Research Article   **Open Access**

Assessment of Adsorption Kinetics in a Quaternary Liquid Phase System using Activated Carbon derived from Oil Palm Empty Fruit Bunch

Olateju I. I.[1], Adeodu A. O.[2], Daniyan I. A.[3]

[1]Department of Chemical Engineering, Afe Babalola University Ado-Ekiti, Nigeria.

[2, 3]Department of Mechanical and Mechatronics Engineering, Afe Babalola University, Ado-Ekiti, Nigeria.

*Corresponding author: Adeodu A. O.
                        Department of Mechanical and Mechatronics Engineering,
                        Afe Babalola University,
                        Ado-Ekiti, Ekiti State, Nigeria.
                        E-mail: aadeodu@abuad.edu.ng,

ABSTRACT

A fixed mass of activated carbon as adsorbent was tested for the removal of organic pollutants (phenol, butanol, butan-2-ol and 2- methyl butan-2-ol) from an aqueous solution via batch adsorption experiment. The effect of the pollutants initial concentrations and contacting (agitation) time on pollutants adsorption was investigated. The purpose of the research is to determine the rate of adsorption (adsorption kinetics) of a quaternary system comprising of phenol, butanol, butan-2-ol and 2-methyl butan-2-ol, using activated carbon as the adsorbent. This will achieve the objective of assessing the adsorbent capacity in removing the organics as a function of time from the liquid phase. The adsorption kinetic of the process was carried out through experimentation and analysis which follows first order kinetic model. The results of the batch experiments adsorption kinetics showed that activated carbon exhibited high sorption capacities toward the organic pollutants and were presented in break through curves. The curves indicated that all the organic components experience high adsorption kinetics within the first 30 minutes, with phenol taken the lead. Phenol and butan-2-ol had reached their peak of adsorption at 120 minutes, and at 150 minutes, they were completely removed from the solution. From the analysis, it was concluded that adsorption using activated carbon as adsorbent favours phenol and butan-2-ol more than the other two organic components. To improve on the design of a multi-component adsorbent reactor and to find the best operating conditions, the fundamental equilibrium and kinetic data for adsorption processes are essential.

Keyword: Adsorbent, Adsorption Kinetics, Break through Point, Equilibrium, Quaternary System

INTRODUCTION

The discharge of organic pollutants in the environment is worrying for both toxicological and esthetical reasons [1]. From experience, petroleum companies, both refineries and depots are majorly associated with some environmental problems of water pollution [2] [3] which could even result in climatic change [4] among other impacts. Water pollution has been a matter of great public concern globally [5] and petroleum industries have been identified as major source of the organic compounds [6] which are primarily water pollutants. Some refineries use deep injection well to dispose effluent water generated inside the plant, and some of these waters end up in aquifers and ground water [7].

Oil production and transportation, can disrupt the human population, animals and the fish life of the region [8]. Oil waste dumping, production pollution and spill wreck havoc on the surrounding wild life and habitat [8]. It threatens the extinctions of several plant and animal, and has already armed many land animals and plant species [8].

Pollutant removal from contaminated or polluted waters by adsorption techniques has been of growing importance due to the chemical and biological stability of organic compounds to conventional water treatment methods and the growing need for high quality treatment [9]. However, commercially available activated carbons are still considered as expensive materials due to the use of non-renewable and relatively expensive starting material such as coal, which is unjustified in pollution remediation application [10]. Therefore, in recent years, this has prompted a growing research interest in the production of activated carbons from renewable and cheaper precursors which are mainly industrial and agricultural

by-products, such as apricot shell [11], male flower of coconut tree [12], jute fibre [13], rubber wood saw dust [14], corn cob [15], bamboo [16] and oil palm fibre [17].

Conversion of coconut husk to activated carbon will serve a double purpose. First, unwanted agricultural waste is converted to useful, value added adsorbents and second, the use of agricultural by-products represents a potential source of adsorbents which will contribute to solving part of the polluted water treatment problem in Nigeria. From previous study, EFB based activated carbon was found to be effective adsorbent for removing chlorophenol and most organic compound from aqueous solution [18]. Similar to surface tension, adsorption is a consequence of surface energy. In a bulk materials, all the bonding requirements (be the ionic, covalent or metallic) of the constituent atoms of the material are filled by other atoms in the material. However, atoms on the (clean) surface experience a bond deficiency, because they are not wholly surrounded by other atoms. Thus it is energetically favourable for them to bond with whatever happens to be available. The exact nature of the bonding depends on the details of the species involved, but the adsorbed materials are generally classified as exhibiting physisorption or chemisorption [19] [20] [21].

A surface already heavily contaminated by adsorbates is not likely to have much capacity for additional binding. Freshly prepared activated carbon has a clean surface. Charcoal made from roasting wood differs from activated carbon in that its surface is contaminated by other products, but further heating will drive off these compounds to produce a surface with high adsorptive capacity. Although the carbon atoms and linked carbons are most important for adsorption, the mineral structure contributes to shape and to mechanical strength. Spent activated carbon is regenerated by roasting, but the thermal expansion and contraction eventually disintegrate the structure so some carbon is lost or oxidized [22-24].

Adsorptive capacity is the effectiveness of the carbon removing desired constituents such as COD, colour, phenol, etc., from the waste water [25]. Depending on the characteristics of the wastewater, one type of carbon may be superior to another since its capacity may be greater at equilibrium effluent concentrations [25].

The amount of material which accumulates depends on the dynamic equilibrium which is achieved between the rate at which material adsorbs to the surface and rate at which it evaporates. The higher the rate of adsorption and the lower the rate of desorption, the greater the fraction of the available surface which will be covered by adsorbed material at equilibrium. When a bed nears saturation, the flow is stopped and the bed is regenerated to cause desorption. The adsorbates can thus be recovered and the adsorbent reused. Regeneration can be accomplished in several way and these lead to the "circle type".

In the regeneration process, the previously adsorbed materials have to be removed from the carbon pore structure. The modes of regeneration are thermal, steam, solvent extraction, acid or base treatment and chemical oxidation [26] [27]. The adsorption of a single component from an aqueous solution onto an adsorbent has been modeled successfully, but relatively little model development has been done for the multi component case that has to be handled in practice. However, the behaviour of breakthrough profiles in a multi component system is entirely different from that in the one-component system.

To improve the design of the adsorbents reactor and to find the best operating conditions, the fundamental equilibrium and kinetic data for adsorption processes are essential [24]. The purpose of this research is to determine the rate of adsorption and evaluate the adsorbent in removing the organics from the liquid phase. The scope of the study is limited to initial concentration of the pollutants and the contacting time which was exhibited by first order kinetics.

METHODOLOGY

Preparation of Activated Carbon

EFB used for preparation of activated carbon in this study was obtained from a local palm oil mill. The pre-heated EFB was loaded in a stainless steel vertical tubular reactor placed in a tube furnace and the carbonization of the precursor was carried out by ramping the temperature from room temperature to 700^0C with heating rate of 10^0C/min. and hold 2hrs. Throughout the carbonization process, purified nitrogen was flown through at flow rate of $150cm^3$/min. The activated carbon was prepared using physiochemical activation method consisting of potassium hydroxide (KOH) treatment followed by carbon dioxide (CO_2) gasification by applying the optimum operating conditions obtained from earlier study [28]. The char produced from the carbonization process was mixed with potassium hydroxide pallets with impregnation ratio of 3:1. The dried mixture was then activated under the same condition as carbonization, but to a final temperature of 844^0C. Once the final temperature was reached, the nitrogen gas flow was switched to CO_2 and activation was held for1.8hrs. The activation was then cooled to room temperature under nitrogen flow and then washed with hot deionized water and 0.1M HCL until the PH of the washing solution reached 6-7

Experimental Procedures and Set-up

The following apparatus and materials were used to carry out the experiment in the laboratory: Spectrophotometer, electromagnetic stirrer, weighing balance, measuring cylinder, volumetric flask, conical flask, funnel, filter paper, cuvette, cctivated carbon, phenol, butanol, butan-2-ol, 2-methylbutan-2-ol.

Experimental Procedure for Adsorption Kinetics

1. The solutions were prepared with the initial concentration of 1.08g/*l* for phenol, butan-2-ol, butanol, and 2-methylbutan-2-ol.
2. A set of five glass tubes, each charged with 20ml solution of the organic components (phenol, butan-2-ol, butanol, 2-methylbutan-2-ol, was used.
3. 1.00g of activated carbon was added to each tubes
4. The tubes were each shaken for 30, 60, 90, 120, 150, 180min. and the solid adsorbent was removed by filtration
5. The equilibrium concentration was determined. The

experiment was conducted in a batch process

Adsorption Kinetics Studies

Adsorption kinetics is a time-dependent process and it is very important to know the rate of adsorption for design and evaluate the adsorbent in removing the organics from gas or liquid.

The rate of adsorption, r_{ads}, of a molecule onto a surface can be expressed in the same manner as any kinetic process. For example, when it is expressed in term of the particle pressure of the molecule in the gas phase above the surface. The rate of adsorption is given by:

$$r_{ads} = k' \, p^x \qquad (1)$$

where:
x = Kinetic order
k' = Rate constant
p = Partial pressure

If the rate constant is then expressed in an Arrhenius form, then we obtain a kinetic equation of the form:

$$r_{ads} = K_o \exp\left(-\frac{Ea}{RT}\right) P^x \qquad (2)$$

Where:
E_a = the activation energy for adsorption
k_0 = the pre-exponential (frequency) factor
The rate of adsorption is governed by
1. The rate of arrival of molecules at the surface
2. The proportion of incident molecules which undergo adsorption

That is, the rate of adsorption (per unit area of surface) can be expressed as a product of the incident molecular flux, F and sticking probability.

$$rads = S. \, F \qquad (3)$$

The flux of incident molecules is given by the Hertz-Knudsen equation

$$F = \frac{p}{\left(2\prod mkT\right)^{1/2}} \qquad (4)$$

where:
p = gas pressure (N/m^2)
m = Mass of one molecule (Kg)
T = Temperature (K)

The sticking probability is clearly a property of the adsorbates/substrate system under consideration but must lie in the range $0 < S < 1$; it may depend upon various factors – foremost amongst these being the existing coverage of adsorbed species (θ) and the presence of any activation barrier to adsorption. Therefore,

$$S = F(\theta)\exp\left(-\frac{Ea}{RT}\right) \qquad (5)$$

where:

E_a = the activation energy for adsorption
F (θ) = function of the existing surface coverage of adsorbed species.

Combining the equations for S and F yields the following expression for the rate of adsorption:

$$R = \frac{F(\theta)p}{\sqrt{2\pi mkT}} \exp\left(-E_a / RT\right) \qquad (6)$$

NOTES
1. The above equation indicates that the rate of adsorption is expected to be first-order with regard to the partial pressure of the molecules in the gas phase above the surface.
2. It should be recognized that the activation energy for adsorption may itself be dependent upon the surface coverage, i.e. E_a = E (θ).
3. If it is further assumed that the sticking probability is directly proportional to the concentration of vacant surface sites (which would be a reasonable first approximation for non-dissociative adsorption) then f(θ) is proportional to (1 − θ); where, in this instance, θ is the fraction of sites which are occupied (i.e. the Langmuir definition of surface coverage).

Adsorption Parameters

Apparent Density: The particle density increases with time as adsorption fills the particle's pores. An associated increase in apparent density, defined as the mass per unit volume of a container occupied by non- stratified dry carbon, will result [29].

Higher density provides greater volume activity and it indicates better quality activated carbon.

Surface Area: Under an electron microscope, the high surface area structures of activated carbon are revealed. Individual particles are intensely convoluted and display various kinds of porosity, there may be many areas where flat surfaces of graphite-like material run parallel to each other, separated by only a few nanometers or so. These microspores provide superb conditions for adsorption to occur, since adsorbing material can interact with many surfaces simultaneously.

The greater the surface area, the higher the number of adsorptive sites available.

Adsorptive Capacity: This the effectiveness of the carbon removing desired constituents such as phenol, colour etc. from the wastewater. Factors affecting adsorption capacity are: surface area of activated carbon, pore size of carbon, solubility of solute in aqueous solution, pH and temperature [30]. Adsorption capacity is proportional to concentration of adsorbate.

Kinetic Parameters: These determine the rate of adsorption and have negligible effect on adsorption capacity. Because adsorption rate is limited by diffusion, variables that influence diffusion have a significant effect on adsorption rate. For example, a higher concentration gradient across the surface of the carbon particle will increase the rate of adsorption, though a

high concentration of the solute can eventually have a negative effect on adsorptive capacity. In practice, the primary carbon variable influencing adsorption rate is the size of the carbon particle. Smaller carbon particles have a greater ratio of surface area to volume, making them more 'accessible' to diffusion from solution [30].

Pore Size Distribution: This defines the available pore volume of a carbon and it is produced through adsorption of liquid and gases under pressure. Molecules encountered in gas phase are generally smaller and more mobile than those in liquid phase application [31]. Therefore, a gas phase carbon has the majority of its pores concentrated in the micropore region. There is a wider range of molecular sizes in liquid phase work and adsorbates are less mobile in water. This means a broader range of pore sizes must be available for ease of movement of adsorption of particular molecular sizes. For liquid adsorption, high pores are better.

Abrasion Resistance: This is the ability to withstand degradation during handling, i.e. for activated carbon to maintain its physical integrity and withstand frictional forces imposed by backwashing. The higher the abrasion number, the more resistant the carbon is to abrasion [31].

NOTE: Backwashing occur from a fixed volume (column) experiment when the bulk density is high.

Temperature: The lower the temperature, the higher (or the increase) the adsorption capacity except in the case of viscous liquid.

Mesh Size: The finer the particle size of an activated carbon, the better the access to the surface area and the faster the rate of adsorption kinetics.

Ash Content: It reflects the purity of the carbon. It is the inorganic residue left after heating of the raw material. Common as constituents of coal-based carbons are silica, alumina, iron, calcium and magnesium.

Ash content reduces the overall activity of activated carbon and the efficiency of reactivation [31]. The lower the ash content, the better the activated carbon.

Contact Time: Sufficient contact time is required for each adsorption equilibrium and to maximize adsorption efficiency.

Breakthrough Curves

Adsorption is a transient process. The amount of material adsorbed within a bed depends both on position and time. As fluid enters the bed, it comes in contact with the first few layers of adsorbent. Solute adsorbs, filling up some of the available sites. Soon the adsorbent near the entrance is saturated and the fluid penetrates further into the bed before all solute is removed. Thus, the active region shifts down through the bed as time goes on. The fluid emerging from the bed will have little or no solute remaining until the bulk of the bed becomes saturated. The break point occurs when the concentration of the fluid leaving the bed spikes as unabsorbed solute begins to emerge. At that point the bed has become ineffective. Usually, a break point composition is set to be the maximum amount of solute that can be acceptably lost, typically ranging between 1 and 5 percent [32].As the concentration wave moves through the bed, most of the mass transfer is occurring in a fairly small region.

This mass transfer zone moves down the bed until it "breaks through".

The shape of the mass transfer zone depends on the adsorption isotherm (equilibrium expression), flow rate, and the diffusion characteristics usually, the shape must be determined experimentally.

The wave front may change shape as it moves through the bed, and the mass transfer zone may broaden or diminish unfavourable and linear isotherms tend to broaden. Favourable Langmuir and Freundlich isotherms may broaden at first, but quickly achieve a constant pattern front, an asymptotic shape. This means that the mass transfer zone is constant with respect to both position and time. When dealing with a constant pattern front, one can make measurements on a small scale apparatus and scale-up the results to a full-size adsorber.

RESULTS

Table 1. Breakthrough Curve Data

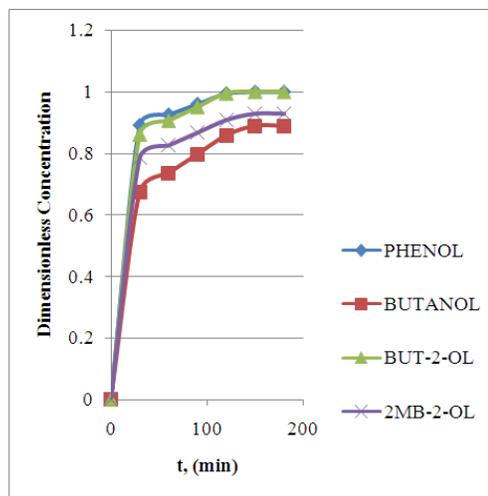| Time,t (min)	Phenol	Butanol	Butan-2-ol	2-methylbutan-2-ol
	Co/Ci	Co/Ci	Co/Ci	Co/Ci
0	0	0	0	0
30	0.8917	0.6745	0.8614	0.7857
60	0.9259	0.7358	0.9059	0.8269
90	0.9602	0.7971	0.9504	0.8681
120	0.9945	0.8585	0.9946	0.9094
150	1.0000	0.8892	1.0000	0.9301
180	1.0000	0.8892	1.0000	0.9301

Figure 1. Breakthrough curves for the simultaneous adsorption of phenol, butanol, butan-2-ol and 2-methylbutan-2-ol

DISCUSSION OF RESULTS

Figure 1 shows the adsorption kinetics of activated carbon as a time dependent process. It evaluates the adsorbent in removing the organics from the liquid phase solution. From the curves, in the first 30 minutes, there was high level adsorption processes in which was most predominant in the adsorption of phenol, followed by butan-2-ol, 2-methylbutan-2-ol and butanol respectively.

Between 30-60 minutes, the dominant rate of adsorption

shifted to butanol by increase concentration of 0.07, followed by butan-2-ol with 0.05 increase in concentration. Subjecting the four organic components to the same process condition, at 120 minutes, phenol and butan-2-ol had reached their pick of adsorption and at 150 minutes, they are completely removed from the solution while 0.1108 (11%) of butanol and 0.0699 (7%) of 2-methylbutan-2-ol remain in the solution.

CONCLUSION

- From the breakthrough curves, the breaking point time of phenol and butan-2-ol is 150 minutes. i. e at that time, the two organic component are totally out of the solution.
- Adsorption using activated carbon favours phenol and buatn-2-ol more than other organic components.

REFERENCES

1. Metivier-Pignon H., Faur-Brasquit Z., Cloirec P. L., (2003). Adsorption of dyes onto activated carbon cloths: Approach of adsorption mechanism and coupling of ACC with ultra filtration to treat coloured waste waters. Separat. Purificat. Technol., 31: 3-11
2. Lin, M. C., Chiu, H. H., Yu, H. S., Tsai, S. S., Cheng, B.H., Wu T.N and Yang, C.Y. (2001). Increased Risk of Petroleum Delivery in Areas with Air Pollution from a Petroleum RefineryPlant in Taiwan.J. Toxicol. Environ Health A. 64(8), 637-644
3. Yang. C. Y., Cheng. B.h., Hsu, T. Y., Tsai, S. S., (2000). Female Lung Cancer Mortality and sex ratio at birth near a petroleum refinery plant. Environmental Research 83 (1) 33-40
4. Skodvin T., and Skjaerseth J. B., (2001). Shell Houston, We Have a Climate Problem, Global Environmental Change 11(2), 103-106
5. Akeredolu F. A and Sonibare J. A., (1997). Measurement of Benzene, Toluene, and Xylene (BTX) within Nigeria Refinery and its Environs by the Carbon Addition Techniques. Journal of Nigeria Society of Chemical Engineers, Lagos, Nigeria Vol.16 No. 1&2, pp. 123-132
6. Cetas F., Odabasi M., and Seyfoghn R., (2003). Ambient Volatile Organic Compound (VOCs) Concentrations around a Petrochemical Complex and a Petroleum Refinery. The Science of the Total Environment 312(1-3), 103-112
7. Adeodu A. O., Daniyan I. A., Yusuff A. S., (2013). Assessment of Soil, Water and Air pollution by heavy metals from Petroleum and Petrochemical Companies in Nigeria. International Journal of Scientific and Engineering Research. Vol.4, Issue 7, Pg 2401-2412
8. Anonymous A. (1979). Environmental Impact. www.epa.gov
9. Basar C. A., (2006). Applicability of the various adsorption models of three dyes adsorption onto activated carbon prepared waste apricot. J. Hazardous Mater. 135: 232-241
10. Attia A. A., Girgis B. S., Fathy N. A., (2008). Removal of Methylene blue by carbon derivatives from Peach Stones by H3P04 activation: Batch and column studies, Dyes and Pigments, 76: 282-289
11. Karigozoglu B., Tasdemir M., Demibas E., Kobyam M., (2007). The adsorption of basic dye (Astrazon Blue FGRL) from aqueous solutions onto Sepiolite fly ash and Apricot shell activated carbon: Kinetic and equilibrium studies. J. Hazard. Mater., 147: 297-306
12. Senthikumaar S., Kalaamani P., Subburaan C. V., (2006). Liquid phase adsorption of Crystal violet onto activated carbons derived from male flower of coconut tree. J. Hazard. Material, 136: 800-808
13. Senthikumaar S., Varadarajan P. R., Porkodik K., Subbhuraan C. V., (2005). Adsorption of Methylene blue onto Jute fibre carbon: Kinetic and equilibrium studies. J. Colloids Inter. Sci., 284: 78-82
14. Kalavathy M. H., Karthikeyan T., Rajgopal S., Miranda L. R., (2005). Kinetic and Isothermal studies of Cu (1) adsorption onto H3P04 activated rubber wood sawdust. J. Colloids Interface Sci., 292: 354-362
15. Tseng R. L., Tseng S. K., Wu F. C., (2006). Preparation of high surface area carbons from corn cob with KOH etching plus C02 gasification for the adsorption of dye and phenol from water. J. Colloids surfaces A: Physiochem Eng. Aspects. 279: 69-78
16. Hameed B. H., Din A. T. M., Ahmad A. L., (2007). Adsorption of methylene blue onto Bamboo based activated carbon: kinetic and equilibrium studies. J. Hazard. Mater, 141: 819-825
17. Tan I. A. W., Hameed B. H., Ahmed A. L., (2007). Equilibrium and kinetic studies on basic dye adsorption by Oil palm Fibre activated carbon. J. Chem. Eng., 127: 111-119
18. Tan I. A. W., Hameed B. H., Ahmed A. L., (2009). Adsorption Isotherms, Kinetic, Thermodynamics and Desorption studies of 2, 4,6 trichloro phenol on Oil palm empty bunch-based activated carbon. J. Hazard. Mater., 164: 473-482
19. Ferrari L., Kaufmann J., Winnefeld F., Plank J. (2010).Interaction of cement Model systems with super plasticizers investigated by atomic force microscopy, zeta potential, and adsorption measurements. J. Colloid interface Sci. vol. 34, No.1, 15-24.
20. Olafadehan O. A. (2010). Chemical reaction kinetics note. Department of chemical engineering, University of Lagos.
21. Wikipedia, (2010). Adsorption. (Http://en .www.wikipedia.org/wiki/Adsorption)
22. Wikipedia, (2010). Activated carbon. (http://en.wikipedia.org/wiki/activated_carbon)
23. Wikipedia, (2010). Adsorption kinetics. http://www.wikipedia.org/wiki/Adsorptionkinectics
24. Xiang Li., Zhong Li., and Luo Ling'al. (2008). Adsorption kinetics of dibenzofuran in activated carbon packed Bed. Chinese journal of chem. Eng. Vol.16, No.2, 203-208.
25. Matthew, F.T., David,W.M. (2007). The role of surface acidity and pore size distribution in the adsorption of 2-methylisobomeol via powdered activated carbon. Carbon vol. 45,858-864.
26. Charles S. M., Li, H., Teppen, B.J., Boyd, S. A., (2006). Quantifying the availability of clay surfaces in soils for adsorption of nitrocyano-benzen and diuron. Environ. Sci. Technol.vol.40, 7751-7756
27. McClenny W. A., Oliver K. D., Jacumin Jr. H. H., Daughtrey Jr. E. H. (2002). Ambient level volatile organic

compound(VOC) monitoring using solid adsorbents-Recent US EPA studies. J.Environ.Monit vol.4, 695-705.

28. Tan I. A. W., Hameed B. H., Ahmed A. L., (2008). Optimization of preparation conditions for activated carbons from Coconut husk using response surface methodology. J. Chem. Eng., 137: 462-470

29. Von Phul. (2002). How activated Carbon influenced the Development of sigma Pure Technology. D-Foam incorporated, Weatherford TX 76086 -1393.

30. Wanen L. McCabe, Julian C. Smith, Peter Harrioh. (1993).Unit Operations of Chemical Engineerig. Fifth edition. McGraw-Hill Chem. Eng. Series. pp 814-816.

31. CPL Caron Link, (2008). Properties of activated carbon. (http://www.activated_carbon.com/1-3.html)

32. EPA, (1995). Remediation case studies: groundwater treatment. Federal remediation technologies roundtable, 1995. EPA/542/R-95/003.

Citation: Adeodu A. O., et al (2014) Assessment of Adsorption Kinetics in a Quaternary Liquid Phase System using Activated Carbon derived from Oil Palm Empty Fruit Bunch. J. of Bioprocessing and Chemical Engineering. V1I3. DOI: 10.15297/JBCE.V1I3.01