A Study of Characterizations and Efficiency of Activated Carbon Prepared from Peel and Bunch of Banana for Methyl Orange Dye Adsorption

O. Prachpreecha[1], K. Pipatpanyanugoon[2] and P. Sawangwong[3]

[1]*Environmental Science Program, Faculty of Science, Burapha University, Chon buri, Thailand*
[2]*Department of Industrial Engineering, Faculty of Engineering, Burapha University, Chon buri, Thailand*
[3]*Environmental Science Program, Faculty of Science, Burapha University, Chon buri, Thailand*

Abstract: *This research studied the characterizations of activated carbon preparation from peel and bunch of banana by using the FT-IR spectroscopy and SEM (scanning electron microscopy). It was found that changed in surface morphology of activated carbon before and after activation, which showed well developed pore structure in activated carbon demonstrating corrosive effect of H_3PO_4 and studied on adsorption efficient of methyl orange dye on activated carbons. The different parameters: peel and bunch of banana dose (0.01 g to 0.1 g), adsorption times (30 to 150 minutes), pH values 3.0 to 11.0 and temperature (15, 30 and 45 ^{o}C).The results showed that peel and bunch of banana (0.05 g) was a bio-adsorbent for methyl orange dye adsorption under the suitable conditions at 90 minutes adsorption time, pH 5.0 and 30 ^{o}C. The equilibrium adsorption isotherm gave a good corresponding to Langmuir isotherm model with the maximum adsorption capacity were found to be 0.86 (mg/g) for peel of banana and 0.89 (mg/g) for bunch of banana. The results indicate that activated carbon prepared from peel and bunch of banana could be low-cost alternative bio-adsorbent to activated carbon in the wastewater treatment for removal of dyes.*

Keywords: *activated carbon, peel and bunch of banana, adsorption, methyl orange dye*

I. Introduction

The wastewaters resulted from industrial process usually consist of a number of contaminants including acids, bases, dissolved solids, toxic compounds and organic dyes. Methyl orange dye is one of the popular dyes also known as acid orange 52, Orange III or tropaelin D which is a simple model of azoic dyes widely used in paper, plastic, food and textile industries in coloring some products resulting environmentally hazardous waste. The discharge of dyes into natural streams and rivers from the industries is one of the major problems as dyes give toxicity to be carcinogenic and mutagenic to aquatic organisms. Methyl orange dye are resistant to aerobic digestion, stable to light, heat and oxidizing agents due to their structure and damaging to the aesthetic nature of the environment [1-2].

Researches have been performed to develop effective treatment technologies for wastewaters containing dyes, such as electro-coagulation, membrane filtration, electrochemical destruction, ion exchange, irradiation, advanced oxidation, ozonation, precipitation and adsorption involving the use of activated carbon [3]. Activated carbon is the most popular adsorbent, which has been used with great success. However, activated carbon is expensive and its regeneration and reuse makes it more costly. Consequently, many researchers have studied the feasibility of using low-cost substances for the removal of various dyes and pollutants from wastewaters [4]. Basically, there are two different processes for the preparation of activated carbon: physical and chemical activation. Physical activation involves carbonization of carbonaceous precursor followed by activation of resulting charcoal in the presence of activating agents. Chemical activation on the other hand, involves the carbonization of precursor in the presence of chemical agents. Chemical activation has more advantages over physical activation with respect to higher yield, more surface area and better development of porous structure oxygenated surface complexes in carbon [5].

In the present study, to observe the applicability of product in treatment system, its characterization has been done for physical, chemical and adsorption properties of activated carbon was prepared from low-cost adsorbent (peel and bunch of banana wastes).Thai banana know as "Kluai Nam Wa" and scientific name is *Musa sapientum* L., is one of the most popular fruit in Thailand. The FT-IR and SEM studies were carried out to see the porosity and surface functional groups development in the product upon activation. The efficiency of activated carbon for methyl orange dye adsorption was then described in isotherm models (Langmuir and Freundlich)

II. Materials and Methods

2.1 Preparation of activated carbons

Thai banana known as "Kluai Nam Wa (*Musa sapientum* L.) was the bio-adsorbent of choice use in this study. The banana waste consisting of peel and bunch used in the study were obtained from a group of agricultural housewives group at Pakthongchai district, Nakhonratchasima, Thailand. The peel and bunch of banana wastes were cut into small pieces (1-2 cm), collected, dried, crushed and washed thoroughly tree times with deionized water to remove the adhering dirt. They then were air dried in an oven at 100–120 ◦C for 24 hours and then bring the peel and bunch of banana had dried in a ceramic packaging for burned in carbolite until the desired temperature (300, 400, 500 600 and 700˚C) by increasing the temperature at a rate of 5˚C/ minutes to the desired temperature at the freezing temperature about 1 hour. After cooling the resulted charcoal burnt carbonized at different temperature was tested iodine number. The selected charcoal of highest iodine number as tested by standard method ASTM D 4607-94 [6] was ground and sieved to be use in the study (at 500 ˚C carbonization temperature was chosen for this study because iodine number were highest). After that the charcoal was carbonized with phosphoric acid (50 % H_3PO_4) and then was burnt to charcoal to be used as a raw material in the synthesis of activated carbon. The charcoal was activated in the carbolite to 600, 700, 800 and 900˚C by increase the temperature at a rate of 10˚C/minutes. When the desired temperature is reached soaked at this temperature for about 2 hours and then left to cool down for 30 minutes at 200˚C. The products were washed thoroughly with hydrochloric acid (5% HCl), followed by hot water many times until pH 6.5-7.0. The activated carbons from both produces were kept dried at a temperature of 120˚C and selected activated carbons of highest iodine number as tested by standard method ASTM D 4607-94 [6] was etherification in order to study the adsorption efficiency after modification (at 800 ˚C carbonization temperature, the iodine number highest of activated carbons from both produces).

2.2 Characterizations of activated carbon preparation from peel and bunch of banana by using the SEM studies and FT-IR determination

To observe the surface pore structure of activated carbons, SEM studies were carried out using scanning electron microscope (LEO, Model 1450 VP, UK). In the present study, conducting material coating on specimen was done with gold metal by vacuum evaporation to get uniform thickness of specimen during analysis and FT-IR determination by using Fourier-Transformed Infra Red (FT-IR*)* spectroscopy (Bruker, Model tensor 27, Germany), where the spectra were recorded from 4000-400 cm^{-1}.

2.3 Batch adsorption experiments

Batch equilibrium adsorption experiments were performed in a set of 125 (mL). Stoppered flasks (Erlenmeyer flasks) using 30 (mL) of methyl orange dye solution with initial concentrations was 3.0 (mg/L) and adsorbent dose range of 0.01 to 0.1 (g). The flasks were placed in a thermostatic shaker at temperature 15, 30 and 45(ºC) and shaken at 150 rpm for 30-150 minutes. A pH value was measured with model Eco Sense pH 10/Temperature Pen YSI Incorated (USA). A Perkin Elmer (USA) model Optima 2100 DV ICP-OES (inductive couple plasma optical emission spectrometer) was used to determine methyl orange concentration. The removal percentage (R%) of methyl orange dye by the adsorbents, amount of the dye adsorbed at time t, q_t (mg.g^{-1}) and at equilibrium, q_e (mg.g^{-1}) were calculated by the following equations (1) respectively

$$R\% = \frac{(C_0 - C_t)}{C_0}x100, \qquad q_t = (C_0 - C_t)x\frac{V}{W}, \qquad q_e = (C_0 - C_e)x\frac{V}{W} \quad ....(1)$$

Where C_0, C_e and C_t (mg/L) are the concentrations of methyl orange dye solution at initial equilibrium and at time (t) respectively, *V* (L) is the volume of the solution and *W* (g) is the mass of dry adsorbent used.

III. Results and Discussion

3.1 Characterizations of activated carbon preparation from peel and bunch of banana
3.1.1 SEM studies

A scanning electron microscope (SEM) was used to examine the surface of charcoal from peel and bunch of banana before activation and activated carbon after activation (Fig. 1 and 2). The SEM images of charcoal showed holes that were spaced out on the surface with smooth edges. While the SEM images of activated carbon show the presence of wide pore which resulted due to chemical activation with H_3PO_4 at 800˚C. The SEM images of charcoal and activated carbon show that activation plays key role in porosity development which is largely responsible for the extent of surface area and adsorptive capacity of carbon [7].
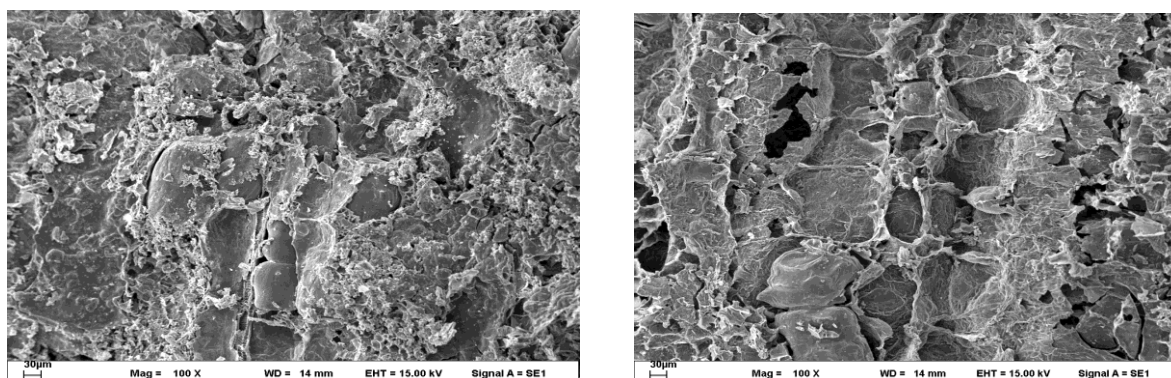
(a1)   (b1)

Fig. 1. SEM images of charcoal from peel of banana before activation (a1)
and activated carbon after activation (b1) with 100x magnifications
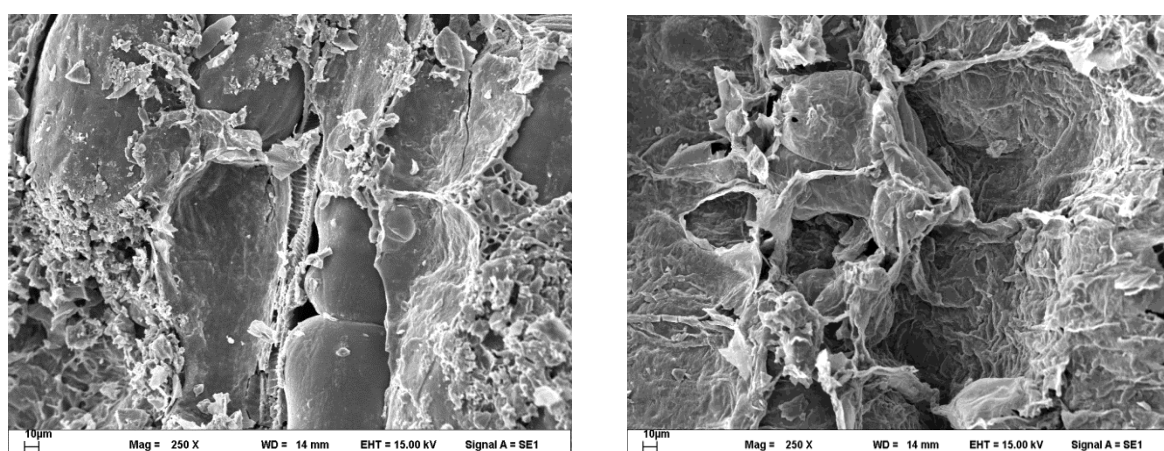
(a2)   (b2)

Fig. 2. SEM images of charcoal from bunch of banana before activation (a2)
and activated carbon after activation (b2) with 250x magnifications

3.1.2 FT-IR determination

The FT-IR is an important technique to qualitatively determinate characteristic functional groups, which make the adsorption behavior possible. Figs. 3 and 4 shows the IR spectrums of charcoal and activated carbon from peel and bunch of banana. There is formation of more surface functional groups on carbon as compared to char due to activation (Table. 1 and 2). The adsorption bands of activated carbon from peel of banana after carbonization at 800˚C were appeared at 3192 cm^{-1} are corresponding to OH stretching of hydroxyl, 1584 cm^{-1} indicate C=O stretching of carboxylic acid or ester, 1449, 1361, 1303, 768, 703 and 617cm^{-1} indicate C-H stretching of alkane, 1110 cm^{-1} indicate C-O stretching vibrations in alcohols, phenols, acids, ethers or esters 881cm^{-1} indicate C-C stretching vibration in aromatic rings [8]. The compared with that of charcoal from peel of banana, the prominent peak intensity at stretching of O-H and C-O were significantly increase, C-H was significantly reduced and not appeared, confirming the damage of polysaccharide or protein in porous carbon materials after carbonization at 800˚C with H_3PO_4 [9].

The adsorption band of activated carbon from bunch of banana were appeared at 2715 and 2285 cm^{-1} are corresponding to P-OH stretching, bands at 1557 cm^{-1} indicate C=C stretching, 1115 cm^{-1} indicate C-O stretching, 931and 670 cm^{-1} indicate C-H stretching. The compared with that of charcoal from bunch of banana the prominent peak intensity at stretching of O-H was significantly reduced and not appeared, after carbonization at 800˚C with H_3PO_4 was appeared P-OH stretching.

Table. 1. Some fundamental IR absorption frequencies of charcoal and activated carbon from peel of banana

Charcoal		Activated carbon	
Band position (cm^{-1})	Possible assignment	Band position (cm^{-1})	Possible assignment
3338	O-H stretching	3192	O-H stretching
2921	C-H stretching	1584	C=C stretching
2850	C-H stretching	1449	C-H stretching
1564	C=C stretching	1361	C-H stretching

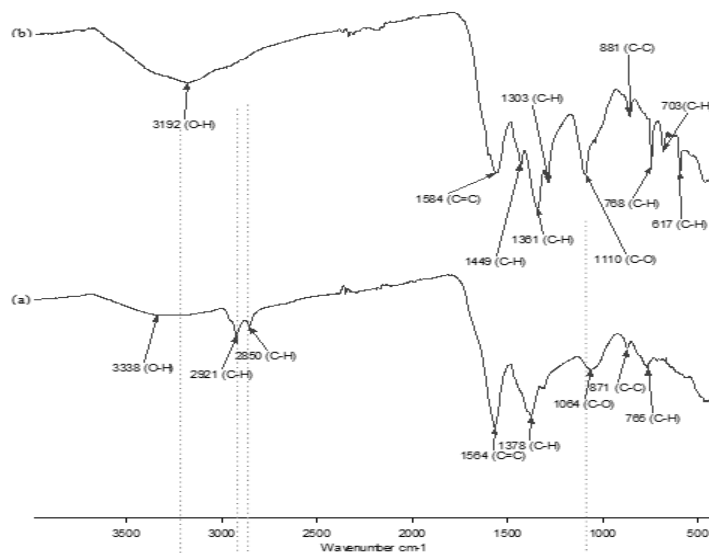| 1378	C-H stretching	1303	C-H stretching
1064	C-O stretching	1110	C-O stretching
871	C-C stretching	881	C-C stretching
765	C-H stretching	768	C-H stretching
		703	C-H stretching
		617	C-H stretching

Fig. 3. FT-IR spectra of charcoal from peel of banana (a) and activated carbon from peel of banana (b)

Table. 2. Some fundamental IR absorption frequencies of charcoal and activated carbon from bunch of banana

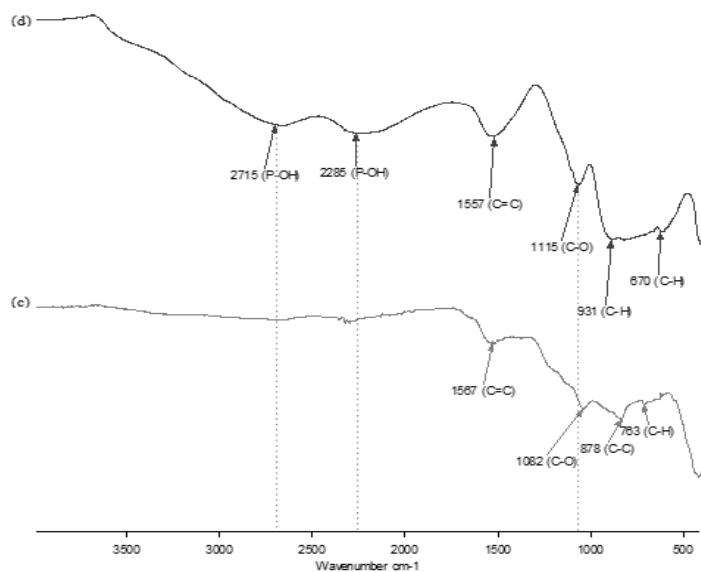| Charcoal		Activated carbon	
Band position (cm⁻¹)	Possible assignment	Band position (cm⁻¹)	Possible assignment
1567	C=C stretching	2715	P-OH stretching
1082	C-O stretching	2285	P-OH stretching
878	C-C stretching	1557	C=C stretching
763	C-H stretching	1115	C-O stretching
		931	C-H stretching
		670	C-H stretching

Fig. 4. FT-IR spectra of charcoal from bunch of banana (c)
and activated carbon from bunch of banana (d)

3.2 Effect of adsorbent dose

An effect of weight activated carbon (peel and bunch of banana)in the range of 0.01 to 0.1(g) was investigated using 3.0 (mg/L) of solution containing methyl orange dye and 90 minutes adsorption time. Fig. 5 showed the increasing of banana peel and bunch weight from 0.01 to 0.05 (g) was corresponded to the higher adsorption abilities from 59.91% to 90.09% for peel of banana and 53.35% to 96.00% for bunch of banana. However, the percentage of adsorption was found to be constant at higher 0.05(g) for peel and bunch of banana because saturated active sides of both were presented. Therefore, 0.05(g) was optimal weight for this study. The increase in the removal of dyes with adsorbent dose due to the introduction of more binding sites for adsorption. The primary factor explaining this characteristic is that adsorption sites remain unsaturated during the adsorption reaction whereas the number of sites available for adsorption site increases by increasing the adsorbent dose [7, 10].
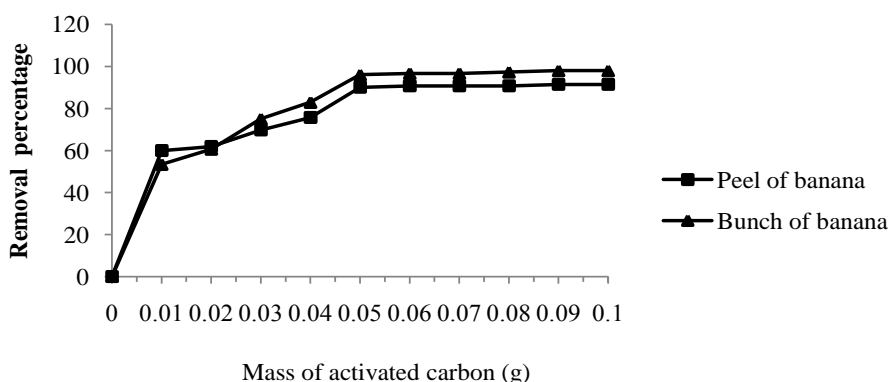

Fig. 5. Methyl orange dye removal efficiency vs. adsorbent dose for peel and bunch of banana

3.3 Effect of adsorption time

The effect of adsorption time between the solution containing methyl orange dye and activated carbon form peel and bunch of banana inside the shaken conical flask. The concentrations of solution containing methyl orange dye used were 3.0 (mg/L). The adsorption times were 30, 60, 90, 120 and 150 minutes. The percentage of adsorbed methyl orange dye with different adsorption time was shown in the Fig. 6.

From the Fig.6, the percentage of methyl orange dye removal from the aqueous solution increased rapidly and reached up to 95.34% for peel of banana and 92.74% for bunch of banana at 90 minutes. It was clearly seen that 90 minutes shaking time could be adopted as an equilibrium time for maximum adsorption. The percentage of methyl orange dye removal was rapid due to adsorption of the dye molecules on the upper surface of the adsorbent. Then it became slow due to slow passing of molecules into the inner structure of the adsorbent [11].
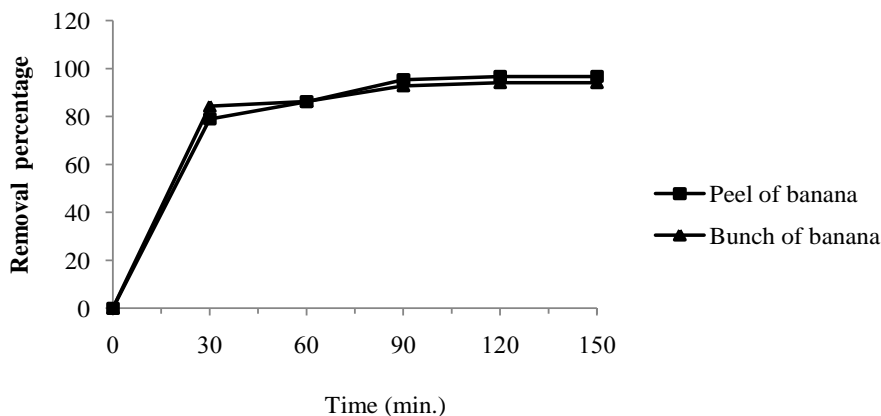

Fig. 6. Methyl orange dye removal efficiency vs. adsorption time for peel and bunch of banana

3.4 Effect of pH value

An effect of pH was studied in the pH range of 3.0 to 11.0 to investigate the adsorption efficiency of activated carbons from both produces under 90 minutes time and 0.05 g dose. From the study, the adsorption of solution containing methyl orange dye was found to continuously increase with pH values from 3.0 to 5.0 and then stayed in maximum at pH 5.0 as shown in the Fig.7. At lower pH, the surface charge may be positively charged which enhance the adsorption process. Moreover, the decrease in the adsorption of methyl orange dye with an increase of pH value is also due to the competition between anionic dye and excess OH-ions in the solution, which may be due to the fact that the high concentration and high mobility OH-ions are preferentially adsorbed compared to dye anions [12].
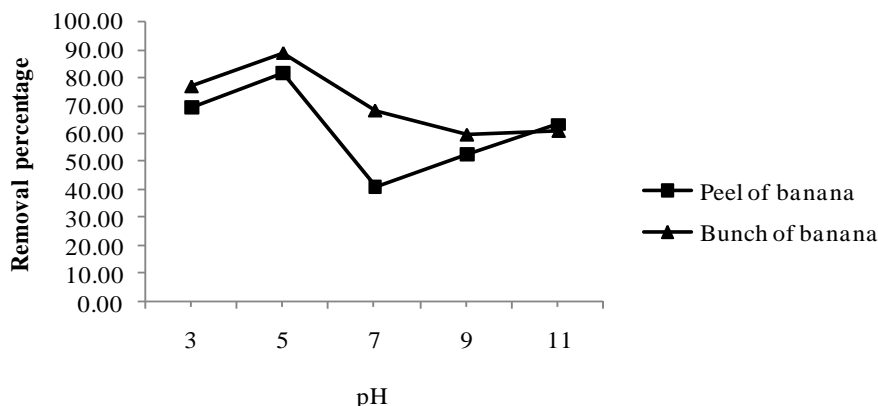

Fig. 7. Methyl orange dye removal efficiency vs. pH values for peel and bunch of banana

3.5 Effect of temperature

An effect of temperature on adsorption for solution containing methyl orange dye were 15, 30 and 45 (^{o}C), 90 minutes adsorption time and optimal pH was 5.0 shown in the Fig. 8. The percentage of adsorption was reached up to 78.94% for peel of banana and 83.53% for bunch of banana at 30 (^{o}C). The temperature has a pronounced effect on the adsorption process from the change in temperature will cause changes in the equilibrium capacity of the adsorbent for adsorption of particular adsorbate. The adsorption of methyl orange dye on activated carbon decreases as the solution temperature increases. It was explained that as the temperature increased, the physical bonding between the organic compounds (methyl orange dyes) and the active sites of the adsorbent weakened [13].
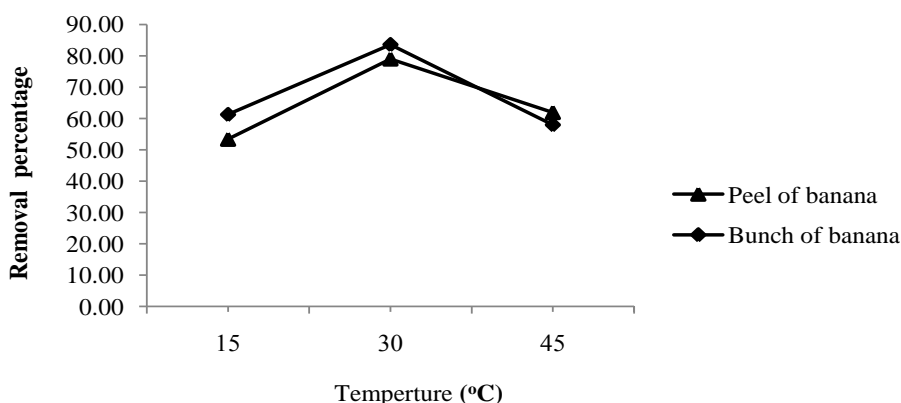

Fig. 8. Methyl orange dye removal efficiency vs. temperature for peel and bunch of banana

3.6 Adsorption isotherm

Experimental isotherm data collected for the adsorption of activated carbon from both produces are fitted in Langmuir and Freundlich adsorption isotherm models.

3.6.1 Langmuir model

The Langmuir isotherm is valid for monolayer adsorption onto a surface with a finite number of identical sites. The Langmuir model is based on the assumption of adsorption homogeneity, such as equally available adsorption sites, monolayer surface coverage, and no interaction between adsorbed species. If dyes adsorption follows the Langmuir model, the adsorption process can be expressed as equation (2).

$$\frac{C_e}{q_e} = \frac{1}{bq_m} + \frac{C_e}{q_m}$$ ……………………………………………………(2)

Where q_m (mg/g) the maximum adsorption capacity and bq_m is the Langmuir constant related to the rate of adsorption [14]. The Langmuir plot of "C_e/q_e" vs "C_e" at 0.5, 1.0, 2.0 and 3.0 (mg/L) is shown in Fig. 9 and 10. The results calculated from the plot are given in Table. 3. The Langmuir adsorption capacity varies from 1.742 to 1.763 (mg/g) for peel of banana and 1.742 to 1.761 (mg/g) for bunch of banana over the range of initial dye concentration studied. The Langmuir isotherm fits the experimental data well ($R^2 = 0.9989$ and 0.9998).

3.6.2 Freundlich model

The Freundlich equation is the empirical relationship whereby it is assumed that the adsorption energy of dye binding to a site on an adsorbent depends on whether or not the adjacent sites are already occupied. The Freundlich isotherm model is usually adopted for heterogeneous adsorption. One limitation of the Freundlich model is that the amount of adsorbed solute increases indefinitely with the concentration of solute in the solution. This isotherm can be described as follows equation (3).

$$\ln q_e = \log k_f + \frac{1}{n} \log C_e$$ ……………………………………………..(3)

Where k_f (mg/g)(L/g)$^{1/n}$ and n are the physical constants of the Freundlich adsorption isotherm. The k_f and n are indicators of the adsorption capacity and adsorption intensity, respectively [15]. The Freundlich constants were obtained from a plot of "log q_e" vs "log C_e" at 0.5, 1.0, 2.0 and 3.0 (mg/L) is shown in Fig. 11 and 12. The results calculated from the plot are given in Table. 4. The Freundlich constant (K_f) is 1.746 (L/mg) for peel of banana and 1.747 (L/mg) for bunch of banana. On increasing the initial dye concentration from 0.5 to 3.0 (mg/L), the adsorption capacity also increases ($R^2 = 0.9564$ and 0.9678).

The both Langmuir and Freundlich models, show the intercept and slope for the straight lines used in the calculations of isotherm constants tabulated in Table. 3. In order to decide which type of isotherm fits the experimental data better, the applicability of the model is established from the regression coefficient R-square (R^2). Langmuir model is more appropriate to explain the nature of adsorption with correlation coefficient is 0.9989 and 0.9998 for activated carbon prepared from peel and bunch of banana while Freundlich model shows poorly fit ($R^2 = 0.9564$ and 0.9678) for activated carbon from both produces, respectively. Langmuir is the more important model for monolayer adsorption, based on the assumption that the adsorption process takes place at specific homogeneous sites within the adsorbent surface and that once a dye molecule occupies a site, no further adsorption can take place at that site, which concluded that the adsorption process is monolayer in nature [16].
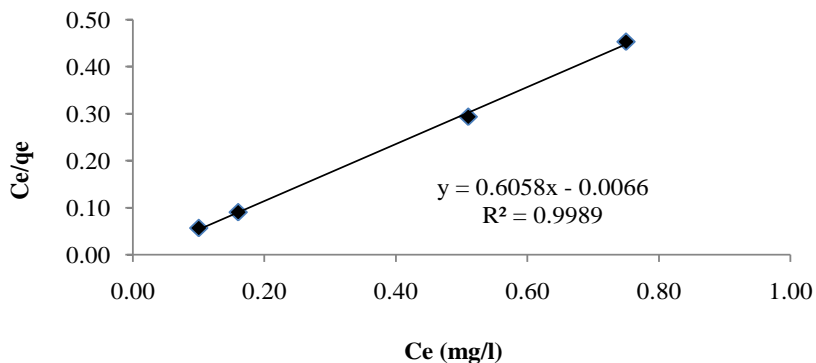
Fig. 9. Langmuir isotherm of methyl orange dye by activated carbon from peel of banana
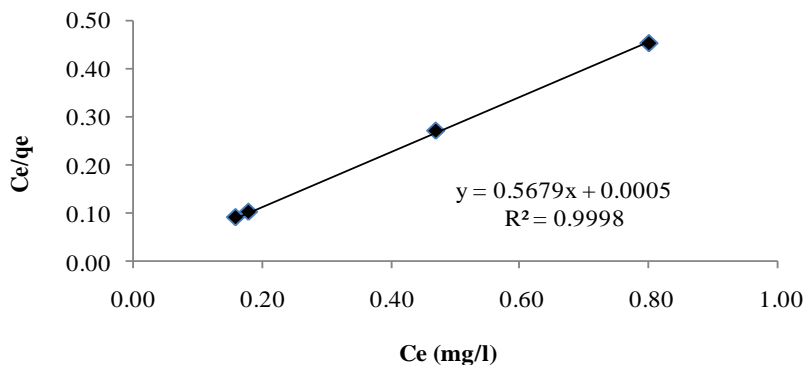

Fig. 10. Langmuir isotherm of methyl orange dye by activated carbon from bunch of banana
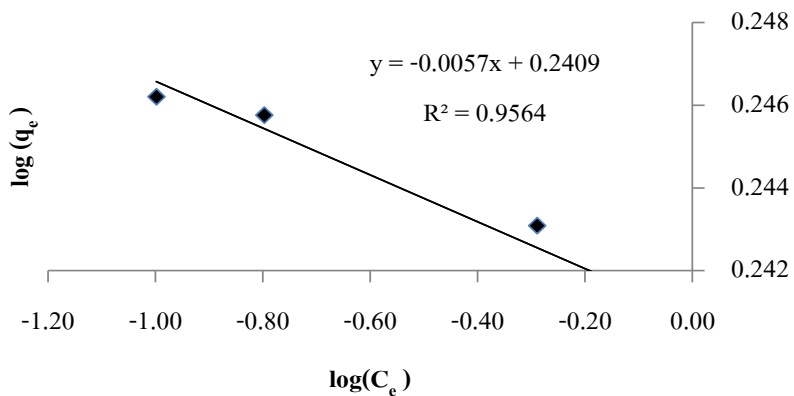

Fig. 11. Freundlich isotherm of methyl orange dye by activated carbon from peel of banana
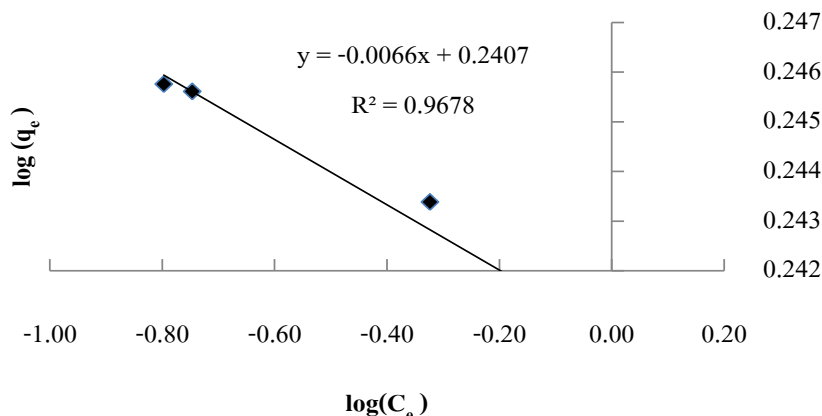
$$y = -0.0066x + 0.2407$$
$$R^2 = 0.9678$$

Fig. 12. Freundlich isotherm of methyl orange dye by activated carbon from bunch of banana

Table. 3. Parameters obtained for the Langmuir and Freundlich equation

Activated carbon	Langmuir equation			Freundlich equation		
	q_m (mg/g)	K_L (L/mg)	R^2	K_F (L/mg)	1/n	R^2
Peel	1.651	91.77	0.9989	1.746	0.0057	0.9564
Bunch	1.761	1135.72	0.9998	1.747	0.0066	0.9678

IV. Conclusions

Activated carbons were prepared from peel and bunch of banana at 800°C by chemical activation with H_3PO_4, was used to successfully for the removal of reactive methyl orange dye from aqueous solutions. Activation process also modifies of more functional groups as compared to charcoal, which surely enhances the performance of adsorbent. The shifting of peaks in FT-IR spectrum confirmed the methyl orange dye adsorption onto activated carbons. The SEM study also made support to it by observing difference in surface morphology of adsorbent before and after activated by H_3PO_4. The activated carbons from peel and bunch of banana was a bio-adsorbent methyl orange dye adsorption under the suitable conditions at 90 minutes adsorption time, pH 5.0 and 30°C. The Langmuir and Freudlich adsorption isotherm models were used for the description of the adsorption equilibrium of methyl orange dye onto the adsorbent. It was found that equilibrium data were best described by the Langmuir isotherm model. Moreover, the adsorption process takes place through electrostatic interaction between adsorbate species in solution and surface of the adsorbent. This adsorption process is expected to economically various environmental applications including treatment of drinking water, removing color from industrial effluents, removal of heavy metals and wastewater treatment system of agricultural.

Acknowledgments

References

[1]. A.G., Abdullah, M.A., Mohd Sallah, M.K., SitiMazlina, M.J., Megat Mohd Noor, M.R., Osman, R., Wagiran and S., Sobri, Azodye removal by adsorption using waste biomass: Sugarcane Bagasse, International Journal of Engineering and Technology, 2(1), 2005, 8-13.

[2]. VC., Srivastava, MM., Swamy, ID., Mall, Adsorptive Removal of Phenol by Bagasse fly ash and Activated Carbon: equilibrium, kinetics and thermodynamic study, Colloids and Surfaces A: Physicochemical and Engineering Aspects, 272, 2006, 89-104.

[3]. V., López-Grimau and M.C.Gutiérrez, Decolourisation of simulated reactive dye bath effluents by electrochemical oxidation assisted by UV light. International Journal of Chemosphere Research, 62, 2006, 106-112.

[4]. U.R., Lakshmi, V.C. Srivastava, I.D. Mall and D.H. Lataye, Rice husk ash as an effective adsorbent:Evaluation of adsorptive characteristics for Indigo Carmine dye. International Journal of Environmental Management, 90, 2009, 710-720.

[5]. M.A., Lillo-Rodenas, D., Carzrola-Ameros and A., Linares-Solano, Carbon, 2003, 265.(41)

[6]. ASTMD., Standard test method for determination of iodine number of activated carbon. Annual book of ASTMD standard Sec. 15, 15.01, 2011, D4607-94.

[7].   R., Malik, DS, W, S. R., Ramteke, Adsorption of malachite green on groundnut shell waste based powdered activated carbon, Waste Manage, 27, 2007, 1129-1138.

[8].   W., Tongpoothorn, M., Sriuttha, P., Homchan, C., Ruangviriyachai, Preparation of activated carbon derived from Jatrophacurcas fruit shell by simple thermo-chemical activation and characterization of their physico-chemical properties. International Journal of Chemical Engineering Research, 89, 2011, 335–340.

[9].   P., Sugumaran, V., Priya Susan, P., Ravichandran and S., Seshadri, Production and Characterization of Activated Carbon from Banana Empty Fruit Bunch and Delonixregia Fruit Pod. Journal of Sustainable Energy & Environment, (3), 2012, 125-132.

[10].   J., Yener, T., Kopac, G, D, T., Dogu. Adsorption of Basic Yellow 28 from aqueous solutions with clinoptilolite and amberlite, Journal of Colloid and Interface Science, 294, 2006, 255-264.

[11].   A.A., Ahmad, B.H. Hameed and N., Aziz, Adsorption of direct dye on palm ash: Kinetic and equilibrium modeling, Journal of Hazardous Materials, 141, 2007, 70-76.

[12].   A., Khaled, A., El Nemr, A, A, A., Ei-Sikaily, Treatment of artificial textile dye effluent containing Direct Yellow 12 by orange peel carbon, Desalination, 238, 2009, 210-232.

[13].   IW., Tan, AL, H, B. H., Ahmad, Adsorption of basic dye using activated carbon prepared from oil palm shell: batch and fixed bed studies, Desalination, 225, 2008, 13-28.

[14].   V., Lugo-Lugo, S., Hernandez-Lopez, C., Barrear-Diaz, F., UrenaNunez, and B., Bilyeu, A comparative study of natural, formaldehy detreated and copolymer-grafted orange peel for Pb(II) adsorption under batch and continuous model, Journal of Hazardous Materials, 161, 2009, 1255-1264.

[15].   M., Ajmal, R.A.K., Rao, R., Ahmad, and J., Ahmad, Adsorption studies on Citrus recticulate (fruit peel of orange): removal and recovery of Ni(II) from electroplating wastewater, Journal of Hazardous Materials, B79, 2000, 117-131.

[16].   A., Afkhami, T., Madrakian, and A., Amini, Mo(VI) and W(VI) removal from water samples by acid-treated high area carbon cloth, Desalination, 243, 2009, 258-264.