STUDY OF ADSORPTION OF COBALT NITRATE IN OIL PALM EMPTY FRUIT BUNCH (OPEFB) FIBRES

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Abstract--

INTRODUCTION

Malaysia has known to be one of the palm oil contributor in the world of palm oil industries. Over 80 million tonnes of dry biomass has been produced by nation of Malaysia and is stated to be risen by 100 million tonnes by year 2020 (Fuadi et al., 2014). Besides, palm oil biomass can be categorized from its oil palm empty fruit bunches (OPEFB), kernel's shell and their oil palm mesocarp fibres (OPMF).

Technology insight has better idea on this biomass which significantly renowned to be one of renewable energy resources in future (Syed-Hassan et al., 2014). Anthropogenic climate change in fossil fuel resources and the depletion of fuel used these days such as a distressed upsurge of oil prices and the uncontrol of global environment issues regarding current fossil fuels consumption had given impact on the current researchers to discover new idea of using these plant-based resources and substitute it as fossil fuel usage (Syed-Hassan et al., 2014).

One of the decision that being seen by the researchers why biomass is seen as new potential substitution is because of it produces less environmental pollution energy as compared to the current energy resources. This is due to lower Sulphur (S) and Nitrogen (N_2) contents in biomass which knowingly high content of these two will impact ______. Besides that, the secretion of neutral Carbon Dioxide (CO2) from biomass can be absorbed by photosynthesis process by trees and its natural conversion reduces Carbon Dioxide (CO_2) emission to the atmosphere. Pogaku et al. (2016) stated realization of Malaysia on the imminent energy security that lies in renewable biomass energy had inspired them to discover more. However, the agriculture's effluents in Malaysia are still under the concept of typical decomposition where its only taken into natural decompose or burn in open space. Thus, this research is alternatively to use OPEFB as biomass material to produce bio-oil through catalytic pyrolysis using Cobalt Nitrate (CO(NO3)2) and discover the adsorption behaviour of the process.

This biological organic complex that abundantly exist on earth are seeing as new energy potential for future unlimited availability of energy. Biomass is specifically comprising of cellulose and hemicellulose structures, extractives, inorganics, lignin and heteroatoms; Nitrogen, Sulphur, Hydrogen and Oxygen which different in each and every single material (M. Auta et al., 2014).

Cellulose is known as major richly available plant's cell walls that derived of natural polymer of D-glucose components, of a six-carbon ring that known as pyranose. And, cellulose is generally about 30 to 50% of total lignocellulosic dry matter (G. Kabir & B.H. Hameed, 2017). Next, hemicellulose or a cell that surrounds the cellulose fibres; link connecting the cellulose and lignin. This cell is a heterogeneous group of branched polysaccharides that has some structural elements of variety of monomers include glucose, galactose, mannose, xylose, arabinose and also glucuronic acid. G. Kabir & B.H. Hameed (2017) stated that hemicellulose fraction is about 20 to 40% of the total dry biomass in lignocellulosic biomass.

Lastly, lignin; the aromatic three-dimensional and a cross-linked phenol polymer. Lignin exists at the outer layer of fibres and plays important role of the structural rigidity and function to hold the fibres of polysaccharides together. Dhyani V. et al. (2017) stated that about 40% of lignin cells filled up the empty spaces of cellulose microfibres that coated with hemicellulose as it actually binds the hemicellulose and cellulose within the plant's cell walls.

The oil palm void tree grown foods bundle fibres or the OPEFB have recycling potential after the OPMF and moreover OPEFB are understood to be a second-generation biofuels beneficial advance from first-generation biomass. This is due to non-compete resources of OPEFB as equated to the first-generation biomass (food supply) which use direct sources of bio-products gaining from vegetable oils, corn, sugar, paddy, etc. (F. Zakaria et al., 2016). OPEFB; contain of high moisture up to 60% of wet OPEFB basis (N. Abdullah & F. Sulaiman, 2013) normally being sun-dry until reach over 20 to 40% of dampness as to prepare for utilization as fuel. The researchers also mentioned on 0.2 kg of oil from OPEFB produced per kilogram of palm oil.

The details summary comparison made of why cobalt is chosen in producing bio-oil in Table 1.1. A simplified conclusion drawn from the comparison is cobalt catalyst show better performance but need to operate at certain temperature and pressure and the feedstock composition (W. Chen, 2017).

Table 1.1 Comparison of cobalt-based and iron-based catalysts (W. Chen, 2017)

Factors	**Cobalt catalysts**	**Iron catalysts**
Cost	~1000 times more expensive cheap	cheap
Preparation	impregnation or precipitation	precipitation
Carbon sources	natural gas	coal, natural gas, biomass
H2/CO ratio	~2	0.5–2.5
Activity	high	relatively low
Chain-growth probability	0.94	0.95
Stability	durable	coking, poisoning aging, attrition *etc.*
Sulphur tolerance	<0.1 ppm	<0.2 ppm
Side reaction	negligible	water-gas-shift

Utilization of OPEFB give benefit of elimination of undesired products such as ketones and N_2 compounds which lead to improvement to bio-oil quality when being treated (F. Zakaria et al., 2016). Besides of generation of bio-oil from OPEFB, its also can be beneficial in other ways such as might transform under fuel to prepare steam to waste-fuel boilers for processing, power-generation with steam turbines, used as fertilizer in plantations in the form of burnt wastes and also being used as mulch; a cost-saving fertilizer which function as a soil conditioning agent by releasing nutrients to the soil via microbes which leads to change constructed of the dirt structure owing to preferred aeration, upsurges those water field limit, also growths those mud pH.

Researchers also nowadays have discovered the function of OPEFB as it converted to bio-oil and bio-char that naturally can solve the disposal and environmental problem and cutting costs of waste treatment over the function that it not fully utilized of covering road surface in plantation areas that leads to higher CO2 emission (F. Abnisa et al., 2013). Additionally, application of OPEFB can be done by combination of thermochemical processes as a whole system that produces a saving energy integrated auto thermal technology which are bio-gasoline, bio-kerosene and bio-solar (F. Abnisa et al., 2013). Anguile J. J. et al. (2013) stated too OPEFB is a good adsorbent for adsorption of metals through the complex function of surface properties, environmental and solution parameters.

Pyrolysis; thermochemical process that uses heat and catalyst to convert biomass into bio-products in fast reaction under few seconds to hours (Dhyani V. et al., 2017). Formerly, pyrolysis, M. I. Jahirul et al. (2012) stated in their research that it is a thermal decomposition process encompasses biomass heating process the practice in the default of oxygen alternately air to prepare a mixture from claiming robust char, condensable fluids and gases. Furthermore, F. Abnisa et al. (2013) stated the pyrolysis operating temperature is normally at high level of heating and the process includes series of exothermic and endothermic reactions.

Pyrolysis in exothermic reaction comprises breaking of biomass into more smaller portions which occur under low temperature during initial stage of pyrolysis as stated by F. Abnisa et al. (2013) and the endothermic reaction took place under increasing of temperature which few of the initial crops are evaporated and break into minor crops. The authors also highlighted there are abundant of revisions have revealed that it can reach to 70 wt.% of conversion biomasses into bio-oil via pyrolysis while approximately about 15-25% yielding of bio-char from pyrolysis process. Moreover, the common temperature for pyrolysis reaction to run is within 400-800ºC that yield gas, liquid and char however, each of the products produced depends on the type of pyrolysis process together with limits and properties involved (J. Akhtar & N. S. Amin, 2012).

Basically, for the medium temperature of biomass decomposition is at 400-550 ºC which yield liquid oils at short residence time, otherwise, gaseous products produced at high temperature when it is keeps increasing and char dominantly favours the low temperature. So, for bio-oil to produce, EFB wastes need to undergo the low temperature. Besides, as according to studies by (J. Akhtar & N. S. Amin (2012) too, production of oil in pyrolysis process can be divided into three main temperatures range which are the fast pyrolysis (≥500 ºC) and slow pyrolysis which at low rate of biomass heating and the last one is low temperature carbonization (≥400 ºC).

Generally, pyrolysis of a biomass is determining through its series of process pathway which has about four stages; as stated by K. C. Sembiring et al. (2015) <220°C is where the moisture progression happens of 220-315°C is for principally hemicellulose breakdown, 315-400°C is for cellulose decomposition and lastly, >400°C for lignin breakdown. As stated by G. Kabir & B.H. Hameed (2016), catalytic pyrolysis of lignocellulose biomass can produce a high-grade bio-oil and a huge range of catalyst can activate or fasten the bio-oil production process as to give a high quality of bio-oil. Catalytic pyrolysis is commonly conducted in fixed bed pyrolizer, fluidised bed pyrolizer or spouted bed reactor (G. Kabir & B.H. Hameed, 2016). Catalyst that is introduced in this study is Cobalt (Co(II)) catalyst to produce the bio-oil. As for Co(II) need to be impregnated into the OPEFB, an adsorption analysis is made to see the amount of Co(II) catalyst that can be maximumly adsorb by OPEFB.

Beforehand, in term of goals to produce bio-oil from pyrolysis process, this bio-oil can be described as a dark brown organic liquid that characterized as highly oxygenated, corrosive, viscous and is labelled as a complex chemical that can be used as substitute synthetic fuel (M. Auta et al., 2014). The researchers also stated that it has high calorific value which the oil also can be used as stabilizer for refined petroleum feedstocks, thermal power stations, gas turbines and not to mention functionality of easily converted to useful chemicals. Thus, in the used of catalyst for evaluating the quality and quantity of bio-oil from biomass pyrolysis as knowingly, the catalyst is boosting the selective determination of the product and subsequently the desired application (M. Auta et al., 2014).

The adsorption process is chosen to be the best solution for Co(II) catalyst to be adsorb into the OPEFB due to it simple design and low-cost process. In this study, the aim is to study on the adsorption of Cobalt Nitrate $Co(NO_3)_2$ catalyst. More advance, many of the researchers have been carried out the studies on the adsorption of Co(II) ions and also others studied solution parameters which are ionic strength effect and ion pair formation were part that influence adsorption on Co(II) ions. In previous study (P. Thilagavathy & T. Santhi, 2014), the concentration of adsorb metal solution was measured and calculated using symbols of metal per unit mass of fibres (q_e) as in the subsequent equation:

$$q_e = (C_0 - C_e)V/W \tag{2.1}$$

$$Adsorption\ percentage = C_0 - C_e/C_0 \times 100 \tag{2.2}$$

where C_0; initial and C_e; equilibrium concentrations (mg/L), respectively. V is the solution volume (L) and W; mass of adsorbent (g).

Thus, in previous studies clarified that adsorption equilibrium can reach much faster at lower initial concentration of metal ions whereabout the penetration of metal molecules onto boundary layer occur before interrelation of adsorbent. Requirement of longer contact time at higher metal concentration needed for these processes (M.S. Sajab et al., 2013). As stated too by H. Javadian (2014), q_e increases when the equilibrium concentration of the solution increases and this increased q_e lead to improved chief reason at higher equilibrium concentration.

Adsorption process as mentioned by S. I. Nor-Azemi et al., (2014) in example of using oil palm mesocarp fibres (OPMF) and Nickel (Ni) ions in biomass treating observation; by doing a chemical treatment in example treating OPMF with 0.1M NaOH beforehand, it reaches the higher efficiency of heavy metals adsorption. So, it forms high nickel concentration when compared by treated OPMF thru 0.1M HCl and untreated OPMF. As here in Figure 2.5 shows the capacity of Ni(II) and Co(II) by different bio-sorbent.

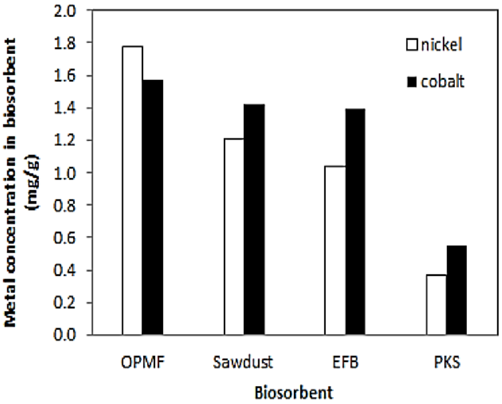

Figure 2.5 Capacity of Ni(II) and Co(II) by different bio-sorbent (F. A. Fuadi et al., 2014)

S. I. Nor-Azemi et al., (2014) also revealed in their research that due to the advanced introduction of the energetic requisite sites in moment of breakdown of cell-membrane result in the high nickel adsorption. Besides, it is discovered that alkali (chemical) treatment help in removing lipid and proteins for metal ions adsorption and also avoid biomass decomposition by destructing the autocatalytic enzymes. Furthermore, in their research too mentioned on high adsorption of metal concentration lead by the release of polymers (polysaccharides) in alkali pre-treatment as due to high attraction side of the polymer towards some metal ions.

As clarified by H. Javadian (2014), adsorption is affected by many factors which in this study highlighted on the initial concentration variation and also the adsorbent dosage. As the author mentioned, for initial concentration; in the test for Co (II) onto copolymer nanofiber, Co(II) will be perfectly absorbed at the little initial concentration together with availability of sorption sites and high surface area which easily for Co(II) sorption. And, when at higher initial concentration, availability of sorption sited becomes limited that make low efficiency of metal sorption.

The adsorption isotherm modelling as explained by Ghosal et al. (2017), is vital in defining the equilibrium relationship among the solute in the solution and on the adsorbent surface as the isotherm parameters sub with kinetic and thermodynamics of adsorption process. The authors also cited that the nature of the reaction at the interface and the quantitative together with qualitative estimation of the efficiency of the adsorbent are also computed from isotherm model. To study the adsorption mechanism and create expectation of maximum adsorption capacity of the adsorbent, Langmuir and Freundlich isotherm models are generally used as in this case respect to EFB fibres.

Freundlich Isotherm

S.A. Sadeek et al. (2015) stated that an empirical equation for the hypothesis for heterogeneous surfaces adsorption process on and adsorption dimensions is linked to the vadsorbed metal concentration called Freundlich isotherm. The same authors also stated that Freundlich isotherm is fit in adsorption at high concentrations of metal ions at equilibrium yet not for the lower concentration. As stated by M.S. Sajab et al. (2013), the Freundlich isotherm explained on alterable adsorption and widely covers monolayer and multilayers homogeneous adsorbent surface and each molecule adsorbed onto the surface on about the adsorbate. Here is the equation involved:

$$log q_e = \log K_f + \left(\frac{1}{n}\right) \log C_e \qquad (2.3)$$

In the above equation; *logK_f* value is the intercept and *(1/n)* value is the slope (S. Sivakumar et al. (2014). In function of plotting *logC_e* against *log q_e*, it gives straight line and the correlation coefficient (R_2 value) indicates the applicability of this isotherm. Besides, calculation for maximum adsorption capacity of the adsorbent can be done by replacing the obligatory equilibrium concentration in Freundlich equation (P. Thilagavathy, T. Santhi, 2014).

Langmuir Isotherm

Anguile J. J. et al. (2013) stated in their research on the Langmuir adsorption isotherm which it describes the relationship between the quantity of gas adsorbed on a surface and the pressure of that gas. Based on S.A. Sadeek et al. (2015), Langmuir isotherm undertakes two key points in the adsorption process by at first, occurrence of adsorption at exact homogeneous adsorption sites in the adsorbent while the second one occurrence of the monolayer adsorption and maximum adsorption as the adsorbed molecules form a saturated layer on the surface of adsorbent. The same authors mentioned that all adsorption sites involved are dynamically alike and the intermolecular force declines as the distance from the adsorption surface upsurges.

Generally, this isotherm is frequently used for adsorption of a solute from a liquid solution. Here is the equation involved:

$$\frac{C_e}{q_e} = \frac{1}{Q_{0^b}} + \frac{C_e}{Q_0} \qquad (2.4)$$

q_e – Amount of dye adsorbed per unit mass of adsorbent (mg g^{-1}).

Q_0 – Monolayer adsorption capacity (mg g^{-1}).

C_e – Equilibrium concentration (ppm).

b – Langmuir constant.

If the activated carbon is linear with correlation coefficient (r) closer to unity indicating that the adsorption data are best fitted to this isotherm. The feasibility of the process is expressed in terms of separation factor RL which is given by the equation:

$$R_L = \frac{1}{(1 + bC_i)} \qquad (2.5)$$

b – Langmuir constant.

C_i – Initial concentration of dye.

The separation factor R_L indicates the nature of isotherm and the feasibility of adsorption process as favourable. The R_L values are found to be in the range 0-1, indicating that the adsorption process is favourable.

Commonly, all of isotherm values are constants were calculated from the slope and intercept of the plots using regression analysis (S. Sivakumar et al. (2014). M.S. Sajab et al. (2013) mentioned in their research that Langmuir isotherm undertakes monolayer coverage of adsorbate over a homogeneous adsorbent surface whereabout it includes every single molecule adsorbed onto the surface requires equal adsorption activation energy. The authors also stated that at higher temperature, greater adsorption can occur which can be facilitated by advanced diffusion rate of adsorbate molecules across the external boundary layer and internal pores of adsorbents.

Theoretical results

S.A. Sadeek et al., (2015) stated, indication for all R_L values normally obtained greater than zero and less than unity as few considerations needed for favourable adsorption of Co(II) ion by the different bio sorbents. Their studies showed that Langmuir equilibrium isotherm fit in defining the metal adsorption process by the studied of bio sorbents as it tells that a monolayer of metal ions form lead to adsorption process occur on the bio sorbent surface with finite number of identical sites, which are homogeneously dispersed over the surface.

On the other side, Freundlich model has two parameters that denotes the quantity of metal ions adsorbed at equilibrium concentration which are adsorption capacity and adsorption intensity of the metal ions. And, *n* value of 1-10 signifies the metal ions adsorption strength on the absorbent which relatively strong adsorption. As in previous studies, some of the authors such as P. Thilagavathy & T. Santhi (2014) had mentioned the comparison of experimental and calculated data made for the validity of the isotherm models.

Based on correlation coefficients in their studies for HAN, it stated that the Freundlich equation gives the best fit over the entire range of concentrations. This model is considered by *1/n*, the heterogeneity factor, which give positive value showing good adsorption of Co(II) onto HAN. Henceforward, the binding for adsorption on heterogeneous surfaces, i.e., surface with non-energetically equivalent sites. Thus, it disclosed favourable adsorption mechanism and high affinity of adsorbate for adsorbent designate that values of *1/n* less than unity or high values of Freundlich constant. Sorption isotherm investigations by H. Javadian (2014) also showed that Freundlich model offers higher correlation factor than other models in sorption process.

METHODOLOGY

Materials & Methods

OPEFB fibres is used in this study. Other elements being used are the Sodium Hydroxide (NaOH) solution in preparation of OPEFB fibres. Ultimate and proximate analyses are made in order to know few elements' amount in the fibres. Cobalt Nitrate (Co(NO3)2) as the catalyst for pyrolysis process which being observed in amount of metal adsorbed by the OPEFB fibres.

Consequently, preparation of Cobalt, Co(II) mix with Nitrate, NO3 solution is done. ICP-OES test is in used as to analyse the metal-loading amount on the EFB fibres whereabout the acid solution (Dihydro-Oxygen, H2O2 and Hydrogen Nitrate, HNO3) are used in the acid digestion method to proceed to the analysis of the metal-loading samples. Fixed-bed reactor is used for catalytic slow pyrolysis process and several parameters are being adjusted in order to achieve high yield of bio-products. Thus, the loaded samples fibres with different range of metal concentrations are being pyrolyzed to get the bio-oil afterwards.

3.3 Biomass Preparation

A local OPEFB fibres are taken from Malaysia. The OPEFB fibres then being dried under the sun for 2 consecutive days to remove the moisture content of the fibres prior to pyrolysis. Then, the OPEFB is continually been dried for 24hrs at 110°C in the conventional oven (F. A. Fuadi et al., 2014). The dried OPEFB is then being shredded for the metal impregnation process afterwards. The samples are then kept in a tight container and place in refrigerator for further use.

3.4 Proximate Analysis

Analyses were carried out to find the moisture, ash, volatile and fixed carbon content of all samples. The moisture content was determined using ASTM E871 Method (Annual Book of ASTM Standard, 1998). The ash content was calculated on dry basis using NREL Standard Analytical Method (Laboratory Standard Analytical Method, 1994) while, the volatile matter content was determined using standard ASTM E872 (Annual Book of ASTM Standard, 2006)

3.5 Ultimate Analysis

The ultimate analysis was carried out using CHNS/O analyser (Perkin Elmer 2400 Series II) to determine Carbon (C), Hydrogen (H), Nitrogen (N), and Oxygen (O) contents of the raw OPEFB samples (S. S. A. Syed-Hassan et al., 2014). All results were given in percentage and the oxygen content was calculated by finding the difference.

3.6 Impregnation of Cobalt Nitrate (Co(NO3)2) onto OPEFB Fibres

The stock solution of Co(NO3)2 is prepared by dissolving their corresponding nitrate salts (Co(NO3)2.6H2O) in distilled water. All chemicals are obtained from Faculty of Chemical Engineering, UiTM Shah Alam, Selangor. The loading of Co(NO3)2 onto OPEFB are studied at various concentration (10-200 mg/L). The impregnation process is conducted by mixing the OPEFB and Co(NO3)2 solution using magnetic stirrer in a beaker for various soaking times (S. N. I. Nor-Azemi et al., 2014).

3.7 Cobalt Loading Determination Using Inductive Coupled Plasma (ICP-OES)

As to make sure that the filtrates having no Co(NO3)2 solution, the soaked solid samples are filtered and rinsed with distilled water several times and detection is done by using Inductive Coupled Plasma (ICP-OES) model iCAP 6000 series. The same steps are repeated for various concentration of Co(NO3)2 solution. Besides, to adjust the initial metal pH from 2.0 to 8.0, 0.1 M of NaOH and 0.1 M of HCl are used and in a case of avoiding Cobalt Hydroxide formation, the experiments are not conducted beyond pH 8.0.

The filtered loaded-OPEFB is then being dried in oven at 110°C for 24 h and after dried, the samples are stored in tight container and placed in a refrigerator for further used. In order to digest the OPMF samples in a microwave digester (Milestone ETHOS) before being tested using ICP-OES Acid, the aqua reqia solution of a mixture of 35% H2O2 and 65% HNO3 is in used for digestion method (S. N. I. Nor-Azemi et al., 2014). Here in this research, the Co(NO3)2 concentration is determined from the solid and not from the filtrates. The digested samples are being analysed and biomass of different capacity in adsorbing metal ions is computed using the equation:

$$q=(Ci-Cref)VW \qquad (3.1)$$

controller of the furnace and the reactor are always synchronised whereas as to create the necessary inert condition for the pyrolysis studies, furnace Nitrogen (99.99% pure) flowed through the reactor at 200 ml/min for 15 min (M. Auta et al., 2014). For each pyrolysis study, the desired input parameters, N2 flow and reaction time are set to be achieved at a heating rate of 100°C/s. The N2 flow of 200 ml/min and the reaction time of 10 min are set for the catalytic pyrolysis.

Nevertheless, the reaction temperature and catalyst loading ratio are varied during the pyrolysis studies. The advanced vapours and gases are received by a condenser attached to the product outlet pipe of the reactor. In the mode of condensing the pyrolysis vapours into bio-oils, the temperature of the condenser is maintained at 5°C by using frozen salt and water mixture (Yiin C. L. et al., 2016). Non-condensable gases are entrained in a gas collector. At the end of the reaction, the reactor is cooled to a temperature close to the ambient temperature. The biochar and bio-oil in the reactor are recovered and weighed. Calculation of the difference between the initial amount of OPEFB and the total amount of the solid and liquid products as to determine the quantity of the gas. The amounts of the pyrolysis products are stated on dry basis and ash-free basis. The liquid yield calculation using this formula (Yiin C. L. et al., 2016):

$$Liquid\ yield(wt.\%)=weight\ of\ biomass-oil\ producedweight\ of\ biomass\times 100 \quad (3.2)$$

Typical reaction condition for the bio-oil used are 5 weight percent of H-Y zeolite catalyst at temperature of 500 °C and nitrogen flow rate of 100 ml/min [5, 6]. (Yiin et al, 2016)