

Adsorption and Dispersion of Nickel on Oil Palm Mesocarp Fiber

Syed Shatir A. Syed-Hassan^{*}, Siti Nor Izuera Nor-Azemi, Farah Aimi Fuadi

Faculty of Chemical Engineering, Universiti Teknologi MARA, Shah Alam, Selangor 40450, Malaysia
shatir@salam.uitm.edu.my

The investigation on the adsorption of metal from aqueous solution onto a biomass is important for several reasons. First, biomass has been widely used as an economical sorbent to remove heavy metals from industrial wastewater. Second, studies have shown that impregnation of metals onto a biomass helps improving thermal conversion of the biomass, for example, by reducing the yields of tar and char and thus enhancing the formation of syngas during biomass gasification. The produced metal-loaded char from thermal conversion of metal impregnated-biomass on the other hand, can be re-used as a catalyst for various reactions such as water-gas shift reaction. In this study, we examine the adsorption of Nickel from aqueous solution onto oil palm mesocarp fiber by varying important parameters such as pH and initial metal concentration. The kinetic study shows that the adsorption of Nickel follows the pseudo-second order kinetic model. Our study also reveals that Nickel disperses well into nano-size particles on the oil palm mesocarp fiber, suggesting the suitability for carrying out thermal conversion of Nickel-loaded oil palm mesocarp fiber in the future. The adsorption of Nickel is lower but sufficient enough to be used as catalyst in biomass thermochemical processes.

1. Introduction

Global environment is currently facing serious problems due to the increased level of metal concentration especially from metal extraction industries, electroplating, refining, battery production, dye and leather industries, etc. (Yalcin et al., 2012). There are various technology have been used to remove heavy metal such as exchange of ion on resins, solvent extraction, separation by membrane and precipitation, but the adsorption is considered as efficient technology to remove heavy metals from industrial wastewaters (Azouaou et al., 2013). Nickel is one of the heavy metals that can cause serious damage to lungs and kidneys. Its carcinogenic characteristic, on the other hand, leads to cancer and skin dermatitis (Denkhaus and Salnikow, 2002). Therefore, the removal or the re-use of Nickel from wastewater is very important. Many studies have shown that biomass is suitable to be used as heavy metal adsorbent. Other than being used as biosorbent, biomass also has become one of the renewable energy resources. The depletion of fossil fuel resources, the rising of oil prices and the environmental issues arising from the fossil fuels consumption (greenhouse effect and global warming) lead to the usage of biomass as a renewable energy resource and considered as an alternative to fossil fuels (Türe et al., 1997). Biomass have been used for various proposes including as cooking and heating fuels, being combusted for electric generation, used in incinerator and used as raw materials for the production of chemicals and synthetic fuels (Boroson et al., 1989). The energy produced from biomass waste has less environmental pollution compared with fossil fuel combustion due to its lower contents of Sulfur and Nitrogen (Tsai et al., 2007). The neutral circulation of Carbon Dioxide from biomass during photosynthesis and its conversion reduces CO₂ emission to the atmosphere thus produce CO₂ neutral energy (Min et al., 2013). Many studies found that metal addition onto biomass helps improving thermal conversion of the biomass, for example, by reducing the yields of tar and char and enhancing the formation of syngas during biomass gasification (Richardson et al, 2010) and the metal loaded biomass also can be used as catalyst for the downstream thermochemical processes such as tar cracking.

Gasification is a method to convert biomass into synthetic gas (CO, H₂) that can produce power and heat, and also fuels and chemicals through Fischer-Tropsch synthesis. Gasification produces 3 main components: gas (CO, H₂, CO₂, smaller hydrocarbons), liquid (bio-oil, tar) and solid residue (char or ash). The raw gas from biomass gasifier is dirty due to the presence of unacceptable level of tar and it has to be cleaned for most applications. Other than that, Nitrogen, Sulfur, alkali metals and Chlorine compounds are also the undesirable gasification products that need to be removed (Richardson et al., 2010). Thus, the high amount of clean syngas production becomes the challenge for its application in industries. In order to enhance the efficiency of gasification process, i.e., to produce clean syngas and to avoid the use of very high reaction temperature, the catalysts are normally used. A part from using conventional catalyst in gasification, catalytically active materials can also be directly impregnated onto the biomass in order to avoid the use of the often expensive support materials. In order to maintain high efficiency of the catalyst, the loading and dispersion of the catalyst onto biomass must be further studied. The poor dispersion and loading of the catalysts onto biomass will affect the lifetimes of the catalysts and also its activity.

In this paper, we discuss the adsorption of Nickel from aqueous solution onto oil palm mesocarp fiber (OPMF), one of the most available biomasses in Malaysia. Several important parameters such as pH and initial metal concentration were varied in this study in order to understand their effects on the adsorption and dispersion of nickel onto OPMF. The kinetic study was done in order to determine the appropriate adsorption kinetic model for OPMF-Nickel system the adsorption isotherm also was studied. The outcomes of this study are important for developing new biomass conversion process, i.e., the thermal conversion of metal-loaded biomass.

2. Materials and methods

2.1 Materials

Some amounts of Ni(NO₃)₂ were dissolved in 1200 mL of distilled water separately to prepare three concentrations. For Nickel solution pH adjustment, 0.1 M NaOH and 0.1 M HCl were used. The same acid and base were used for pre-treatment of OPMF before being loaded with Nickel.

2.2 Biomass preparation

The OPMF were collected from Sime Darby Plantation Sdn Bhd, Malaysia. The collected OPMF were oven dried for 24 h at 110 °C in conventional oven after directly sun dried for two days to remove the moisture content (Ohmukai et al., 2008). Then, the dried samples were ground and sieved to obtain particle size between 125 µm and 300 µm. The samples were stored in a tight container and were placed in a refrigerator for further use.

2.3 Characterization of biomass

To determine the functional groups of raw OPMF and Nickel loaded OPMF, the Fourier Transform Infrared (FTIR) analysis was carried out using PerkinElmer 2000 spectrometer with the range of wave number 500-4000 cm⁻¹. The Carbon (C), Hydrogen (H), Nitrogen (N), and Oxygen (O) contents of the raw OPMF were detected using elemental analyser CHNS-O (FlashEA 1112 Series). The sulfur content in palm oil wastes was found by many studies (Sulaiman and Abdullah, 2011) to be very low (less than 0.1 wt%), thus it was not determined in this study. The X-ray diffraction (XRD) analysis by using Rigaku Ultima IV, Cu Kα radiation (40kV/40mA) was done in order to prove the presence of Nickel phases on the OPMF surface and to determine the Nickel crystallite size by using Scherrer equation.

2.4 Nickel Loading onto OPMF

The loading of Nickel onto OPMF were studied at various solution pH (2.0-8.0) and using various Nickel concentration (in the range reported for industrial wastewater) with the highest ratio of fiber to Nickel is 20:1 by mass as in Yu et al., (2006) study which is between 505-1,682 ppm. The mixture of OPMF and Nickel solution was stirred by magnetic stirrer in a beaker for various soaking times. The solid samples that have been soaked and filtered were rinsed with distilled water several times until the filtrates having constant pH (Yu et al., 2006) and no Nickel detected using ICP-OES (iCAP 6000 Series). The same steps were repeated for various concentration of Nickel solution and various Nickel pH solutions. 0.1 M of NaOH and 0.1 M of HCl were used to adjust the initial metal pH from 2.0 to 8.0. The experiments were not conducted beyond pH 8.0 to avoid Nickel Hydroxide formation. The loaded-OPMF that has been filtered was dried in oven at 110 °C for 24 h. The dried samples were stored in a tight container and placed in a refrigerator before used in further analysis. Acid digestion method by using aqua regia solution was done in order to digest the OPMF samples in a microwave digester (Milestone ETHOS) before being tested using ICP-OES. This step is different from other adsorption experiments – Nickel concentration in this

study was determined from the solid while other methods usually determine Nickel concentration from the filtrates. Thus, the Nickel concentration in this study is quite lower if compared with previous studies.

3. Results and Discussion

3.1 Raw Material Analyses

The ultimate analysis of raw OPMF as in Table 1 shows that the OPMF consisted of moderately high contents of Oxygen and carbon, low Hydrogen and Nitrogen content. The elemental composition of OPMF in this study is comparable with previous study (Abnisa et al., 2013). Figure 1 show the FTIR analysis of untreated OPMF and OPMF treated with NaOH and HCl. There are slight changes of infrared spectra for OPMF that have been treated with NaOH where it is weaker than the others. The most significant band showed by Figure 1 occurred at $2,922\text{ cm}^{-1}$ which may be due to the presence of C-H_n groups that usually contain compounds of alkyl, aliphatic and aromatic. The broad peak between $3,600\text{-}3,100\text{ cm}^{-1}$ represent carboxylic acids (O-H groups) that usually acid and methanol. From Figure 1, the untreated raw OPMF shows a broad peak between $3,600\text{-}3,100\text{ cm}^{-1}$ and the peak becomes lesser after being treated with NaOH and HCl. The absorbance of the peaks in the treated OPMF samples were substantially lower than those in the raw sample indicating that bond stretching occurred to a lesser intensity due to the exchange of hydrogen ions with Na and Cl ions. Other functional group is C=C that showed by peak between $1,632\text{-}1,450\text{ cm}^{-1}$ which represent benzene and aromatic skeletal mode. All these groups or some of them is expecting to be responsible for the adsorption or ion-exchanging with the Ni(II) ions.

Table 1: Ultimate analysis of raw OPMF

| Ultimate analysis (wt%) | | | |
|-------------------------|------|------|-------|
| C | H | N | O |
| 46.38 | 8.12 | 4.80 | 40.70 |

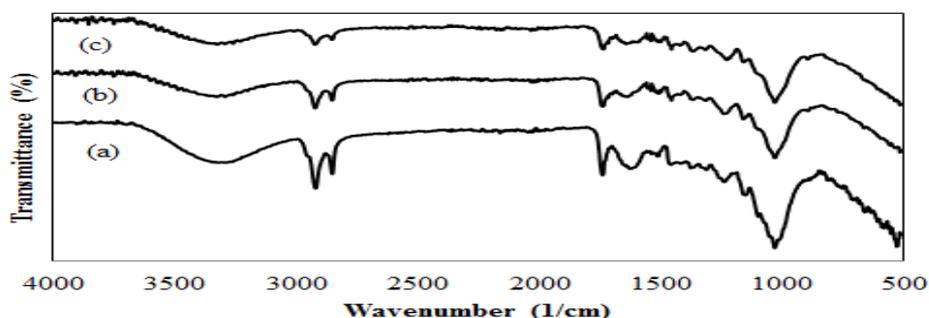


Figure 1: FTIR analysis of Raw OPMF (a) untreated, (b) treated with 0.1M HCl (c) treated with 0.1M NaOH

3.2 Adsorption of Nickel

Nickel loading was found to increase with increasing Nickel concentration as shown by ICP-OES analysis in Table 2. This characteristic of adsorption shows that the initial Nickel ion concentrations affecting the biomass surface saturation (Zafar et al., 2008). Intraparticle diffusion at higher Nickel concentration causes the hydrolyzed ions to diffuse at slower rate compared with lower Nickel concentration.

Table 2: Nickel loading by raw OPMF at different initial nickel concentration

| Sample name | Nickel loading (ppm) | | | |
|-------------|------------------------------------|----------------------------------|-----------------------|--------------------|
| | Initial nickel concentration (ppm) | Final nickel concentration (ppm) | Nickel loading (mg/g) | Nickel removal (%) |
| Raw OPMF | 1,682 | 1,537 | 1.44 | 1.71 |
| Raw OPMF | 842 | 738 | 1.21 | 2.87 |
| Raw OPMF | 505 | 420 | 0.85 | 3.37 |

The adsorption process at lower concentration of Nickel occurs quicker thus resulting in higher percentage of Nickel removal. pH metal solution is important in affecting the metal adsorption/loading by influencing surface properties of biomass, metal speciation in solution and degree of ionization (Chen et al., 2010). Figure 2 shows the Nickel loading onto untreated raw OPMF at pH 2.0 to 8.0. The trend of the Nickel loading in Figure 2 varies slightly for higher pH. As can be seen in Figure 2, the percentage of Nickel loading onto untreated raw OPMF is higher at higher Nickel solution pH due to high content of negative functional groups that attracts Ni(II) ions onto binding sites, resulting in lower electrostatic repulsion between Nickel ions and the surface. At lower pH, the competition between H⁺ ions and Ni(II) ions is greater than at higher pH, thus restrict the adsorption of Nickel, resulting in lower Nickel loading percentage.

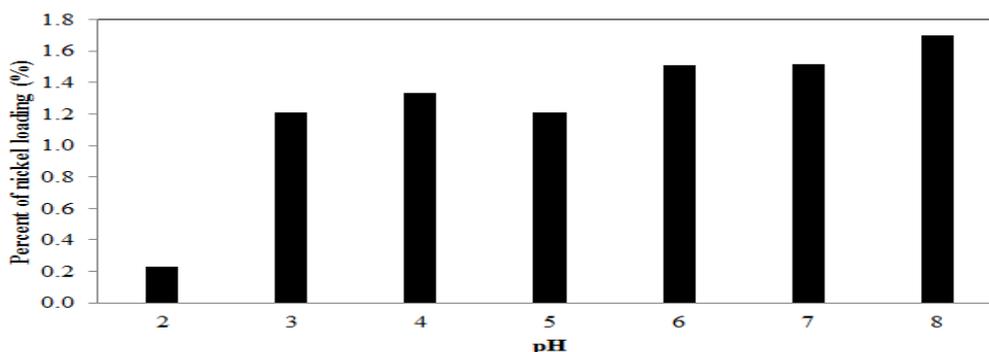


Figure 2: Percentage of nickel loading onto untreated raw OPMF at various nickel solution pH

3.3 XRD analysis

Figure 3 shows XRD analysis for nickel-loaded untreated OPMF at three different initial Nickel concentration (1,682, 842 and 505 ppm). It was observed that for OPMF loaded with initial Nickel concentration of 1,682 ppm, the peak for various Nickel Nitrate phases was clearly seen compared with the other two samples, at peak $2\theta = 22.19, 26.94, 34.50, 50.49, 67.94, 68.46$. The characteristic of XRD peak of Nickel Nitrate phase crystalline was obvious at $2\theta = 26.94$ as shown in Figure 3 (c), with the crystallite size of 55.2 nm according to Scherrer equation. Meanwhile, the peaks for nickel nitrate phases for the other nickel concentrations (Figure 3 (a) and (b)) seem lower than the previous one. For sample OPMF with initial Nickel concentration of 842 ppm, the Nickel Nitrate phases peaks detected were similar with the earlier one but the crystallite size is lower (40.3 nm). Meanwhile, the sample OPMF with initial concentration of 505 ppm, the Nickel Nitrate phases peaks not so clear and only detected at $2\theta = 22.06, 26.97, 34.94$ with the Nickel Nitrate crystallite size of 67nm. Thus, overall, for all initial Nickel concentration, the Nickel Nitrate crystallites on OPMF detected by XRD were in nano size range of 40-70 nm. The dispersion of the Nickel catalyst must be well dispersed and lower peak intensity means better dispersion of catalyst on support (Lu et al., 2013).

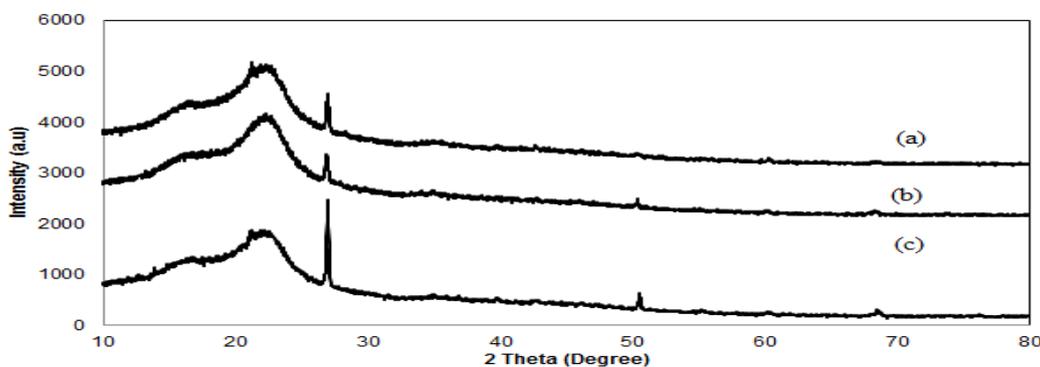


Figure 3: XRD analysis of nickel-loaded untreated OPMF with different nickel concentration (a) 505 ppm, (b) 842 ppm, (c) 1,682 ppm

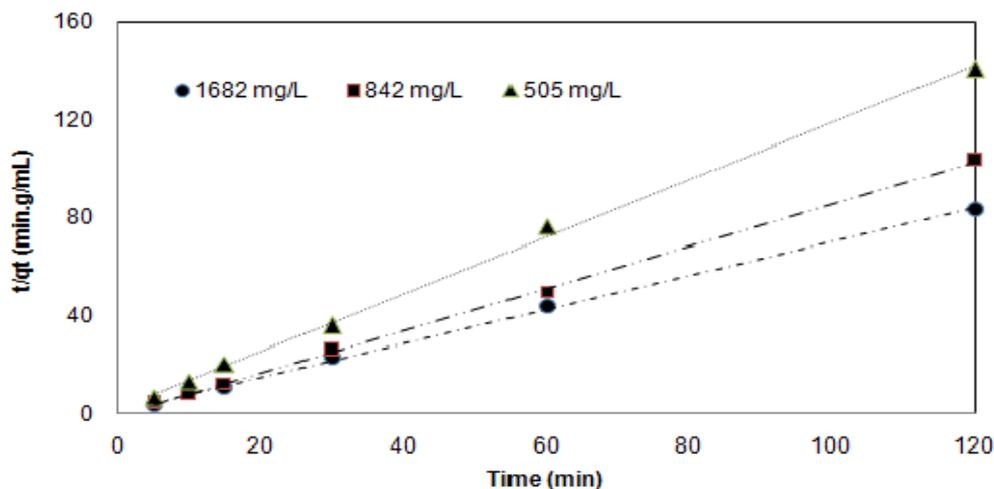


Figure 4: Pseudo-second order kinetic model of Nickel loaded untreated OPMF at various concentrations (Volume of Nickel Nitrate solution:1,200 mL, Mass of OPMF:200 g, pH of Nickel solution:7)

3.4 Adsorption kinetic

Adsorption kinetic model was used to determine the dynamic behaviour of sorption process (Chen et al., 2009). In this study, two kinetic models were applied – the Lagergren's first order (adsorption rate based on adsorption capacity) and the Pseudo-second order (explain chemisorption involving ion exchange and forces). Figure 4 showed the pseudo-second order kinetic plot for nickel loaded OPMF at various initial concentration where the q_t (mg/g) is the amount of Ni(II) adsorbed at time t . By comparing both results, the data fitted well using pseudo-second order with the R^2 (all above 0.99) higher than first order model for all Nickel concentration studied. Thus, the adsorption of Nickel by OPMF is heterogeneous system and the limiting step is chemisorption (Yadav et al., 2013).

4. Conclusion

This study shows that the loading of Nickel onto OPMF is influenced by initial concentration and initial pH of Nickel solution. The loading of Nickel varies slightly at higher pH. The higher value of initial pH of Nickel solution results in higher Nickel loading and the higher initial Nickel concentration having higher Nickel loading onto OPMF. Various types of functional groups in raw OPMF responsible for the Nickel adsorption, and the pre-treatment of raw material using NaOH and HCL show changes of the FTIR intensity bands, especially for the carboxylic group which show that this group mainly responsible for the Na and Cl ions attachment onto OPMF surface/matrix. From the XRD analysis, it is evidenced that several Nickel Nitrate phases are present on the untreated OPMF surface for all initial Nickel concentration with nano crystallite size in the range of 40-70 nm. All the Nickel Nitrate phases dispersed well especially at lower initial Nickel concentration. The kinetic model for Nickel adsorption by untreated OPMF is well described by pseudo-second order where chemisorption is the rate limiting step. The removal of Nickel by using OPMF is quite low in this study as it was measured from the solid and not from the filtrates. The outcomes of this study are important for developing future biomass conversion process such as the application of Nickel-loaded biomass as material in the gasification process that can enhance the production of syngas.

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