PREPARATION AND CHARACTERIZATION OF ACTIVATED CARBON FROM HYPHAENE THEBAICA SEED SHELLS; EQUILIBRIUM STUDY

[1]Nasma D. Eljack

[2]Abdelhakiem Ibraheem

[1]Department of Chemistry, Tarabah University College, Taif University, KSA
[2]Department of Chemistry, Faculty of Science, University of Khartoum

Corresponding author:
Nasma_74@hotmail.com

ABSTRACT

In this study activated carbons (AC) from hyphaene thebaica seed shells has been prepared via pyrolysis followed by chemical activation method. Ferric chloride and zinc chloride were used as activators to produced FeAC and ZnAC respectively. The chemically activated carbons were characterized in terms of iodine number, percentage yield, moisture content, ash content and surface area beside spectroscopic analysis. FT-IR measurements reveals the existence of a different functional groups, as a result of XRD analysis the prepared AC has a less content of inorganic compounds than the precursor. The surface physical morphology of hyphaene AC was shown using scanning electron microscopy (SEM). SEM images of these materials showed a high pours carbon and irregular distribution with heterogeneous morphology of the surface. Average pores diameter, total pores volume and BET surface area of the prepared carbons had been obtained from BET isotherms as follow; 2.8315 nm, 0.4232 cm3/g and 548.8 m2/g for ZnAC and 2.9410 nm, 0.3885 cm3/g and 561.95 m2/g for FeAC respectively. It's clear that both ZnAC and FeAC have similar characteristics regarding their surface properties. The adsorption of two heavy metal ions namely; Cu(II) and Cr(III) onto FeAC were investigated. Adsorption equilibrium isotherms of these metal ions were found to fit Langmuir isotherms exhibiting maximum adsorption of 128.487 mg/g for Cr(III) and 121.496 mg/g mg/g for Cu(II). The results indicated that hyphaene AC exhibits large surface areas, high porosity, high iodine value and low ash and moisture contents. According to these properties, hyphaene AC can be consider as adsorbent materials for a wide range of applications.

INTRODUCTION

Activated carbon (AC) is an amorphous, porous carbonaceous material that reacts with gases during the pyrolysis process to increase the number of pores. AC become an important research area because of its excellent properties such as, large surface area, nontoxicity, enrich of pores, and the ability of modifying its surface with different functional groups. For these reasons, AC has been widely used as adsorbent material for many applications [1–3]. They can be used to remove contaminants from gas and liquid phases with high efficiency, for example, they can be used to treat and purify wastewater and air pollution. As synthesized carbon is expensive, the demand for the synthesis of relatively cheap carbon for various applications is an interesting and promising area[4–8]. Agricultural waste is considered as a good source of AC because it is not expensive, renewable, safe, available at large quantities and simply to access; additionally, contain high carbon and low ash. [9-12]

Characterization of Activated Carbon

Characterization of activated charcoal is essential to classify it for specific applications, and it mainly depends on the properties of the precursors such as ash content, moisture content, iodine value and surface properties, as well as the method of activation used.

Iodine Value

Iodine value is the number of iodine (in milligrams) absorbed by one gram of AC. This value is the measure of the amount of micropore found within the AC. Iodine value is the most important parameter used to characterize AC activity and efficiency. The higher iodine value the higher the microporosity of the AC.

Surface area

The adsorption efficiency is depending on how large the specific surface area of the adsorbent. The pore volume limits the size of adsorbate on the other hand the surface area limits the amount of adsorbate.[18] The specific surface area (m^2/g) of AC is usually obtained from gas adsorption isotherm (N_2 or Ar at their boiling points) using the Brunauer-Emmett-Teller BET theory.[19-21]

Surface Functional Group of Activated Carbon

Generally, AC surface is approximately neutral so polar molecules are less adsorbed compared with nonpolar one. The presercuers chemical structure affects the surface properties and offer a potentially easily and cheap method for modifying the surface of AC. Various chemical groups containing oxygen, nitrogen and other heteroatoms have been recognized. As the activated carbons have a porous structure with disordered spaces, this enables heteroatom to combined easily to the surface during synthesizing and activation. Various spectroscopic methods have been used to identify surface functional groups such as infrared (IR).

Pore structure

Pore size distribution properties are key indicators of a carbon capacity for removing adsorbates. The gas phase adsorbates are generally smaller than those in liquid phase; therefore, a gas phase AC has the majority of its pores concentrated in the micropore region.[21]

Adsorption Isotherms

There are different isotherm models that used to describe the adsorption for a variety of systems.

Langmuir isotherms model is as follow:

$$q_e = q_{\max} \frac{K_L C_e}{1 + K_L C_e} \qquad (1)$$

EXPERIMENTAL

Material and methods

Sample source

Hyphaene seed shells were collected as plant wastes from Khartoum area (Sudan) and were used as an activated carbon precursor.

Chemicals and Instruments

Ferric chloride, Zinc chloride, Chromium(iii)Chloride hexahydrate, Cupric Chloride, Hydrochloric acid, Sodium hydroxide, Sodium thioslufate, Starch, Iodine solution. All these chemicals of analytical grade and were used without further purification.

Atomic Absorption spectrometry (AAS) Savanta serial No AA7638GBC (Australia), Autoclave model 23-200 Germany, Hot stirrer Model: LMS-1003 Scott science UK. Infrared spectroscopy: (FT-IR 84005 Shimadzu Japan),

Scanning electron Microscope (SEM) Model: H-8100 England, X-ray Diffraction (XRD) (Panan analytical X'Pert³ MRD (Netherlands). Muffle furnace Model: WACS-104 Korea, pH-Meter model: JENWAY 3505 UK, Shaker. Specific surface area BET (Quantachrome Instruments German).

Deionized water was used in preparing solution.

Experimental procedure

Dried hyphaene seed shell was homogenized and let to impregnated in $FeCl_3$ or $ZnCl_2$ for 24 hours, then the sample prepared for pyrolysis and carbonization as described by the method of Caturla,[22]. The prepared carbons were labeled as FeAC or ZnAC.

Adsorption of metal ions onto hyphene activated carbon

A stock solution of 1000 mg/L of standardized Cu or Cr ions were prepared from their chloride salts. Further dilution was made to obtained solution of the desired concentration.

The adsorption of these ion solution on both FeAC and ZnAC were carried out in aqueous solution at $25\,^{\circ}C$, in general, (3g) of the active carbon were put into 20 ml of aqueous solution containing metal ions, the pH of solution was adjusted to 6.8 using 0.1 M NaOH and the mixture put into electrical shaker. The supernatants were filtered at different time interval, and the remain metal concentrations were determined using atomic absorption spectrophotometer.

Characterization of Hyphaene seed shell Activated Carbon

The yield percent

The following equation is used to calculate the yield for the prepared carbons;

The yield (%) = $\dfrac{\text{weight of final activated carbon}}{\text{weight of dried shell}} \times 100$

Moisture Content

2 grams of hyphaene activated carbon (FeAC or ZnAC) was placed in a silica crucible, then heated to $120\,^{\circ}C$ in an oven for 1 hr, and left to cool at a dedicator. After cooling the weight of dried sample was measured. The percentage of the moisture content was obtained using the following equation;

$$\text{Moisture content \%} = \frac{\text{loss in weight (g)}}{\text{Initial weight(g)}} \times 100 \qquad (12)$$

Ash content is evaluated with the same equation.

Iodine value test

In order to standardize iodine solution, 10 mL of 0.1N iodine solution was taken in a conical flask, 2 drops of starch solution were added then titrated against 0.05 N sodium thiosulphate till the end point. Burette reading corresponds to blank reading is (B)

0.2 g of AC was placed into a flask. 40ml of 0.1N iodine solution was then added, the mixture was shaken properly for 4 minutes and then filtered. The filtrated was collected in a dry flask and then 10ml of the filtrate was titrated against standard sodium thiosulphate solution using starch as indicator. Burette reading is (A)

Iodine value was estimated as follow;

Iodine value: C x conversion factor mg/g $\qquad (14)$

Where $\qquad$ C = B-A

$$\text{Factor} = \frac{\text{Mol wt.of iodine (127) x normality of iodine x 40}}{\text{Wt.of carbon} \times \text{Blank reading}} \qquad (15)$$

RESULTS AND DISCUSSION

Physical and Chemical Characterization of Hyphaene Seed shell Activated Carbon

Hyphaene seed shell activated carbons were characterized using different methods. The physical and chemical properties of the prepared carbons are summarized in Table 1.

Fourier Transform Infrared Measurements

FT-IR spectroscopic measurements of FeAC and ZnAC were conducted using FT-IR spectrometer in KBr pellets in the range of 400 - 4000 cm^{-1} with a resolution of 4 cm^{-1}.

From the FTIR analysis of the two samples (see IR spectra in supplementary material), it can be noticed that both samples had same peaks and values which is to justify that they are from the same source. Broad bands with two maximum peaks can be noticed at 3735.86 cm^{-1} for FeAC and 3739.72 cm^{-1} for ZnAC were corresponded to O-H stretching mode of hydroxyl groups. Bands at 2920, 2850, and 1380 cm^{-1} which were present in the two samples were corresponded to a C-H Asym. stretching and sym. bending, while the bands between 1530 and 1740 cm^{-1} corresponded to C=C alkene stretch. Bands at 2358 cm^{-1} were observed to be strong in FeAC and very strong in ZnAC which is corresponded to a C-H stretching probably from aldehyde group. This difference indicates that Hyphaene reacted differently with the two activators.

X-Ray diffraction

The wide-angle X-ray scattering of samples was measured using an X-ray diffractometer with Cu K α radiation.

The diffraction peaks of FeAC were appeared at 2θ angles of 35.396º, 43.0.36º and 56.935º These diffraction strongest lines are marked by their corresponding miller indices (200), (200), and (222). On the other hand, the diffraction peaks of ZnAC were appeared at 2θ angles of 35.282º, these diffraction strongest lines are marked by their corresponding miller indices (200) (see XRD scans in supplementary material).

Scanning Electronic Microscope (SEM)

The prepared carbons were analyzed using SEM to show the structure of the pores and the external morphology of the samples. The SEM images of ZnAC and FeAC impregnated activated carbon were shown in Figures 1 and 2. It's clear that both the samples show a high level of poursty with a big surface area.

BET analysis of activated carbon

Bet isotherm measurements of both ZnAC and FeAC were conducted using N_2 as adsorptive material at 77.3 K and saturated vapor pressure = 101.03 kpa. The surface area of hyphene AC as well as the mean pore diameters were obtained from the Bet isotherms of both samples. (see the isotherms at supplementary material).

The most important characteristics of AC are surface area and iodine number and the results on Table1 showed that the Bet surface areas of ZnAC and FeAC are 548.8 and 561.95 m^2/g, respectively (see Bet plots in supplementary material). These values are lower than those reported by Bamufleh[23] for AC prepared from date stones using zinc chloride. The iodine numbers of FeAC and ZnAC are in agreement with those reported by Ekpete and his coauthors[24] for activated carbon prepared from Plantain Fruit Stem. The SEM images of the prepared activated carbons indicated that the surface of hypheane AC was very rough and enriched in pores. It is clear that impregnation with $FeCl_3$ and $ZnCl_2$ had an important effect on increasing both surface area and micropores.

The low amount of moisture and ash contents hypheane AC indicates that the presircure has a less particle density. The lower the ash value, the better the activated carbon to be used as adsorbent. Abdullah et al.[25] reported that, the ash values that make a carbon suitable for absorption should be within a range of 1 –20% thus, hypheane AC is a better adsorbent if the ash value is to be considered. The iodine number is usually used to estimate the surface area of activated carbon at room temperature[26, 27]. It is a measure of the porosity and adsorbent capacity of the AC.

Adsorption Equilibrium
Atomic Absorption Spectrometer was used to estimate the concentration of remaining metal ions after each adsorption process using standard procedures.

The adsorption equilibrium data in Tables 2 and 3 and Figures 3 and 5) obtained for the adsorption of Cu^{2+}, and Cr^{3+} ions respectively onto FeAC were fitted with the Langmuir isotherm model (Eq. (1) and are presented as shown in Figures 4 and 6. Several authors [8, 24-27] showed the successful application of Langmuir isotherm for the correlation of experimental adsorption data. The equilibrium findings show that the maximum uptake of Cu^{2+}, and Cr^{3+} on FeAC was 128.487 and 121.496 mg/g, respectively. It is clear that the maximum adsorptions of the two metal ions is nearly the same. These findings suggest that hypheane AC is preferable for adsorption applications.

Table 1: Physical and chemical properties of hyphaene seed shell activated carbons

Properties / Type of AC	FeAC	ZnAC
% Yield	25.8	26.0
pH	6.8	6.8
% Moisture Content	0.0476	0.0837
% Ash content	1.8058	2.1104
Iodine number mg/g	360.27	338.68
Average pores diameter (nm)	2.9410	2.8315
Total pores volume (cm^3/g)	0.4232	0.3885
BET surface area m^2/g	561.95	548.8

Table 2: Effect of time on the adsorption of Cr^{3+} onto FeAC at pH = 6.8 and 25°C.

C_0 ppm / Time min	5	10	15	20
	q_t mg/g			
0	0.01	0.401	0.065	0.28
3	0.091	0.082	0.103	0.611
5	0.135	0.101	0.225	0.72
10	0.143	0.124	0.422	0.804
20	0.146	0.247	0.483	0.838
40	0.144	0.27	0.469	0.828
q_e mg/g	32.37	64.87	97.54	127.15

Table 3: Effect of time on the adsorption of Cu^{2+} adsorption onto FeAC at pH = 6.8 and 25°C.

C_0 ppm / Time min	5	10	15	20
	q_t mg/g			
0	0.032	0.109	0.297	0.673
3	0.11	0.229	0.543	1.57
5	0.203	0.333	0.769	1.72
10	0.389	0.507	0.822	1.897
20	0.366	0.58	0.812	1.995
q_e mg/g	30.89	62.80	94.59	120.03

Figure1. SEM images of hyphaene seed shell FeAC
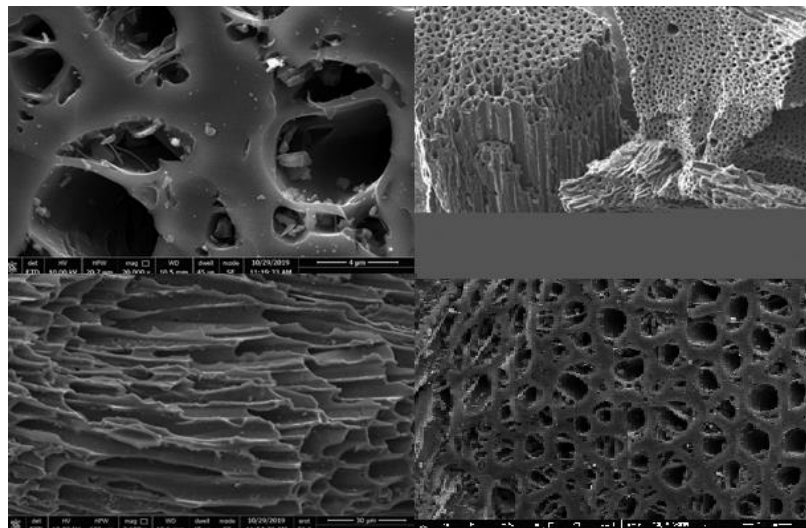
Figure 2. SEM images of hyphaene seed shell ZnAC
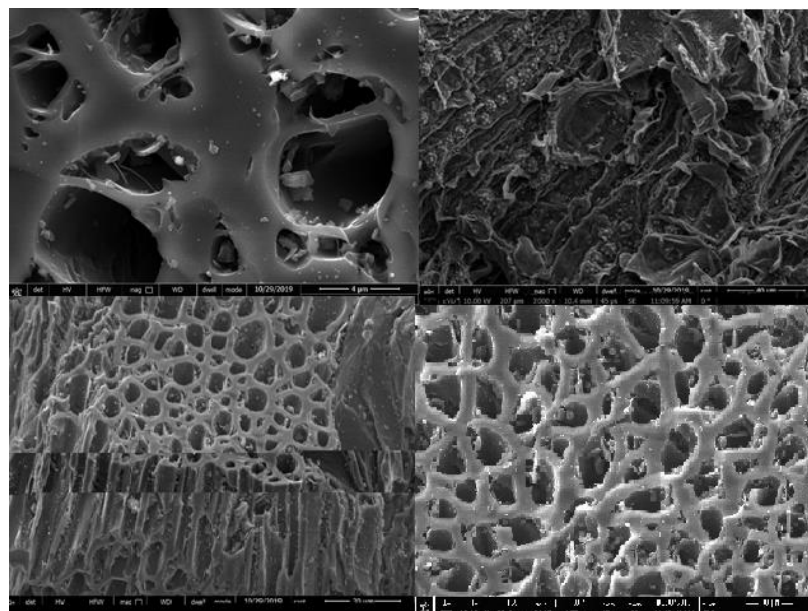
Figure.3. Effect of time on the amount of Cr^{3+} adsorbed onto FeAC at pH == 6.8 and 25°C.
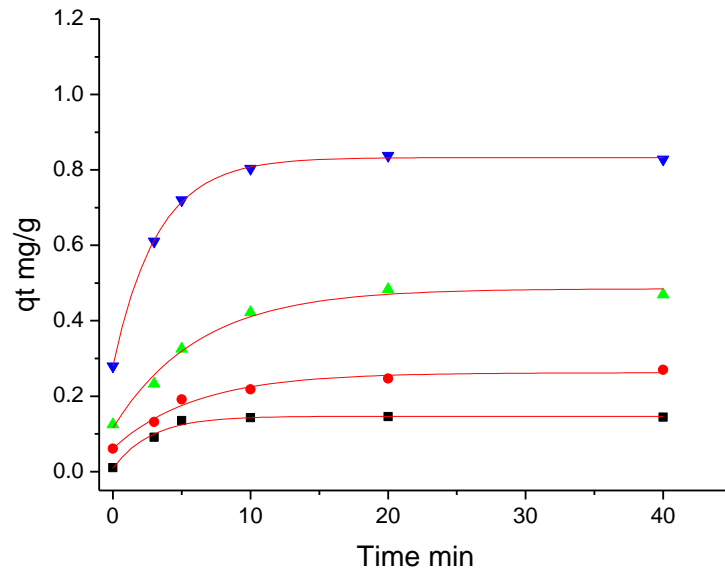
Figure.4. Equilibrium adsorption isotherm (Langmuir isotherm) of Cr^{3+} adsorbed onto FeAC at pH = 6.8 and 25°C.
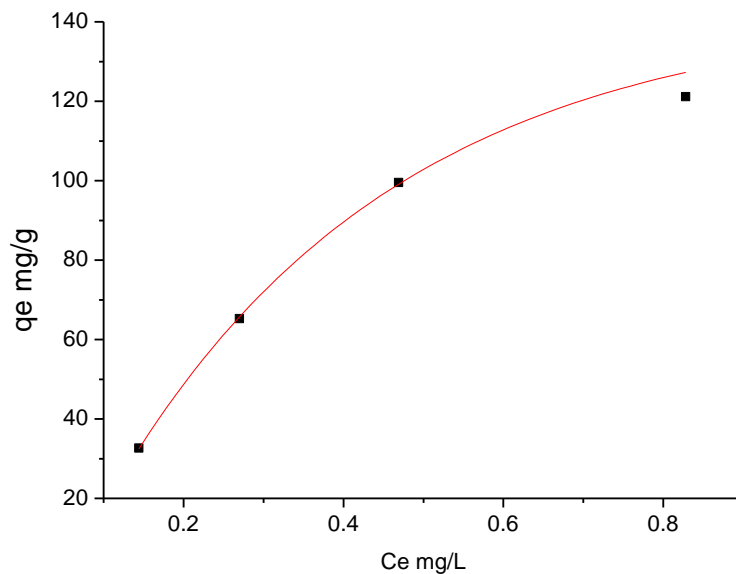
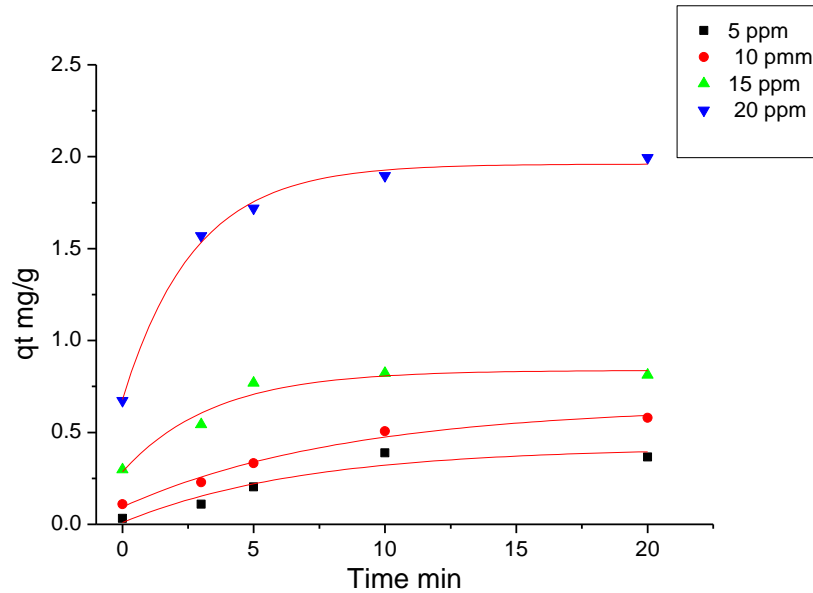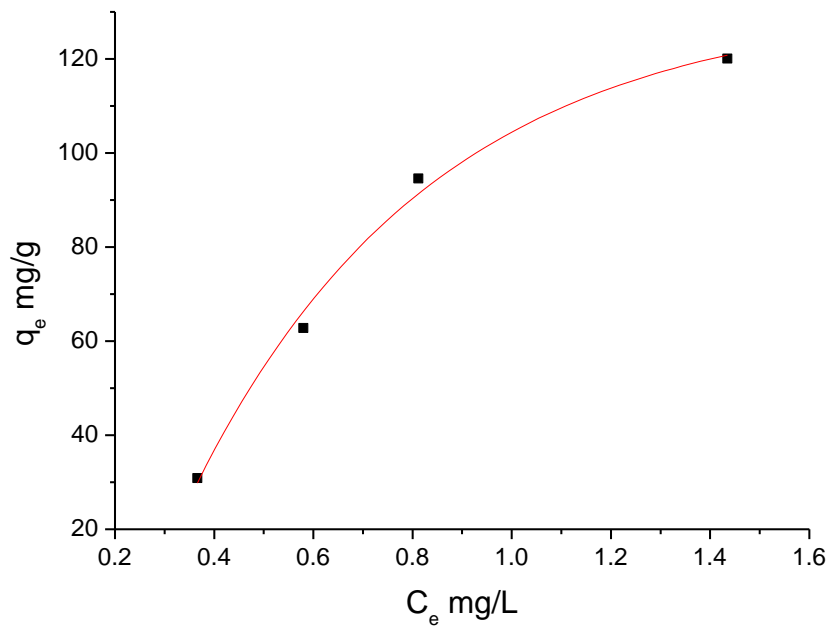**Figure5. Effect of time on the amount of Cu^{2+} adsorbed onto FeAC at pH = 6.8 and 25°C.**

Figure 6. Equilibrium adsorption isotherm (Langmuir isotherm) of Cu^{2+} adsorbed onto FeAC at pH = 6.8 and 25°C.

Eljack and Ibraheem, 2022

CONCLUSION

In this work, activated carbons from hyphaene seed shells were prepared by chemical activation using $FeCl_3$ and $ZnCl_2$ as chemical activators. The findings show that the two activators used has nearly the same effect in the efficiency of the carbon as adsorbent material. The prepared carbons were characterized and analyzed using different methods. Equilibrium measurements of the adsorption of two heavy metals on the prepared ACs were performed. The results revealed that highly porous carbons with higher adsorption capacities were prepared. In conclusion, hyphaene seed shell AC can be classified as an effective adsorbent for removing heavy metal ions from aqueous solutions and polluted wastewaters.

REFERENCES

Al-Qodah, Z. & Shawabkah, R. (2009). Production and characterization of granular activated carbon from activated sludge. Braz J Chem. Eng.., 26(1), 127–136. DOI:10.1590/S0104-66322009000100012

Jiang, Z. et al. (2003). Activated carbons chemically modified by concentrated H_2SO_4 for the adsorption of the pollutants from wastewater and the dibenzothiophene from fuel oils. Langmuir, 19(3), 731–736. https://doi.org/10.1021/la020670d

Vidhyadevi, T. et al. (2014). Optimization of the process parameters for the removal of reactive yellow dye by the low cost Setaria verticillata carbon using response surface methodology: thermodynamic, kinetic, and equilibrium studies. Environ Prog Sustain Energy, 33(3) 855–865. DOI: 10.1002/ep.11859

Athab, A. et al. (2015). Modification of carbon nanotubes surface using different oxidizing agents, Environ Anal Chem, 2(3), 1–2. DOI: 10.4172/jreac.1000e112

Muhammed, G. et al. (2015). Synthesis of multi-walled carbon nanotube by using ethanol as a carbon source, Chem Sci J, 6, 1–2. DOI: 10.4172/2150-3494.1000e106

Abdulrazzak, F. H. & Hussein, F. H. (2014). Effects of nanoparticle size on catalytic and photocatalytic activity of carbon nanotubes-titanium dioxide composites. Environ Anal Chem, 2, 1–2, 2014. DOI: 10.4172/2380-2391.1000e110

Shaheed, M. A. & Hussein, F. H. (2015). Preparation and applications of titanium dioxide and zinc oxide nanoparticles. Environ Anal Chem, 2, 1–3. DOI: 10.4172/2380-2391.1000e109

Kilic, M. et al. (2011). Adsorptive removal of phenol from aqueous solutions on activated carbon prepared from tobacco residues: equilibrium, kinetics and thermodynamics. J Hazard Mater. 189, 397–403. doi: 10.1016/j.jhazmat.2011.02.051

Unlu, N. & Ersoz, M. (2006). Adsorption characteristics of heavy metal ions onto a low cost biopolymeric sorbent from aqueous solutions. J Hazard Mater, 136(2), 272-80. doi: 10.1016/j.jhazmat.2005.12.013.
Dubey, S. et al. (2007). Adsorption of chromium (VI) on low-cost adsorbents derived from agricultural waste material: a comparative study. J Hazard Mater, 45(3), 465-70.
doi: 10.1016/j.jhazmat.2006.11.041

Kurniawan, T. et al. (2006). Comparison of low-cost adsorbents for treating wastewater laden with heavy metals. Sci. Total Environ, 366(2-3):409-26. doi: 10.1016/j.scitotenv.2005.10.001.

Sud, D. et al. (2008). Agricultural Waste Material as Potential Adsorbent for Sequestering Heavy Metal Ions from Aqueous Solutions. Bioresour Technol, 99(14), 6017-27.
doi: 10.1016/j.biortech.2007.11.064.

Fu, F. & Wang, Q. (2011). Removal of Heavy Metal Ions from Wastewaters. J Environ Manag, 92(3), 407-418
doi: 10.1016/j.jenvman.2010.11.011

Chiban, M. et al. (2011). Characterization and Application of Dried Plants to Remove Heavy Metals, Nitrate, and Phosphate Ions from Industrial Wastewaters. Clean (Weinh), 39(4), 376 – 383.
https://doi.org/10.1002/clen.201000127

Sabry, S. et al. (2013). Heavy metals removal from aqueous solutions and wastewaters by using various byproducts. The J Environ Manag, 15(128), 514-21. DOI: 10.1016/j.jenvman.2013.05.061

O'Connel, D. et al. (2008). Biores. Heavy metal adsorbents prepared from the modification of cellulose. Bioresour Technol..doi: 10.1016/j.biortech.2008.01.036.

Gueu, S. et al. (2006). Heavy Metals Removal in Aqueous Solution by Activated Carbons Prepared from Coconut Shell and Seed Shell of the Palm Tree. J Appl Sci, 6(13), 2789-2793DOI: 10.3923/jas.2006.2789.2793

Mestre, J. et al. (2011). Waste derived activated carbons for removal of ibuprofen from solution: role of surface chemistry and pore structure. Bioresour Technol. doi: 10.1016/j.biortech.2008.09.039.

Sing, K. et al. (1985). Reporting physisorption data for gas/solid systems with special reference to the determination of surface area and porosity. Pure Appl Chem, 57, 603-619. DOI: 10.1351/pac198254112201

Harkins, W.D. & Jura, G. (1943). An adsorption method for the determination of the area of a solid without the assumption of a molecular area, and the area occupied by nitrogen molecules on the surfaces of solids, 11, 431-432. J Chem Phys. https://doi.org/10.1063/1.1723871

Mikhail, R. et al. (1968). Investigations of a complete pore structure analysis. I. Analysis of micropores. J Colloid Interface Sci, 26(1), 45-53. https://doi.org/10.1016/0021-9797(68)90270-1

Caturla, F. et al, (1991), Preparation of activated carbon by chemical activation with $ZnCl_2$,
Carbon, 29, 999-1007. DOI:10.1016/0008-6223(91)90179-M

Bamufleh, H.S. (2009). Single and binary sulfur removal components from model diesel fuel using granular activated carbon from date stones activated by $ZnCl_2$. Appl Catal A Gen, 365(2):153-158. DOI: 10.1016/j.apcata.2009.05.054

Ekpete, O. et al. (2017). Preparation and Characterization of Activated Carbon Obtained from Plantain (Musa paradisiaca) Fruit Stem. J Chem, (1), 1-6 https://doi.org/10.1155/2017/8635615

Abdullah, A. et al. (2013). Preparation and characterization of activated carbon from gelam wood bark (Melaleuca cajuputi). Malaysian J Anal Sci, 1 (2001) 65-68.

Guo, Y. & Rockstraw, D. A. (2007). Physicochemical properties of carbons prepared from pecan shell by phosphoric acid activation. Bioresour Technol. 98(8),1513-21. DOI: 10.1016/j.biortech.2006.06.027

Royer, B. et al. (2009). Applications of Brazalin pine-fruit shell in natural and carbonized forms as adsorbents to removal of methylene blue from aqueous solutions: kinetics and equilibrium study. J Hazard Mater. 30, 164(2-3), 1213-22. doi: 10.1016/j.jhazmat.2008.09.028