Comparative Study on Activated Carbon Prepared from Various Fruit Peels

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ABSTRACT: This study is a comparative study on the properties of activated carbon (AC) prepared from Pomegranate, kiwi , banana and mandarin peels which they present in the local Saudi markets. The characteristics of the prepared activated carbon were studied via determination of the percentage of ash and moisture contents, surface area, microstructure using scanning electron microscope (SEM) and function groups present via FTIR. Stepwise remediation method was used for studying the removal efficiency of the prepared activated carbons for Cu(II) ions from aqueous solutions under different conditions of contact time, initial heavy metal concentration (25–1000 mg/L) and solution pH (2–10). The results showed that the activated carbon samples showed higher removal efficiency compared to the dried fruits peels from which they are produced. The activated carbon derived from banana and kiwi peels showed higher efficiency for Cu(II) removal while these derived from mandarin and pomegranate peels showed acceptable results.

KEYWORDS : Removal, Copper, activated carbon, chemical activation, fruit peels.

I. INTRODUCTION

Toxic heavy metal laden wastewater has become a public health concern because of its non-biodegradable and persistent nature. Species such as; Cr, Co, Ni, Cu, Zn, Cd, Hg, and Pb have been resulted from various sources such as landfill, agricultural activities, and industrial wastewater [1-4]. These species are mobilized and carried into food web as a result of leaching from waste dumps, polluted soil and water. The concentrations of these metal species increase in at every level of food chain and are passed onto the next higher level in a phenomenon called bio magnification [5]. Different methods used for the removal of heavy metal species like filtration, chemical precipitation, coagulation, solvent extraction, electro dialysis, ion-exchange, membrane process and adsorption [6-8]. Among the above heavy metals, Copper (II) which discharge in the wastewater from various industries such as electroplating industries, pulp and paper mills, fertilizer petroleum refineries, aircraft and finishing, motor vehicles and non-ferrous metalwork[9,10]. Copper is generally considered to be toxic to man at concentration exceeding 5mg/L. The Word health Organization's guide line for drinking water based on its staining properties is 1mg/L [11]. Excessive intake of copper over 1.0 mg/L from drinking results in hemochromatosis and gas-trointestinal catarrh diseases because it is accumulated in the livers of human and animals. In recent years, various adsorbents have been used for removal of Cu(II) [12]. Since copper is an essential metal in a number of enzymes for all forms of life, problems arise when it is deficient or in excess. However, the carcinogenic character of copper is accepted and epidemiological evidence, such as the higher incidence of cancer among coppersmiths, suggests a primary carcinogenic role for copper. In addition, copper is phytotoxic and, indeed, has been used as an algicide to control algal blooms. It can, therefore, cause plant damage if, for example, it is present at too high a concentration in sewage sludge that is applied to agricultural land.

In recent years, the search for low-cost adsorbents that have metal-binding capacities has intensified. This has led many workers to search for cheaper alternates such as coal, fly ash, silica gel, wool wastes, agricultural wastes, wood wastes, and clay minerals [13-15]. Activated carbon (AC) has been proven to be an effective adsorbent for the removal of a wide variety of organic and inorganic pollutants from aqueous or gaseous media. It is widely used due to its high surface area, well-developed internal microporosity, and wide spectrum of surface functional groups [16-18]. While the effectiveness of ACs to act as adsorbents for a wide range of contaminants is well documented, research on AC modification is gaining prominence due to the need to develop the affinity of AC for certain contaminants to facilitate

their removal from water. There are two processes for the preparation of activated carbon: physical or chemical activation. Physical activation involves carbonization of a carbonaceous materials followed by treatment by activated reagent like CO_2 or steam[19]. In chemical activation ,a raw material is impregnated with an activating reagent such as $ZnCl_2$, H_3PO_4, KOH…etc. Chemical activation is preferred over physical activation owing to the higher yield, simplicity, lower temperature and shorter time needed for activating material, and good development of the porous structure[20]. The main objective of this study to compare between the effectiveness of activated carbon derived from different four fruits peels by simple chemical activation method towards the removal of copper ions from aqueous solutions.

II. MATERIAL AND METHODS

Fresh Pomegranate, kiwi, mandarin and banana peels were collected from local stores in Riyadh, KSA . The collected peels were first washed by distilled water, then dried in sun light for 7 days then in oven at 100◦C for 24 hrs. After drying, the peels were crushed and sieved to 125 mm sieve. The activated carbon was prepared by chemical activation. This was done by boiling 40 g of the fruit peel powder with 120 mL of concentrated H_3PO_4 (1:3 weight ratios) for 6 h in an air condenser system. After cooling, the final products were filtrated and washed several times with $NaHCO_3$ solution and distilled water till neutral pH was reached. After that, the resultant activated carbon was dried at 110 ◦C for 24 h, and subsequently was weighed to determine the yield of the product. Finally it was stored in tightly closed bottles. Table 1 showed the designation of the carbon samples.

Table 1: Samples designation

Sample	Designation
Dry Pomegranate peel	PP
Dry kiwi peel	Kw
Dry mandarin peel	M
Dry watermelon peel	B
Activated carbon derived from Pomegranate peel	PPAC
Activated carbon derived from kiwi peel	KwAC
Activated carbon derived from mandarin peel	MAC
Activated carbon derived from banana peel	BAC

Chemical characterization of the prepared AC were studied via determination of moisture and the ash contents and surface area. To test the moisture content, the activated carbon prepared was weighed, oven dried (100 °C, 24 h), and reweighed. The ash content was determined by igniting the moisture free activated carbon in furnace (500 °C, 1 h) followed by second ignition (700 °C, 4 h), and weighing.
Scanning electron microscope (SEM) was used for studying the texture of the various fruit peels and the prepared activated carbon samples. This was carried out by using a JEOL (JEM2010) scanning electron microscope. FTIR spectra of the chemically activated carbon samples were obtained using a Fourier transform infrared spectrometer (BIO-RAD FTS-40).

Removal studies

Removal process of Cu(II) ions by the prepared carbon samples derived from different fruit peels were studied by column extraction method [21]. Effects of initial concentration of heavy metal solution, contact time and initial pH of the solution were studied.

  Effect of initial concentration of heavy metal solution: 1.5 g of various activated carbon samples were weighed to packed different 200 mm high, 10 mm diameter glass columns. Then 25 mL containing 25, 50, 100, 500 and 1000 mg/L of Cu ions were added keeping the column closed for 1 hr . Then the column was open and the elution was allowed to flow. The elution was reloaded again into the column and the pervious step repeated to 2nd solution loading

cycle. The concentration remaining of each heavy metal in the elution in each solution loading cycle was measured using atomic absorption spectroscopy (AAS) model Z-8100 polarized Zeeman. The removal (R) efficiency was calculated according to the following equation [22]:

$$R \% = (C_i - C_f) / C_f . 100 \dotsb \qquad 1$$

Where: R is the of the removal efficiency and C_i and C_f is the concentration of the heavy metal ion in solution before and solution loading cycloprocess (mg/L).

Effect of solution pH : The effect of pH on the removal of Cu(II) ions by various carbon samples was studies as follow: 1.5 g of various activated carbon samples were weighed to packed different 200 mm high, 10 mm diameter glass columns. Then 25 mL containing 100 mg/L of Cu ions at initial pH: 2,4,6,8 and 10 were added to the column keeping it closed for 1 hr. The remaining concentration of Cu(II) in the elution were measured byAAB. The removal efficiency (*R*%)was calculated by equation 1.

 Effect of contact time: 25 mL of Cu(II) solution of initial concentration 100 mg/L and pH 6 were added to 0.5 gm of activated carbon packed into the glass column. The glass column closed for time intervals; 10, 20, 30 and 60 minutes. Then the column was opened and the elution allowed to follow throw its tape and collected. The remaining concentrations of Cu(II) ions in the elution was measured by AAB and R% was calculated using equation 1.

### III. RESULTS AND DISCUSSION

Samples characterization

Table 2 shows the physical characterization of activated carbons derived from various fruit peels.

Table 2: physical characterization of activated carbon samples

| Parameter	sample			
	PPAC	KWAC	BAC	MAC
Moisture content (%)	3.11	1.99	3.5	**4.9**
Ash content (%)	5.9	4	6.2	**8.5**
S_{BET} (N_2 adsorption) (m^2/g)	128.23	137.5	115.2	**109.56**

SEM

micrographs of the dry fruit peels and the activated carbon samples were illustrated in Fig.1. SEM for dried fruit peels showed particles which varies according to the type of fruit , Fig1; a-d. After chemical activation by phosphoric acid, Fig.1;e-h, dramatic effects occurred on the solid surface which is responsible for pitting and fracturing erosion of the surface. Such improved the pore structure of the prepared activated carbons which increase the efficiency of the activated carbon [24].
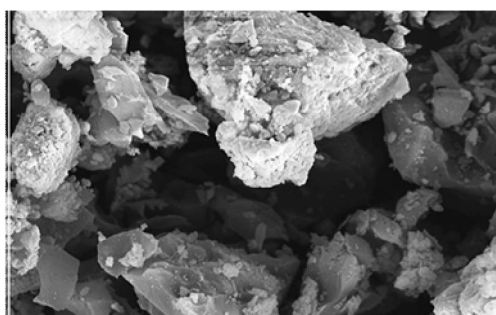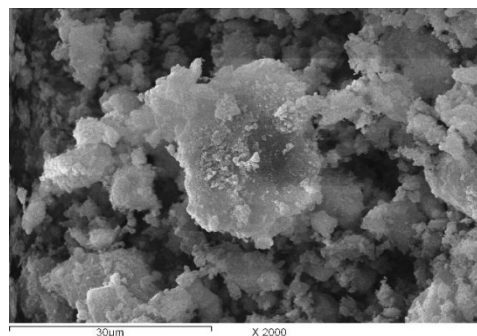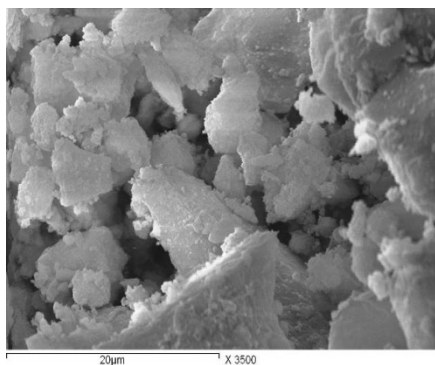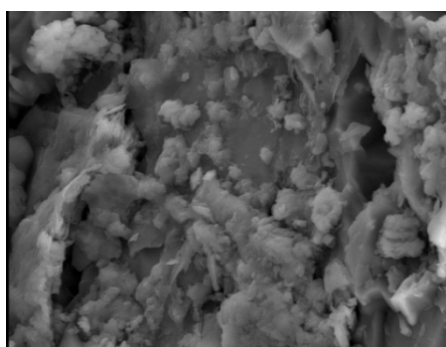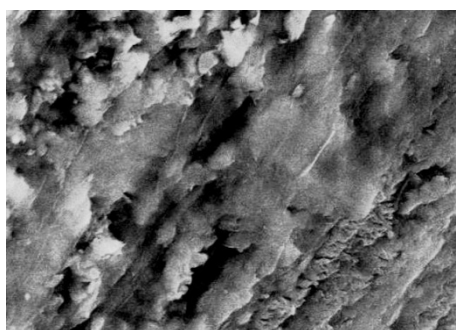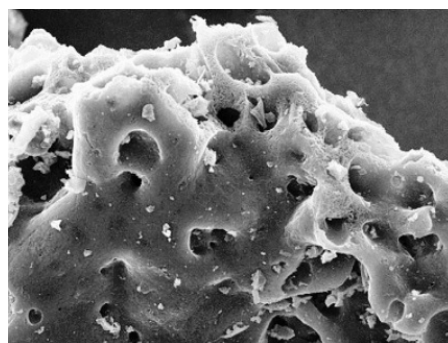

(a)
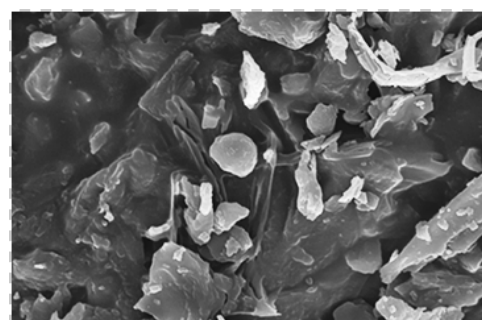
(b)
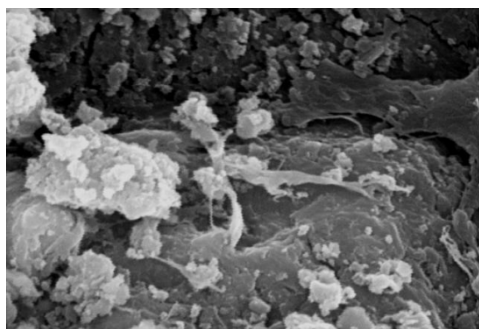
(C)

(d)

(f)

(e)

(g)

(h)

Fig.(1): SEM for fruit peels and activated carbons (a)KW (b)PP (c) B (d) M (e)PPAC .1 (f)KWAC (g)BAC (h)MAAC

FTIR spectra of the various activated carbon samples are shown in Figure 2. FTIR tests were carried out as a qualitative analysis to determine the main functional groups present in the activated carbon samples. All activated carbon samples showed a broad bands in 3300-3500 cm^{-1} region, which indicates the O-H stretching of hydroxyl group. C=O stretching band from kenotic or carboxylic groups formed at 1745.3 cm^{-1}. C=C stretching in aromatic rings formed at 1618.96 cm^{-1}. C–O–C stretching band in ethers formed at 1126.2 cm^{-1} . These functional groups have responsibility for adsorption sites [25]. BAC, PPAC and KWAC samples showed the presence of C=C stretching of

alkynes group was detected at 2826-2862 cm^{-1} . and P=O functional group at 1126 cm^{-1} which could potentially increase the adsorption ability of these carbon samples[26].
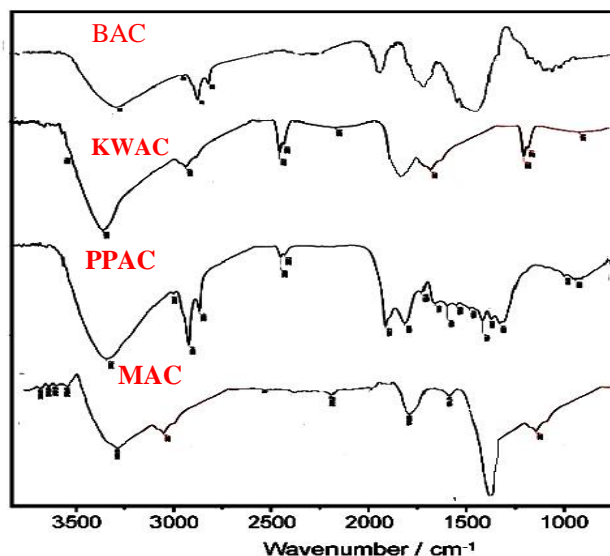

Fig.2 : FTIR of Activated Carbon

Removal of Cu (II) ions

Effect of pH

The pH of the wastewater is one of the imperative factors governing the adsorption of the metal ions. The effect of pH on the percentage of removal of Cu(II) ion by the various fruit peels and the activated carbon samples after 1st and 2nd cyclic solution load was studied from a range of pH= 2 to 10 and illustrated in Figs.3. For various fruit peels studied, the percentage of removal after second load of removal treatment was higher than that after the first load of removal treatment, and the activated carbon samples showed higher removal percentage than the non activated samples, dried fruit peels, all over the rang of pH studied. Also, all the studied samples showed percentage of removal which increase by increasing the pH values from 2 to 6~ 8. In pH range 8-10 the percentage of removal decreased in all the studied samples. M, MAC, PP and PPAC samples showed maximum percentage of removal at pH 6, while KW,KWAC, B and BAC samples showed the maximum at pH 8. This could be explained by decreasing the number of negatively charged adsorbent sites and increasing the number of positively charged sites at low pH values. This did not favor the adsorption of positively charged cations like Cu(II) due to electrostatic repulsion. Increasing the pH values to become near the neutral or alkaline values will lead to deprotonation of the acid sites on the adsorbent surface and the surface becoming negatively charged with high attractive properties. This leads to increase in the surface diffusion of Cu(II) ions into the adsorbent surface which highly increased the percentage of removal. Similar results were reported by previous investigators. Some researchers stated that the increase in metal biosorption after pre-treating the biomass, could be due to the removal of surface impurities and exposure of latent binding sites for metal biosorption [27]

Effect of Initial Element Concentration

Removal percentage at different initial pollutant concentrations gives information about the removal capacity of the adsorbent [28]. The removal percentage (R%) of Cu(II) ions by the various fruit peels at different initial concentrations from 25 to 1000 mg/L was studied and illustrated in Fig. 4. For all the studied fruit peels, the percentage of removal decreased as the initial concentrations of Cu(II) ions in solution increased. About 11- 20 % of the removal efficiency was decreased by increasing the concentration of Cu(II) ions in solution from 25 to 1000 mg/L. Banana and kiwi peels showed the highest R% to copper ions while mandarin and permanganate peels showed a comparable results. The decrease of R% by increasing the initial concentrations of heavy metal can be explained by the fact that all the

adsorbents had a limited number of active sites, which would have become saturated above certain concentration. Besides, increasing of the initial metal concentration results in a decrease in the initial rate of external diffusion[29]. Also increasing the initial metal concentration decreases the driving force for adsorption (Conc. of metal ions / conc. of active sites) which decreases the metal ions diffusion from solution into the adsorbent platelets.

For activated carbon samples the change of R% with the initial Cu(II) ions was shown in Fig.5. Activated carbon samples showed higher R% to copper ions than the fruit peels whatever the initial concentration of Cu(II) ions in the solution. About 100% of copper ions were removed by activated carbon samples derived from banana peels at initial concentrations 25 mg/L. 96% was removed by activated carbon derived from kiwi or mandarin while 92% was recorded for active carbon derived from permanganate peels at the same initial concentration. At higher initial concentration, 1000 mg/L, 90% of copper ions were removed by both KWAC and BAC while 82 and 71 % was recorded for MAC and PPAC samples. The variation of R% by various carbon samples related to the difference in pore structure and the function groups present on the surface which are responsible for the uptake and removal of p   o   l   l   u   t   a   n   t
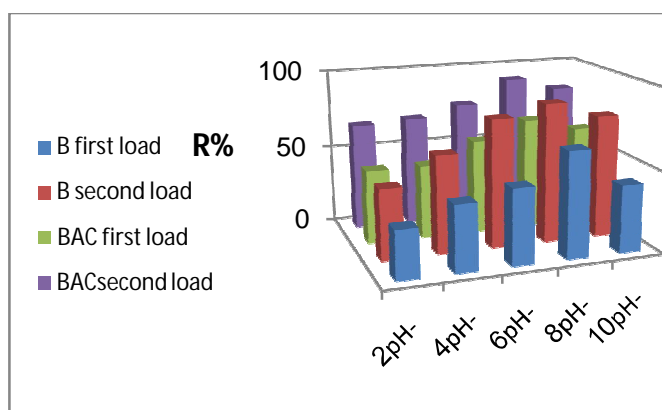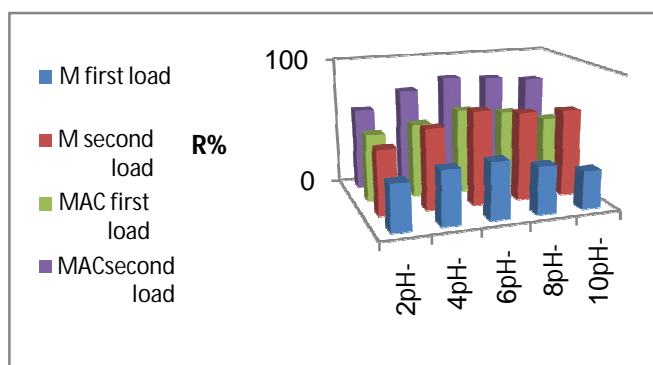
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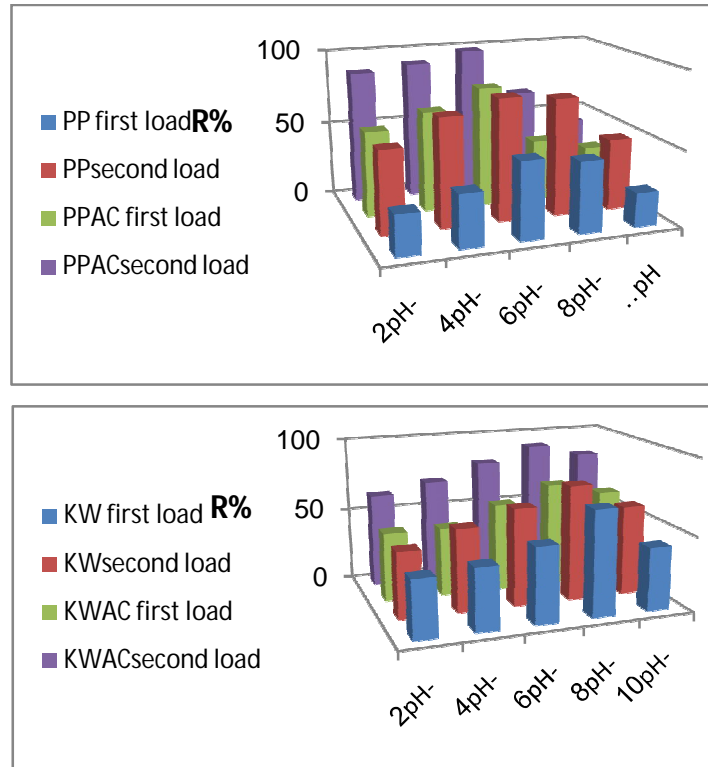
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Fig.(2): **The effect of pH on of percentage of removal of Cu (II) using various fruit peels and activated carbons after 1st and 2nd removal load..**
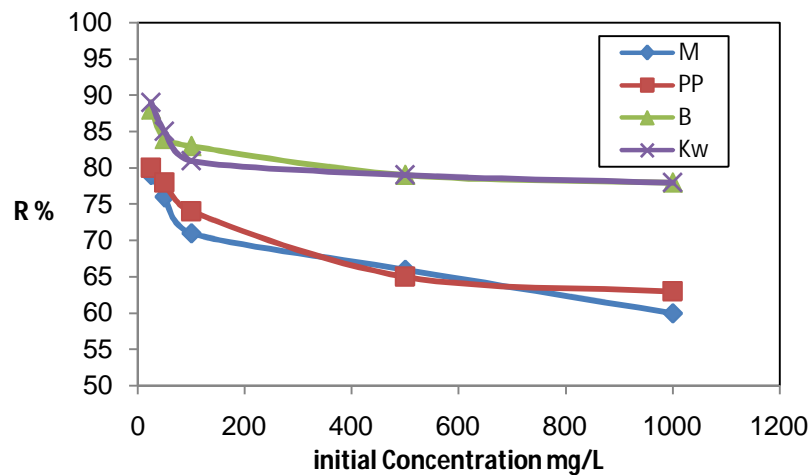

Fig.4: The variation of percentage of removal of Cu(II) ions into various fruit peels.
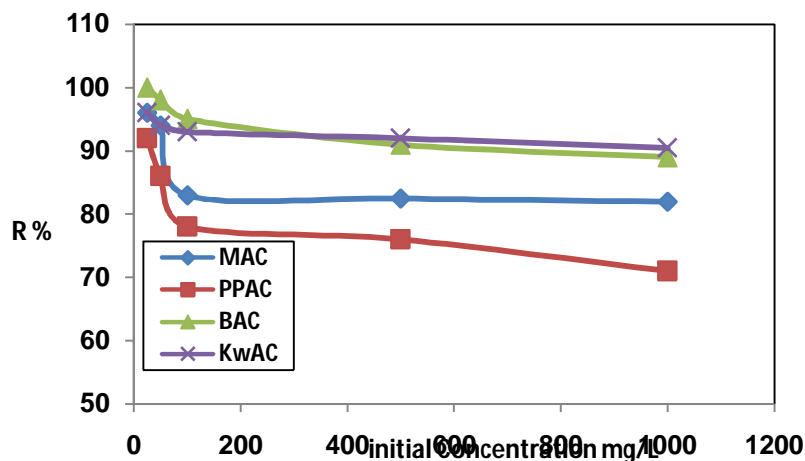
Fig.5: The variation of percentage of removal of Cu(II) ions into various activated carbon sample

Effect of Contact Time

Studying the effect of contact time on the removal of a certain pollutant is an important process to understand the rate of removal. The relation between the percentage of removal of Cu(II) ions and the time of contact into fruit peels or the activated carbons are represented in Fig. 6 and 7. According to the results illustrated in Fig.(6), the removal process of Cu(II) ion by the fruit peels can be divided into two stages; one fast stage in the first 20 minutes in which the diffusion of the Cu(II) ions from the bulk of the solution to the surface of the adsorbent was high. About 51~ 53% of Cu ions were removed by mandarin and permanganate peels while 63% were removed by kiwi and banana peels in this stage This fast stage was followed by a gradual stage of removal from 20 to 60 minutes in which the diffusion of the pollutant ions to the pore structure and the internal surface of the adsorbent was slow due to the activated sites became nearly engaged and unavailable.

The activated carbon samples showed percentage of removal for Cu(II) ions higher than their fruit peels at all the investigated contacted times. Activated carbon samples derived from banana peels showed the highest percentage of removal (about 92% of copper ions are removed after 1 hr) between all the studied fruit peels while the carbon samples derived from kiwi and mandarin showed a comparable values (84% and 81% respectively) of removal percentage and permanganate showed the lowest (71%).
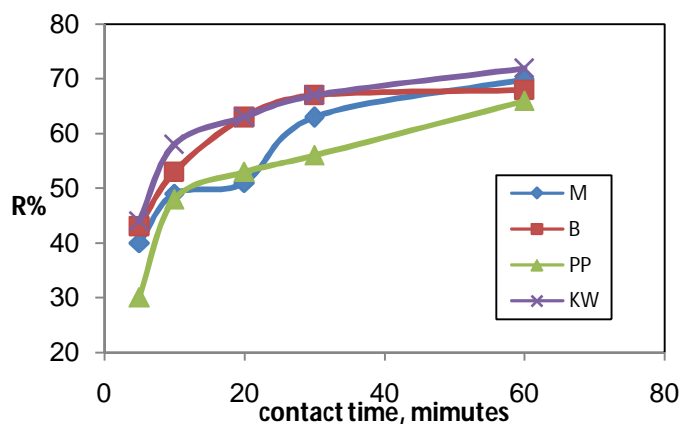

Fig. (6): Removal efficiency (%) for various fruit peels at different contact times.
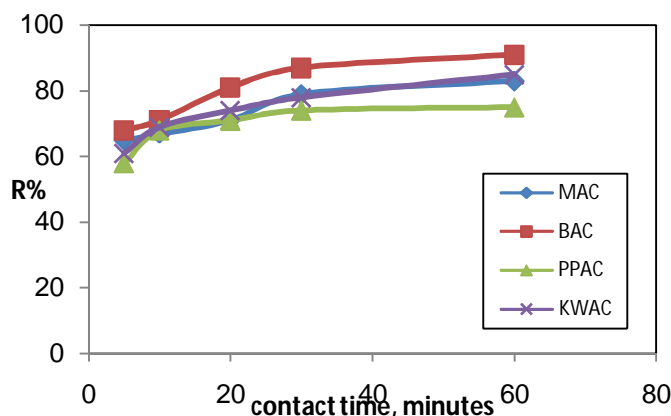
Fig. (7): Removal efficiency (%) for various activated carbon samples at different contact times.

IV. CONCLUSION

Activated carbon produced by chemical treatment using phosphoric acid showed higher removal efficiency compared to the dried fruits peels from which they are produced . The activated carbon derived from banana and kiwi peels showed higher efficiency for Cu(II) removal while these derived from mandarin and pomegranate peels showed acceptable results.

V. ACKNOWLEDGEMENT

REFERENCES

[1]   Coleman, N.J., D.S. Brassington, A. Raza, A.P. Mendham , Sorption of Co^{2+} and Sr^{2+} by waste derived 11 Å tobermorite. *Waste Management*, 26: 260-267, 2006.

[2] Aksu, Z., Determination of the equilibrium, kinetic and thermodynamic parameters of the batch biosorption of nickel(II) ions onto *Chlorella vulgaris*. *Process Biochemstry*, 38: 89-99, 2002.

[3]Zhao D., Jaroniec M., Hsiao B.S., . Editorial for themed issue on 'Advanced materials in water treatments'. *Journal of Materials Chemistry* 20, 4476-4477. , 2010,DOI: 10.1039/C005140N.

[4]Means J.L., D.A. Crerar, M.P. Borcsik, and J.O. Duguid, Adsorption of Co and selected Actinides by Mn and Fe oxides in soils and sediments. *Geochimica et Cosmochimica Acta*, 42:1763- 1773, 1978.

[5]Pandey, P.K., Y. Verma, S. Choubey, M. Pandey and K. Chandrasekhar, 2008. Biosorptive removal of cadmium from contaminated groundwater and industrial effluents. Bioresource Technology, 99 (10) : 4420-4427, 2008.

[6]Ahluwalia, S.S. and D. Goyal, Microbial and plant derived biomass for removal of heavy metals from wastewater. Bioresource Technology, 98(12): 2243- 2250, 2007

 [7] Ajmal, M., R.A.K. Rao and B.A. Siddiqui, 1996. Studies on removals and recovery of Cr(VI) from electroplating wastes. Water Res., 30: 1478-1482, 1996

[8] Ajmal, M., R.A.K. Rao, R. Ahmad, J. Ahmad L.A.K. Rao, . Removal and Recovery of Heavy   metals from electroplating wastewater by using kyanite as an adsorbent J. Haz. Mat., 87: 127-137,2001

[9]Forstner, U. and C.T.W. Wittman, 1981. Metal Pollution in the Aquatic Environment, Springer, New York, pp: 211,1981.

[10] Jenkins, D.W., 1976. In the Proceedings of the International Conference on Environmental Sensing and Assessment, Vol.1, Willey Inter science.New York, 1976.

[11]WHO, 1984. Guidelines for Drinking Water Quality Recommendations, Vol. I, WHO, Geneva, 1984.

[12]Sari A., Tuzen M., Citak D., Soylak M., Equilibrium, kinetic and thermodynamic studies of adsorption of Pb(II) from aqueous solution onto Turkish kaolinite clay, *Journal of Hazardous Materials* , **149**, 283–291, 2007.

[13] K. Kadirvelu, K. Thamaraiselvi, C. Namasivayam, Removal of heavy metals from industrial   wastewaters by adsorption onto activated carbon prepared from an agricultural solid waste, Biores. Technol. 76 (2001) 63–65

[14] K. Kadirvelu, P. Senthilkumar, K. Thamaraiselvi, V. Subburam, Activated carbon prepared from biomass as adsorbent: elimination of Ni(II) from aqueous solution, Biores. Technol. 81 87–90,2002

[15] W.C. Leung, M.F.Wong, H. Chua,W. Lo, P.H.F. Yu, C.K. Leung, Removal and recovery of heavy metals by bacteria isolated from activated sludge treating industrial effluents and municipal wastewater,Water Sci. Technol. 41 (12) 233–240, 2002.

[16]W. Qiao, Y. Korai, I. Mochida, Y. Hori, T. Maeda, Preparation of an AC artifact: oxidative modification of coconut shell-based carbon to improve the strength, Carbon 40 351–358, 2002 .

[17]S. Haydar, M.A. Ferro-García, J. Rivera-Utrilla, J.P. Joly, Adsorption of p- nitrophenol on an AC with different oxidations, Carbon 41 387–395, 2003.

[18]M.F.R. Pereira, S.F. Soares, J.J.M. Órfão, J.L. Figueiredo, Adsorption of dyes onn ACs: influence of surface chemical groups, Carbon 41 811–821, 2003.

[19]C.Bouchelta, M.S. Medjran, O. Bertrand,J. Bellat,J. Anal. Appl. Pyrol. 28 70–77, 2008.

[20]Y.F. Jia, K.M. Thomas, Adsorption of cadmium ions on oxygen surface sites in AC, Langmuir 16 1114–1122,1999.

[21]K. Kelly-Vargas, M. C. Lopez, S. R. Tellez, E.R. Bandala and J. L. Sanchez-Salas , Biosorption of heavy metals in polluted water using different waste fruit cortex, Physics and Chemistry of the Earth 37–39 26–29, 2012.

[22] El-Ashtoukhy, E.S., N.K. Amin and O. Abdelwahab. Removal of lead(II) and copper(II) from aqueous solution using pomegranate peel as a new adsorbent, Desalination, 223: 162-173,2008.

[23] Basta AH, Fierro V, El-Saied H, Celzard A, 2-Steps KOH activation of rice straw: an efficient method for preparing high-performance activated carbons. Bioresource Technol 100: 3941-3947,2009.

[24]Rao, M.M., Ready D.D.K.K, Venkateswarl. P and Seshaiah. K., Removal of Mercury from Aqueous Solution Using Activated Carbon Prepared From Agriculture by-product/Wast. J. Environmental Management., 90(1):634-643,2008.

[25]Wahi, R., Ngaini, Z., and Jok, U.V. (2009). *Removal of Mercury, Lead and Copper from Aqueous Solution By Activared Carbon of Palm Oil Empty Fruit Bunch*. World Applied Science Journal (Special Issue for Environment): 84-91,2009

[26]Krishnan, K.A., Anirudhan, T.S. ,Removal of cadmium(II) from aqueous solution by stream activated sulphurised carbon prepared from sugar-cane bagasse pith: kinetic and equilibrium studies. Water SA 29: 147,2003.

[27]Nadeem, R., M.A. Hanif, V. Shaheen, S. Perveen M.N. Zafar and I. Iqbal, . Physical and chemical modification of distillery sludge for Pb (II biosorption. Journal of Hazardous Materials 150: 335-342,2008.

[28]G. S. El Shafei, I. N. Nasrb, A. S. M. Hassanb, S. G. M. Mohammad, Kinetics and thermodynamics of adsorption of cadusafos on soils, J. Hazard. Mater. 172 1608–16,2009.

[29]Gode, F. and E. Pehlivan, Removal of Cr(VI) from aqueous solution by tow Lewatit- anion exchange resins, J. Hazard. Mater., 119: 175-182, 2005.