Development of Palm Date Pits Activated Carbon Adsorbent for Textile Effluent Treatment

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Abstract- **The adsorption of Cr (VI) on palm date pits activated carbon (DPAC) and commercial activated carbon (CAC) has been carried out. Adsorption studies were carried out for contact time and metal ion concentration. The palm-date pits were crushed, dried and sieved to different mesh sizes for moisture content determination. The samples were subjected gradually to pyrolysis reaction in a furnace. Phosphoric acid (H₃PO₄) was used forthe carbon activation.The study indicated that both adsorbents were effective in removing Cr (VI) from aqueous solution. The percentage removal increased with the increased contact time and reached its peak at 30minutes. The removal of Cr (VI) ions by adsorption from industrial wastewater was done in a batch process. The palm date pits was used as a raw material to develop activated carbon. Palm Date Pits was the choice raw materials because of its availability and suitable to produce activated carbon with reasonably large adsorption capacity at a cheaper production cost. Metal ion concentration, pH, and agitation speed were observed to influence the adsorption of Cr (VI).**

Keywords: Palm Date Pits, Activated Carbon Adsorbent, Textile effluent.

I. INTRODUCTION

Our environment consists of atmosphere, earth, water and space. In normal circumstances, if it remains clean, it is enjoyable. Unfortunately, on account of the various activities of man such as industrialization, construction, transportation etc., the composition and complex nature of the environment gets changed. These activities although desirable for human development and welfare, lead to generation and release of objectionable materials such as heavy metals into the environment [1]. This work seeks to contribute to keeping the environment free of these heavy metals. The environment can be made clean by curbing industrialisation. At the moment the threatening environmental pollution requires an immediate sanitation where removal of heavy metals from the textile industrial effluent wastewater is a prevailing responds. Also, in other to keep pace with the rapid increase in heavy metals pollution, a country like Nigeria should device means to arrest its industrial activities toward producing toxic metals. This work is based on the industrial effluents wastewater pollution and narrowed down to removal of Chromium (VI) from the industrial effluents. The presence of Cr (VI) in the aquatic systems has become a serious problem, which in turn pollutes the environment. Resent work done [2-4]showed that heavy metals and anions concentrations in water samples from Challawa industrial area of Kano state contains significant concentration of chromium ions as well as Cu, Zn, Mg, Mn,

Co, Pb, Ni,and Fe which were found higher than the WHO/EU and FAO/WHO limit. Studies on its removal are increasing with great deal of attention given to improving the existing techniques and inventing new technologies to remove Cr (VI) ions from the contaminated wastewaters [1]. Cr (VI) is among the heavy metals classified as toxic that pose risks to human health and its toxicity varies with threshold limiting value (TLV) = $2\mu g/m^3$ to $5000\mu g/m^3$[5]. Adsorption on activated carbon technique for removal of Cr (VI) ions from wastewater effluents of industries and use of equipment for the method of analysis are widely carried out.

In Nigeria today, industrial growth is high and as well the emission of toxic metals into the environment through effluents. It is anticipated that this work will abate the environmental pollution caused by the toxic Cr (VI) ions in industrial wastewater, since it is known to be carcinogenic, which represents a serious threat to the human health and the ecosystem. Additionally, in the Savannah region of Nigeria, palm dates are produced and commonly consumed in large quantity. The pits are disposed as load waste causing environmental nuisance. Thus, the aims of this research are: To curtail the release of this toxic metal ion known to be carcinogenic agent from discharge surface water by adsorption on activated carbon; to determine the efficacy of using the technique in batch process; to study if the activated carbon produced from date pit can serve as an alternative source of activated carbon against the use of the commercial activated carbon; to obtain data which can be used as means to characterize the adsorptive behaviour of the date pits by determining its adsorptive isotherms; and to assist local industries to meet the required standard of Cr (VI) content in their wastewater and industrial solution before they are discharged into the surface water bodies. To achieve this aim our objectives includes the use of the locally prepared activated carbon (palm date pits) to remove the Cr (VI) ions in a batch process, determine the adsorption capacity of the palm date pits activated carbon for the removal of Cr (VI) from wastewater and compare the adsorption efficiencies (capacity) of the acid activated palm date seed and that of commercial activated carbon in the removal of Cr (VI) from industrial solution or wastewater.

The manufacturing process consists of two phases consisting the precursor is developed into activated carbons using gases. This is generally done by using one or combining the following processes involves material with carbon content is pyrolysed at temperatures in the range 600–900°C in absence

of air (usually in inert atmosphere with gases like argon or nitrogen). The carbonization process is complete drying and then heating to separate by-products, including tars and other hydrocarbons from the raw material as well as to drive off any gases generated. The environment in which the carbonization takes place should not support combustion. Raw material or carbonized material is exposed to oxidizing atmospheres (carbon dioxide, oxygen or steam) at temperatures above $250^{o}C$, usually in the temperature range of $600^{o}C – 1200^{o}C$. The steam burns off the decomposition products from the carbonization phase to develop a porous, three-dimensional graphite lattice structure [6].

Impregnation with chemicals such as acids like phosphoric acid or base like potassium hydroxide, sodium hydroxide or salts like zinc chloride followed by carbonization at temperatures in the range of $450^{o}C–900^{o}C$. It is believed that the carbonization/activation step proceeds simultaneously with the chemical activation. This technique can be problematic in some cases, because for example, zinc trace residues may remain in the end product. However, chemical activation is preferred over physical activation owing to the lower temperatures and shorter time needed for activating material. Meanwhile, several studies of chemical activation have been conducted with zinc chloride, which has been found to maximize the adsorptive capacity and bulk density of locally produced activated carbons [7].Thus adsorption capacity depends on,Physical and chemical characteristics of the adsorbent (carbon) Physical and chemical characteristics of the adsorbate Concentration of the adsorbate in liquid solution Characteristics of the liquid phase (e.g. pH, temperature) Amount of time the adsorbate is in contact with the adsorbent (residence time). The carbonaceous materials have highly developed internal surface area and porosity, sometimes described as solid sponges. The large surface area results in a high capacity for adsorbing chemicals from gases to liquids. Activated carbons are versatile adsorbents with wide range of applications. One of the largest uses of activated carbon is for water treatment. The carbons are added to remove compounds that affect taste and odour of water. Increasing use of activated carbon is found also in industrial wastewater and gas treatment due to the necessity of environmentally friendly processes and also for material recovery purposes. The food industry is also a major consumer of activated carbon where it is used to remove compounds that adversely affect colour, taste and odour. In the mineral industry, activated carbons are used to recover gold from leached liquors. Medicinal uses and the pharmaceutical industry also answer for a large part of the consumption. Catalysis is another area where the structure and features of activated carbon are favourable. In gas applications, activated carbons are extensively used in filters in industrial applications as well as in general air conditioning applications. An important industrial use of activated carbon is solvent recovery. Volatile organic compounds are used in a wide variety of applications and they create unacceptable environment problems if vented straight to the atmosphere.

Activated carbons are also used for storage of hydrogen and natural gas [9].

II. METHODOLOGY

A. Preparation of activated carbon from palm date pits

The palm-date pits were crushed, dried and sieved to different mesh sizes in which weight before and after drying were noted to know the moisture content.100g of each mesh sizes were weighed out for activation.The H_3PO_4 acid (85%) was prepared with distilled water at a ratio 70% acid and 30% distilled water. The total H_3PO_4 solution = 440ml at H_3PO_4 (85%) = 308ml and distilled water at 132ml. Each 100g sample was then mixed with the H_3PO_4 in a beaker as paste so as to allow for impregnation. The paste was left for about 48hours.The samples were put into ceramics used for activation with the aid of pyrolysis reaction in a furnace. After gradual observation, the furnace temperature was then left at a steady temperature of $600^{o}C$ for the next 2 hours. The total time for the pyrolysis reaction was about 3 hours. The pyrolyzed sample is then crushed into powder form[5].The sample is then treated with H_3PO_4 in an incubator at $110^{o}C$ for about 24hours and soaked with distilled water until the solution pH is stable. The adsorbent produced is then soaked in Na_2CO_3 until any residual acid is removed. The Phosphoric acid (H_3PO_4) activated carbon obtained is dried overnight in an oven at a temperature $110^{o}C$, cooled at room temperature and stored in a desiccator until it is ready for use[5].After pyrolysis, the palm date pits activated samples were partially dried under the sun and then crushed into their different mesh sizes due to the sticking together of the samples.The palm date pits activated carbon was washed repeatedly with distilled water (pH = 6.75) until the samples reach a pH between 6 and 7. The pH is achieved by adding a buffer solution (Na_2CO_3) to control the pH. 1 molar solution of the buffer was prepared by dissolving 26.5g into 250ml distilled water.All samples were then weighed ready for experimental analysis.

B.Batch adsorption experiment

All reagents used are of analytical grade. Batch equilibrium experiments are carried out using the Palm Date Pits Activated Carbon (DPAC) and the Commercial Activated Carbon (CAC) as adsorbents. Aqueous solution of the metal Cr (VI) of 1000mg/L was prepared from $K_2Cr_2O_7$ as a source of the heavy metal in the synthetic waste water. The stock solution (1000mg/L) of Cr (VI) is prepared by dissolving 2.8g of $K_2Cr_2O_7$ into 1 litre of distilled water. 100mg/L stock solution is thus prepared from the 1000mg/L as the preferred stock solution in 100ml of distilled water. A series of flasks containing the respective solutions of varying concentrations from 5 – 25 mg/L was prepared from the stock solution. Adjustment of pH is carried out using NaOH. Agitation of the system under investigation was carried out using a magnetic stirrer at 300rpm[5].

To maximize the heavy metal (Cr) removal by the adsorbent, batch experiments are conducted at ambient temperature using the optimum conditions of all pertinent factors such as

dose, pH, agitation speed and contact time. Adsorption was also carried out in the reaction mixture consisting of 1g/L of adsorbent and 100ml of the respective solution with varying chromium concentration from 5 to 25mg/L.

C. Adsorbent Characteristics

The Palm Date Pits Activated Carbon (DPAC) was produced into different mesh sizes of 2.36mm, 1.18mm, 850µm, 425µm and 212µm. The table below gives the moisture content of the DPAC [9].

TABLE 1
MOISTURE CONTENT OF PALM DATE PITS ACTIVATED CARBON

Mesh size (mm)	Weights		Moisture content (g)
	Before heating (g)	After heating (g)	
2.360	282.34	270.06	12.28
1.180	412.00	396.19	16.81
0.850	422.05	403.63	18.42
0.425	345.58	330.28	15.30
0.212	746.50	711.68	34.82

TABLE 2
DENSITY OF THE ADSORBENTS

Adsorbents	Density(g/ml)
Commercial Activated Carbon	0.95
Palm Date Activated Carbon (2.36mm)	0.96
Palm Date Activated carbon (1.18mm)	0.70

TABLE 3
BASIC COMPOSITIONS OF DATE-PALM PITS

Components	Percentage (%)
Moisture	4 – 10
Protein (N x 6.25)	5 – 7
Oil	7 – 10
Crude fibre	10 – 20
Carbohydrates	55 – 65
Ash	1 – 2

TABLE 4
MAJOR COMPONENTS OF RAW PALM-DATE PITS

Compounds	Phase	Wt %
Amorphous Phase[C, O, H(Organic)]	Major	92
Potassium Barium Phosphate Hydride[$KbaPO_3O_9.H_2O$]	Minor	5
Potassium Hydroxide Hydride [$KOH.H_2O$]	Minor	2.5
Potassium Carbon Sulphur [K_2CS_2]	Minor	0.5
Hydrogen Phosphate [$H_4P_2O_7$]	Minor	-

To determine the effect of contact time on adsorption of chromate ion using the different activated carbon produced, a stock solution of 100mg/L of $K_2Cr_2O_7$ was prepared from which a 22mg/L Cr (VI) solution was prepared by serial dilution with distilled water.

A total time of 120min having interval of 5min was considered. The adsorption density (q_e) was evaluated as shown in the equation below.

$$q_e = \frac{(ini\ conc\ of\ adsorbate - final\ equil\ conc\ of\ adsor)}{mass\ of\ adsorbent} \times Vol\ of\ sol$$

Residual concentration (mg/L) = the final concentration of the adsorbate after time t.

Amount absorbed (mg/L) = Initial concentration of the solution – residual concentration of the adsorbate.

q_e is the adsorption density (mg of adsorbate per g of adsorbent) and given as

Additional % uptake (percent removal efficiency) was evaluated, define as:

$$Eff = \frac{ini\ conc\ of\ adsor - final\ equilib\ conc\ of\ adsor}{initial\ conc\ of\ adsorbate} \times 100$$

III. RESULTS AND DISCUSSION

A. Effect of contact time

The plot of adsorption density versus time for DPAC and CAC presented in Figure 1 and 2 were used to analyse the results. In Figure 1, it can be seen that a gradual and low increase in adsorption of chromium ion was observed for 5 to 20mins and at 30min an optimum value was reached, a drop was noticed up to 75mins of contacting the ions with the DPAC.The mass/mass (q_e) of chromium ion to DPAC of 370mg/g minimum adsorption density for a maximum time of 52min was evident. As the contact time was approaching another optimum this second optimum was not reliable due to the instability of the mass/mass ratio recorded as the adsorption of chromium ion outshoot the suppose prevailing mass of the DPAC. Therefore the 1100mg/g (at 75min) value seen in adsorption chart of figure 1 which lead to a drop in adsorption density is due to bleeding (desorption) of the chromate ion back into the fluid phase, this is undesirable, but it is a characterized by the weak binding forces of ions at pH of 7.2 on the DPAC surface. Figure 2 shows a rather uncontrollable bleeding. The mass/mass of chromium ion to CAC data requires a more irregular proportionating in experiment involving adsorption at a prolonged contact time. Taking advantage of mass conversation of a total of 22mg/L for each reaction time, the mass balance confirmed that the outshoot of the adsorbed chromium ion was a bleeding phenomenon.

The adsorption trend thus signifies that after the contact time of 30 and 75minutes respectively, bleeding occurred in the adsorbent (CAC) by transporting back the chromium adsorbed back into the solution which is also known as desorption. Comparison of the adsorption density of the chromate ions using the CAC and the DPAC was presented in Figure 3.
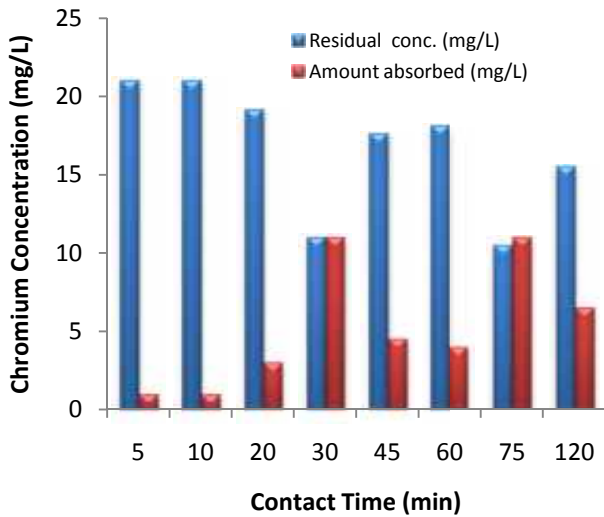
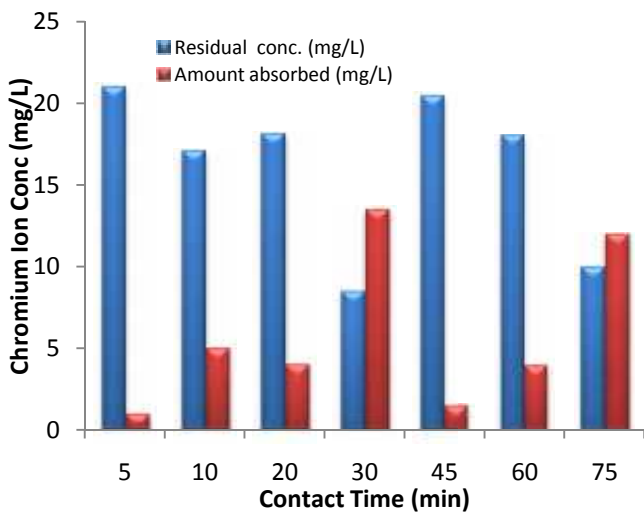Figure 1: Effect of contact time on the removal of chromium (VI) by DPAC

Figure 2: Effect of contact time on the removal of chromium (VI) by CAC

In Figure 3, at contact time of 5 minutes, the adsorption density was equal for both the CAC and DPAC while at contact time of 10 minutes to 45 minutes; the CAC had higher adsorption density. At contact time range of 45 minutes to 60 minutes, the adsorption density of the DPAC was higher than that of CAC. While in the time range of 60 minutes to 75minutes, the adsorption density of both CAC and DPAC were equal. The adsorption density of both adsorbents decreased but the DPAC showed higher adsorption density within the contact time range of 75minutes to 120minutes. The decrease in the adsorption densities at the contact time intervals signifies that bleeding occurred in the adsorbents by transferring back the chromium adsorbed back into the solution which is also known as desorption. This bleeding can be attributed to the surface area of the activated carbon, pH of the adsorbate, temperature of the surrounding, sorbent interaction, particle size inconsistent voltage which in turns affect the agitation speed and the inter-particle bonds that exists between the adsorbate and the adsorbent due to an

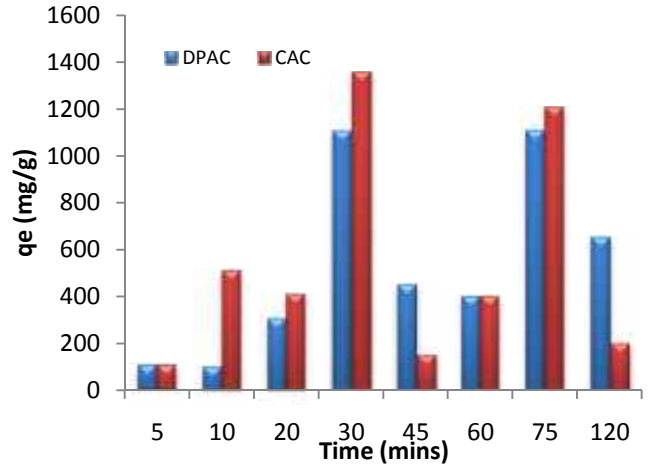exchange of electrons [10]. The effect of pH and temperature is however vital to the adsorption density.

Figure 3: Comparison on the effect of contact time on the removal of chromium (VI) by CAC and DPAC

B. Effect of Metal Ion Concentration

The effect of metal ions concentration on the adsorption capacity of Palm Date Pits Activated Carbon (DPAC) and the Commercial Activated Carbon were studied under optimum conditions. Adsorption of chromium on DPAC and CAC was carried out.

Figure 4 and 5 show the effect of initial concentration on the adsorption density of CAC and DPAC chromate ions.It is observed that the adsorption of chromium on CAC increased with increasing initial concentration of Cr (VI). This can be as a result of an increase in the number of the metal ions competing for the available binding sites in the adsorbent for complexationof Cr (VI) ion at higher concentration levels.
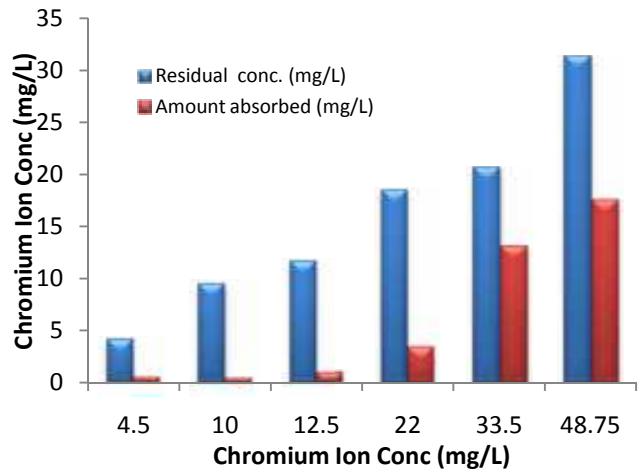

Figure 4: Effect of chromium concentration on the removal of chromium (VI) by CAC

Figure 5 shows the adsorption of chromium on DPAC increase with increasing initial concentration of Cr (VI) with the exception of the 4.5mg/L and 10mg/L concentrations. These initial concentrations were observed to have the same adsorption density and the adsorption density decreased as the concentration was increased to 12.5mg/L. However, as the

concentration increased from 12.5mg/L to 48.75mg/L, the adsorption density increases. This trend can be said to be as a result of an increase in the number of the metal ions competing for the available binding sites in the adsorbent for complexationof Cr (VI) ion at higher concentration levels. The comparison of the effect of chromium concentration on the removal of Cr (VI) using both CAC and DPAC are studied and presented in figure 6.
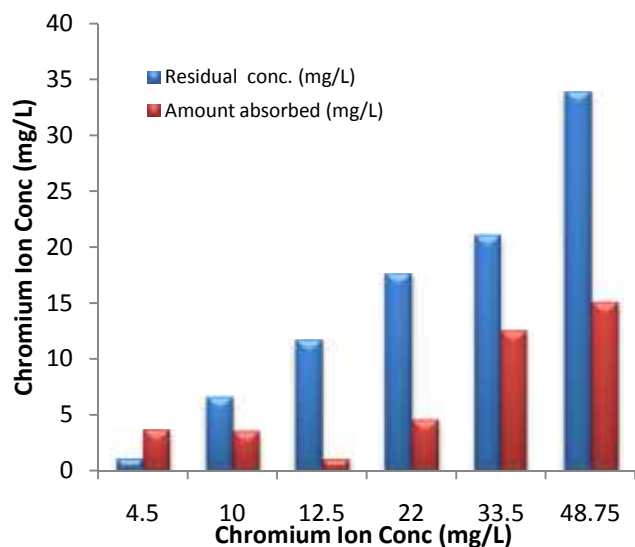

Figure 5: Effect of chromium concentration on the removal of chromium (VI) by DPAC

Figure 6 shows the comparison between the Commercial Activated Carbon (CAC) and the Date Palm Pits Activated Carbon (DPAC) on the effect of chromium concentration on the removal of Cr (VI). At low concentration (4.5mg/L and 10mg/L), the adsorption density for DPAC is greater than that of CAC. However, the adsorption density for CAC at 4.5mg/L and 10mg/L is equal and that of DPAC is also equal at 4.5mg/L and 10mg/L. The trend showed that at low concentrations, the DPAC has higher adsorption density than CAC but as the concentration increases, the reverse is the case. On the whole, it was observed that CAC had the highest values of $1/n$ (1.728) indicating that it has the highest rate of adsorption of Cr (VI) in the solution followed by DPAC with $1/n$ value of 0.767. This implies that, although, the rate at which CAC adsorbed Cr (VI) in the solution is high, its adsorption capacity for the Chromium solution is minimal at k = 1.896 compared to that of DPAC because of its higher k value at 54.217. Palm Date Pits as the choice of raw materials which depends on the availability of locally waste materials was suitable to produce activated carbon with reasonably large adsorption capacity at a cheaper cost.Metal ion concentration, pH, and agitation speed were observed to influence the Cr (VI) uptake. This is largely attributed to the surface chemistry of the activated carbon.
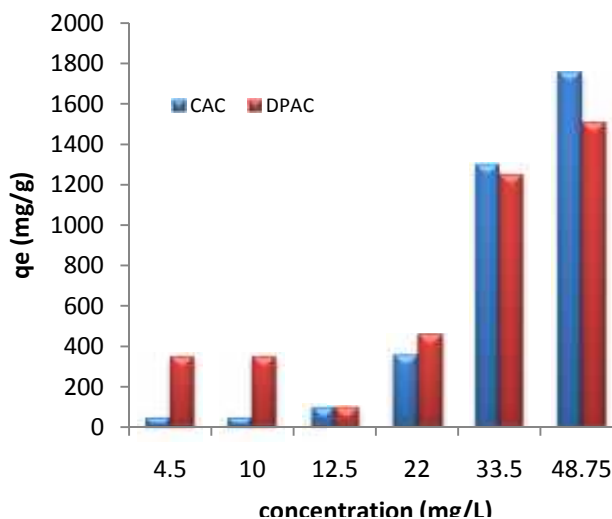

Figure 6: Comparison on the effect of chromium concentration on the removal of chromium (VI) by CAC and DPAC

IV. CONCLUSION

The adsorption of Cr (VI) on palm date pits activated carbon (DPAC) and commercial activated carbon (CAC) was studied. Adsorption studies were carried out for contact time, and mass/mass ratio of metal ion concentration to DPAC as well as a mass/mass ratio of metal ion concentration to CAC adsorbent. The study indicated that both adsorbents were effective in removing Cr (VI) from aqueous solution. The percentage removal increased with the increased contact time and reached its peak at 30minutes and 75 minutes after which bleeding occurred for DPAC while for CAC, the peak time was only at 30 minutes (although, a high adsorption density also occurred at 75 minutes) after which bleeding also occurred.This bleeding can be attributed to the surface area of the activated carbon, pH of the adsorbate, temperature of the surrounding, sorbent interaction, particle size, it is revealed from the studies that the treatment of industrial effluent by activated carbon can be used to reduce the chromium concentration found in textile industrial effluent.

References

1. Khopkar S.M Environmental Pollution Analysis [Book]. - New Delhi-110002 : New Age International (P) limited, 2001. - pp. 1-20.
2. Akinola, M.O., Njoku, K.L. and Ekeifo, B.E. (2008) Determination of Lead, cadmium and chromium in the Tissue of economically important plant growth Around a Textile Industry at Ibseshe, Ikorodu Area of Lagos State, Nigeria. Advances in Environmental Biology 2(1): 25- 30.
3. Akan, J.C., Ogugbuaja, V.O., Abdulrahman, F.I. and Ayodele, J.T. (2009) Heavy metals and anionic Levels in some samples of vegetable Growth within the vicinity of Challawa Industrial Area Kano State, Nigeria. American Journal of Applied Sciences 6 (3): 534 – 542.
4. Adeogun A.O. and Chukwuaka, A.V. (2010), Differential sensitivity of Saggital Otalith Growth and Somatic growth in Oreochromis Niloticus Exposed to Textile Industrial Effluent. Life Science Journal 7(2).
5. Nomanbhay S.M. and Palanisamy K. (2005). Removal of Heavy Metal from Industrial Wastewater using Chitosan Coated Oil Palm Shell Charcoal, Electronic Journal of Biotechnology, Vol. 8 (1):43-53.
6. **Armenante P.M. (2001). Adsorption with Granular Activated carbon. Journal of New Jersey Institute of Technology.**

7. Al-Zharani M.A. Nesratnam S and M.H. Essa Preparation of Phosphoric acid-activated Carbon using Palm Date Pits: Physio-chemical Adsorptive Properties Journal- 1-17

8. Zanzi R. Bai X, Capdevila P. and E. Bjornbom Pyrolysis of Biomass in Presence of Steam for Preparation of Activated Carbon, Liquid and Gaseous Products. (2001). 6th World Congress of Chemical Engineering, Melbourne, Australia.1-8.

9. Omar G.A. Production of Activated Carbon from Local Palm Date Pits for Pollution Removal [Report] : Master of Science Thesis / King Fahd University of Petroleum and Minerals. - Dharan, Saudi Arabia, 2003. - pp. 16-19

10. Allen S. J. and B. Koumanova Decolourization of Water/Wastewater using Adsorption (Review) Journal of the University of Chemical Technology and Metallurgy, Vol.40:175-192.