

Article

## Preparation and Characterization of Poly(ethyl hydrazide) Grafted Oil Palm Empty Fruit Bunch for Removal of Ni(II) Ion in Aqueous Environment

Ili Syazana bt Johari <sup>1</sup>, Nor Azah Yusof <sup>1,2,\*</sup>, Md Jelas Haron <sup>3</sup> and Siti Mariam Mohd Nor <sup>1</sup>

<sup>1</sup> Department of Chemistry, Faculty of Science, Universiti Putra Malaysia, Serdang UPM 43400, Selangor, Malaysia; E-Mails: ili@putra.upm.edu.my (I.S.J.); mariam@science.upm.edu.my (S.M.M.N.)

<sup>2</sup> Institute of Advanced Technology, Universiti Putra Malaysia, Serdang UPM 43400, Selangor, Malaysia

<sup>3</sup> Chemistry Unit, Centre of Foundation Studies for Agricultural Science, Universiti Putra Malaysia, Serdang UPM 43400, Selangor, Malaysia; E-Mail: mdjelas@gmail.com

\* Author to whom correspondence should be addressed; E-Mail: azah@science.upm.edu.my; Tel.: +603-8946-6782; Fax: +603-8943-5380.

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**Abstract:** Poly(ethyl hydrazide) grafted oil palm empty fruit bunch (peh-g-opefb) fiber has been successfully prepared by heating poly(methylacrylate)-g-opefb at 60 °C for 4 h in a solution of hydrazine hydrate in ethanol. The chelating ability of peh-g-opefb was evaluated based on removal of Ni(II) ions in aqueous solution. Adsorption of Ni(II) by peh-g-opefb was characterized based on effect of pH, isotherm, kinetic and thermodynamic study. This cheap sorbent based on oil palm empty fruit bunch fiber has a great future potential in water treatment industries based on high adsorption capacity, biodegradability and renewability.

**Keywords:** nickel ions; oil palm empty fruit bunch; grafted polymer; sorbent

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### 1. Introduction

Ni(II) is one of the heavy metals which is very commonly raised regarding environmental pollution and health problems [1]. The major contributor of Ni(II) in the environment is from industrial- and chemical-based agricultural activities such as mineral processing, paint formulation, electroplating,

porcelain enameling, copper sulphate manufacture, steam electric power plant [2], fossil fuel consumption, disposal of nickel compounds and alloys [3], aircraft industries [4], mining, smelting and refinery works [5]. In addition, it has also been widely used as dental alloy for orthodontic appliance [6].

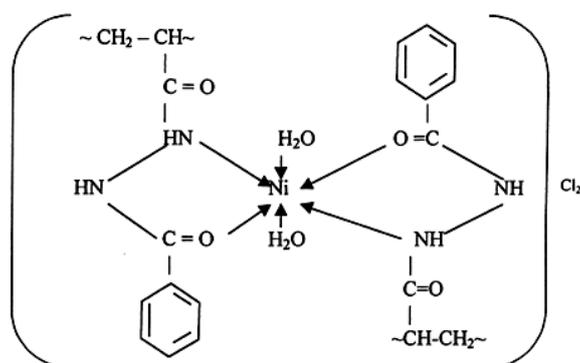
The uptake of Ni(II) into the human body is mainly via inhalation and ingestion which eventually results in the deposition and accumulation of nickel in the body system. The accumulation of nickel will lead to adverse effects including pulmonary fibrosis, renal edema and skin dermatitis, gastrointestinal distress [7], lung fibrosis, cardiovascular and kidney diseases, and the most serious effect is the carcinogenicity of the element [5].

In order to overcome this problem, researchers have tried to develop a method to reduce the concentration of toxic heavy metals in waste water to an acceptable level for environment and human health [8]. Many methods were applied by previous researchers to remove metal from aqueous systems including solvent extraction, precipitation, ultra-filtration, electrode-deposition, cementation, evaporation [9], ion-exchange and reverse osmosis [10]. However, adsorption was found to be the most appropriate technique because of its simplicity and high efficiency characteristics in metal removal and recovery.

In recent years, the use of the agricultural based adsorbents has become popular, particularly on an industrial scale, since they are able to reduce the operational cost and are environmental-friendly. Malaysia is one of major producers of palm oil [11]. Therefore, the abundant waste produced after the oil palm extraction is worthy of being explored since it is able to reduce the waste management problems. In this work, the oil palm empty fruit bunch (opefb) waste was grafted with methyl acrylate to obtained pma-g-opefb and then it was converted to peh-g-opefb. The final product was used as an adsorbent for removal of Ni(II) from aqueous solutions since it is known that hydrazide forms a stable complex with metal ion [12].

Figure 1 shows an example of complex formation of poly (acryloyl benzoic hydrazide) with nickel ion [13].

**Figure 1.** A complex of poly(acryloyl benzoic hydrazide) with nickel ion [13].



## 2. Experimental Section

### 2.1. Preparation of Poly(methyl acrylate) Grafted Oil Palm Empty Fruit Bunch (Pma-g-opefb)

The oil palm empty fruit bunch (opefb) fiber was grind using a stainless steel grinder, washed with hot water, rinsed with acetone and dried in oven at 60 °C for 24 h. The fiber was then sieved using

180 micron sieve in order to obtain homogenous fiber size. About 30.0 g of the opefb was suspended under nitrogen atmosphere into 500 mL of distilled water containing 20 mL hydrogen peroxide (6%) as initiator, 1.60 g of ferrous ammonium sulfate as co-initiator and 50 mL of purified methyl acrylate monomer. The mixture was heated at 75 °C for 3 h. After washing the grafted product with acetone, the pma-g-opefb was dried in oven at 60 °C. The details of the preparation of pma-g-opefb have been previously described [14]. The final weight was measured and grafting percentage ( $P_g$ ) was calculated using the following formula:

$$P_g (\%) = (W_2 - W_1)/W_1 \times 100\% \quad (1)$$

where  $W_2$  and  $W_1$  are the weights of purified grafted product and initial weight of opefb respectively.

## 2.2. Preparation of Peh-g-opefb

Peh-g-opefb was prepared by weighing 1.0 g of pma-g-opefb and refluxed for 4 h with 100 mL of hydrazine hydrate solution in ethanol (15% v/v). Then, the final product was filtered and washed several times with ethanol and dried in oven at 60 °C.

## 2.3. FTIR of Peh-g-opefb

The functional group presence in opefb, pma-g-opefb and peh-g-opefb were determined using Fourier Transform Infrared Analysis (FTIR) spectrometer (Perkin Elmer Spectrum 100 Series) using KBR pellets. The infrared spectra were recorded in the range of frequency of 400 to 4000  $\text{cm}^{-1}$ .

## 2.4. Adsorption Studies

### 2.4.1. Effect of pH on Ni(II) Adsorption

The uptake of metal ions was carried out by mixing 0.10 g of peh-g-opefb with 20 mL of 100 mg/L of metal solution at various pH in centrifuge tube. Sodium acetate was used as a buffer for pH 4 to 6 while HCl solution was used for pH 1 to 3. The sample was filtered and the amount of remaining metal ions in the solution was determined by inductively coupled plasma optical emission spectrophotometer (ICP-OES) model Perkin Elmer Instruments, Shelton, CT, USA (Optima 2000DV).

### 2.4.2. Effect of Initial Concentration and Temperature on Nickel Ni(II) Adsorption

The effect of initial concentration of metal ion solution was evaluated by mixing 0.10 g of peh-g-opefb fiber with 20 mL of metal ion solution at different concentration (50–1000  $\text{mg}\cdot\text{L}^{-1}$ ) at optimum pH. The experiment was carried out at different temperatures (25, 50 and 75 °C) in order to determine thermodynamic parameters.

### 2.4.3. Kinetic Study

Metal ions uptake was carried out by mixing 0.10 g of peh-g-opefb fiber with 20 mL of metal ion solution (100  $\text{mg}\cdot\text{L}^{-1}$ ) at different time interval (30, 90, 120, 250, 360, 480, 720, 840, 960 and 1200 min).

After each time interval, the sample was filtered and the amount of remaining metal ions in the solution was determined by ICP-OES.

### 3. Results and Discussion

#### 3.1. Characterization of Peh-g-opefb

The pma-g-opefb was successfully prepared with percentage grafting of 117.24%. The FTIR spectra of all opefb, pma-g-opefb and peh-g-opefb are shown in Figure 2.

**Figure 2.** FTIR spectra of opefb, pma-g-opefb and peh-g-opefb.

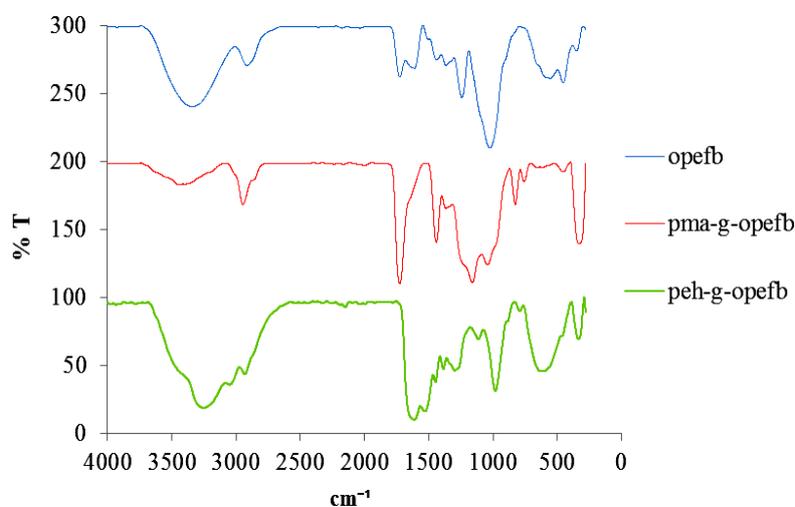


Figure 2 shows broad absorption band appear at around 3500–3200  $\text{cm}^{-1}$  in opefb indicates the O–H stretching attributing to hydroxyl group of cellulose, absorbed water, hemicelluloses and lignin in opefb [15]. However, the intensity of the hydroxyl absorption band decreased in pma-g-opefb due to the formation of macroradicals fiber after reaction of opefb with hydroxyl radicals during the grafting process. In peh-g-opefb, a broad absorption band was observed at about 3300  $\text{cm}^{-1}$  and 3100  $\text{cm}^{-1}$  indicating the N–H stretching from amine group. The presence of the absorption band is in agreement with the N–H stretching observed for poly (acrylamidrazone-hydrazide) which appear at 3319  $\text{cm}^{-1}$  and 3180  $\text{cm}^{-1}$  [16].

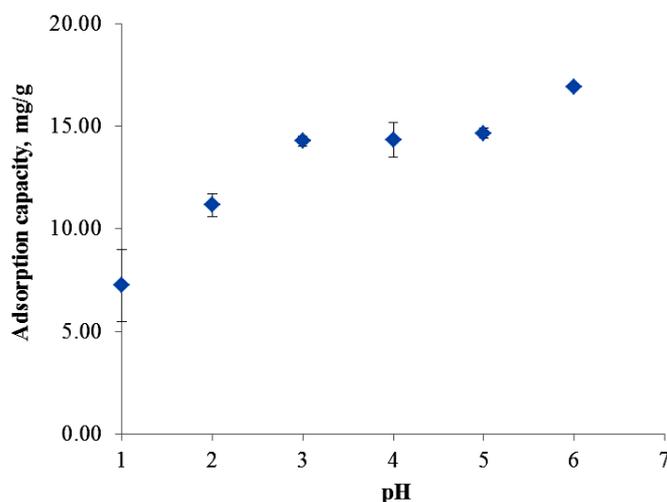
The FTIR spectrum of pma-g-opefb gives one absorption band at 1741  $\text{cm}^{-1}$  corresponding to C=O stretching of an ester functional group of the poly (methyl acrylate). When the pma-g-opefb is converted to peh-g-opefb, there is an obvious disappearance of carbonyl ester absorption band at 1741  $\text{cm}^{-1}$  and appearance of new absorption band around 1650  $\text{cm}^{-1}$  representing C=O stretching from amide in peh-g-opefb which is due to the conversion of majority of the ester group to hydrazide [17]. Furthermore, another absorption band observed at about 1580  $\text{cm}^{-1}$  indicating N–H bending in peh-g-opefb. This result was in agreement with Liu *et al.* which report the presence of N–H bending absorption band at around 1560  $\text{cm}^{-1}$  in poly(acrylamino-phosphonic-carboxyl-hydrazide) [18]. The existence of an absorption band at around 2900  $\text{cm}^{-1}$  in all grafted opefb, ungrafted opefb and peh-g-opefb is due to the C–H stretching from cellulose and lignin [14].

### 3.2. Effect of pH on Nickel (II) Adsorption

The result shows that the adsorption capacity towards nickel ion was low at pH 1 and 2. The low uptake of nickel ions in strong acidic medium may be attributed to the protonation of amine groups which leads to a strong electrostatic repulsions with the metal ion [19–21]. Hence, the protonated amine group obtained in lower pH medium has reduced the available binding sites for the adsorption of nickel ions. As the pH increased, the hydrazides on the adsorbents' surface mainly turn into dissociated forms that allowed an increase in the uptake of nickel ions due to more binding sites with negative charge [19]. The optimum pH for Ni(II) removal by peh-g-opefb is pH 6 and therefore, it was used for subsequent experiments.

Figure 3 indicates the adsorption capacity of peh-g-opefb towards nickel ion at different pH.

**Figure 3.** Adsorption capacity of peh-g-opefb towards nickel ion at different pH.



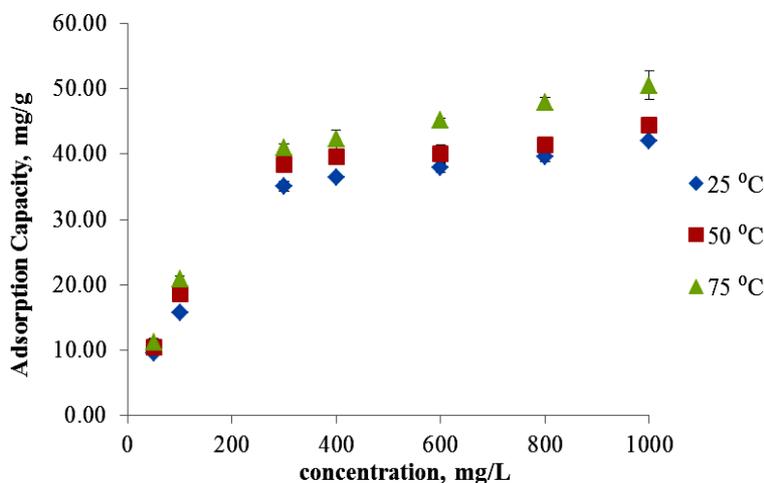
### 3.3. Effect of Initial Concentration on Ni(II) Adsorption

The result indicates that the adsorption capacity of nickel ions by peh-g-opefb is increased from  $9.52 \text{ mg}\cdot\text{g}^{-1}$  to  $41.74 \text{ mg}\cdot\text{g}^{-1}$  at  $25 \text{ }^\circ\text{C}$ ,  $10.61 \text{ mg}\cdot\text{g}^{-1}$  to  $45.29 \text{ mg}\cdot\text{g}^{-1}$  at  $50 \text{ }^\circ\text{C}$  and  $11.86 \text{ mg}\cdot\text{g}^{-1}$  to  $52.17 \text{ mg}\cdot\text{g}^{-1}$  at  $75 \text{ }^\circ\text{C}$  as the initial concentrations increased from  $50 \text{ mg}\cdot\text{L}^{-1}$  to  $1000 \text{ mg}\cdot\text{L}^{-1}$ .

Figure 4 shows the effect of different initial concentration of nickel ions on adsorption of Ni(II) by peh-g-opefb.

At low Ni(II) concentration ( $100\text{--}300 \text{ mg}\cdot\text{L}^{-1}$ ), the adsorption capacities significantly increase with increase initial concentration. This suggests that the increase of amount of the metal ions in the solution enhanced the interactions between metal ions and the active sites on the surface of adsorbent [22]. The initial concentrations of metal ions act as an important driving force to overcome all mass transfer resistance of metal ions between the aqueous and solid phase [4]. However, at the high concentration range ( $400\text{--}1000 \text{ mg}\cdot\text{L}^{-1}$ ) of Ni(II), there is only a slight increment on the adsorption capacity, indicating that peh-g-opefb is becoming saturated and fewer sites are available for metal adsorption [23].

**Figure 4.** Effect of initial concentration of nickel ions on adsorption capacities by peh-g-opefb at different temperature.



### 3.4. Effect of Temperature Ni(II) Adsorption

In temperature study, the result reveals that the uptake of nickel ion increased as the temperature increased, indicating that the adsorption of Ni(II) onto peh-g-opefb is an endothermic process. The increase in temperature increased the number of metal ions with sufficient energy to react with the active sites on the adsorbent surface [24,25]. Furthermore, increase in temperature may produce a swelling effect within the internal structure of the adsorbent, hence increase the interaction between metal ions and the active sites on the adsorbent [26].

### 3.5. Adsorption Isotherm

The isotherm study is a fundamental aspect in determining the nature of adsorption between adsorbent and the metal ions. It indicates how the metal ions are distributed between adsorbents and the metal solutions at equilibrium phase [8]. The adsorption data were analyzed using Langmuir, Freundlich and Temkin isotherm models.

The Langmuir isotherm model assumes that the surface of peh-g-opefb is homogenous and the adsorption potential towards Ni(II) is constant [27,28]. Langmuir isotherm model can be expressed using the following equation

$$C_e/q_e = C_e/Q_0 + 1/Q_0b \quad (2)$$

where  $Q_0$  is the maximum adsorption at monolayer ( $\text{mg}\cdot\text{g}^{-1}$ ),  $C_e$  is the equilibrium concentration ( $\text{mg}\cdot\text{L}^{-1}$ ),  $q_e$  is amount of metal adsorbed at equilibrium ( $\text{mg}\cdot\text{g}^{-1}$ ) and  $b$  is Langmuir constant ( $\text{L}\cdot\text{mg}^{-1}$ ).

The Freundlich isotherm model deals with the heterogeneous surface adsorbent which assumes that different sites involve different adsorption energies [20,27,28]. It can be expressed using the following equation

$$\ln q_e = \ln K_F + \ln(C_e/n) \quad (3)$$

where  $K_F$  is the Freundlich constant ( $\text{mg}\cdot\text{g}^{-1}$ ) indicating adsorption capacity and  $n$  is the Freundlich constant indicating intensity of the adsorption.

Lastly, the Temkin isotherm model assumes that adsorption is characterized by a uniform distribution of binding energies and expressed by the following equation [28].

$$q_e = (RT/b) \cdot \ln A + (RT/b) \cdot \ln C_e \quad (4)$$

where  $RT/b = B$ .  $A$  and  $B$  are constants where  $B$  is related to the heat of adsorption.

Based on the obtained results, Ni(II) adsorption by peh-g-opefb follows Langmuir isotherm model with high correlation coefficient  $R^2 > 0.99$ . Based on the  $R^2$  values, the data also fit the Freundlich and Temkin isotherm models. However, the relationship was statistically less significant in comparison to the Langmuir model. Therefore, it can be concluded that Ni(II) uptake onto peh-g-opefb involves a monolayer adsorption.

Table 1 summarized the isotherm data of Langmuir, Freundlich and Temkin model for the adsorption of Ni(II) onto peh-g-opefb.

**Table 1.** Langmuir, Freundlich and Temkin isotherm constants, maximum adsorption capacities  $q_{max}$ , and correlation coefficients  $R^2$  for nickel (II) adsorption at various temperatures.

| Temperature<br>(°C) | Langmuir isotherm                  |                              |        |        | Freundlich isotherm                   |        |        | Temkin isotherm |        |        |
|---------------------|------------------------------------|------------------------------|--------|--------|---------------------------------------|--------|--------|-----------------|--------|--------|
|                     | $q_{max}$<br>(mg·g <sup>-1</sup> ) | $b$<br>(L·mg <sup>-1</sup> ) | $R^2$  | $R_L$  | $K_F$<br>[mg/g(L/mg) <sup>1/n</sup> ] | $n$    | $R^2$  | $\ln A$         | $b$    | $R^2$  |
| 25                  | 42.19                              | 0.0415                       | 0.9981 | 0.1087 | 9.86                                  | 4.3975 | 0.9619 | 1.6643          | 5.0065 | 0.9395 |
| 50                  | 44.44                              | 0.0661                       | 0.9959 | 0.0717 | 16.12                                 | 6.2461 | 0.9888 | 4.7376          | 3.8720 | 0.9862 |
| 75                  | 51.02                              | 0.0545                       | 0.9936 | 0.0790 | 22.12                                 | 7.8678 | 0.9330 | 7.2172          | 3.5543 | 0.9731 |

The favorability of the adsorption process was predicted in terms of dimensionless constant separation factor, ( $R_L$ ). Using the  $b$  value obtained from the Langmuir isotherm equation, the separation factor,  $R_L$  can be calculated using following equation

$$R_L = 1/(1 + b \cdot C_0) \quad (5)$$

where  $C_0$  is the initial concentration of nickel (II) (mg·L<sup>-1</sup>) and  $b$  is the Langmuir constant (mL·mg<sup>-1</sup>).

The  $R_L$  values indicate whether the isotherm is irreversible ( $R_L = 0$ ), favorable ( $0 < R_L < 1$ ), linear ( $R_L = 1$ ) or unfavorable ( $R_L > 1$ ). The obtained data shows that the  $R_L$  values for nickel (II) adsorption onto peh-g-opefb are favorable at all temperatures with all  $R_L$  values are  $0 < R_L < 1$ .

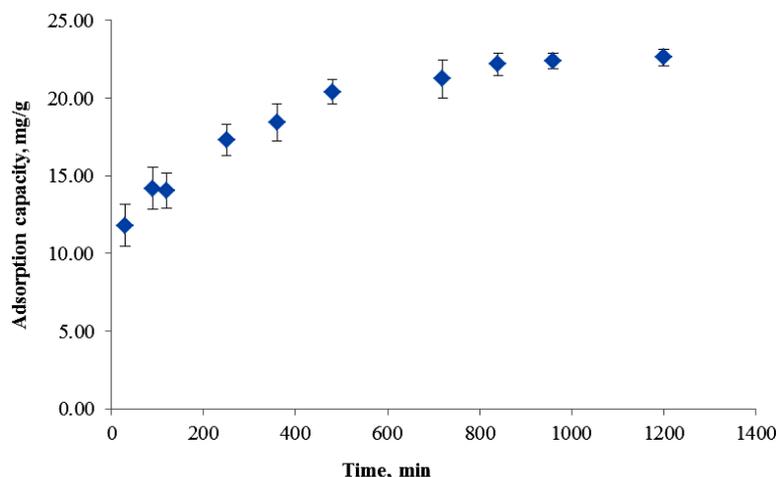
In addition, the  $n$  value obtained from Freundlich equation was able to give an indication as to the favorability of adsorption. According to Reddy *et al.*, the values of  $n$  in the range of 2–10 represent good, 1–2 moderately difficult and  $<1$  is poor adsorption [29]. Therefore, based on the data calculated, values of  $n$  for nickel (II) adsorption onto peh-g-opefb at all temperatures studied were in the range of 2–10 indicating a favorable adsorption process and this is in agreement with the  $R_L$  values.

### 3.6. Adsorption Kinetic

Kinetic study is another important parameter to determine the rate of adsorbate uptake in solid-liquid phase interface in the adsorption system [22]. Adsorption capacities data are plotted *versus* time to investigate the effect of time on equilibrium phase of the adsorption.

Figure 5 shows that the adsorption capacity gradually increases until it reaches equilibrium after about 720 min.

**Figure 5.** Adsorption capacity towards Ni(II) ion at different times.



In order to determine the mechanism and characteristics constant of the adsorption, two kinetic models which are the pseudo-first order and pseudo-second order kinetic models were applied to the experimental data. The pseudo first order kinetic model is expressed as follows

$$\ln(q_e - q_t) = \ln q_e - (k_1 \cdot t)/2.303 \quad (6)$$

where  $q_t$  is the amount of adsorbate on the sorbent at time ( $\text{mg} \cdot \text{g}^{-1}$ ),  $q_e$  is the amounts of adsorbate on the sorbent at equilibrium ( $\text{mg} \cdot \text{g}^{-1}$ ) and  $k_1$  is the first order rate constant ( $\text{min}^{-1}$ ).

Ho and McKay [30] proposed that pseudo-second-order kinetic model based on assumption that adsorption process follows second order chemisorption. The pseudo second order kinetic model can be written as follows

$$t/q_t = 1/(k_2 \cdot q_e^2) + t/q_e \quad (7)$$

where  $q_t$  is the amount of adsorbate on the sorbent at time  $t$  ( $\text{mg} \cdot \text{g}^{-1}$ ),  $q_e$  is the amounts of adsorbate on the sorbent at equilibrium ( $\text{mg} \cdot \text{g}^{-1}$ ) and  $k_2$  is the second order rate constant [ $\text{g} \cdot (\text{mg} \cdot \text{min})^{-1}$ ].

The kinetic constant with the correlation of coefficient for pseudo-first-order and pseudo-second-order kinetic models were calculated and the data show that the  $q_e$  calculated were much lower ( $15.92 \text{ mg} \cdot \text{g}^{-1}$ ) than the experimental value ( $22.78 \text{ mg} \cdot \text{g}^{-1}$ ) for pseudo-first order model indicating that nickel (II) adsorption is not occurring exclusively onto one site per ion [4].

On the other hand, the pseudo-second-order kinetic model gives  $q_e$  calculate ( $23.81 \text{ mg} \cdot \text{g}^{-1}$ ) close to  $q_e \text{ exp}$  ( $22.78 \text{ mg} \cdot \text{g}^{-1}$ ) for nickel (II) adsorption onto peh-g-opefb with the  $R^2 > 0.99$  confirming the applicability of pseudo second order kinetic model. It is also can be concluded that the overall rate of nickel (II) adsorption process was controlled by the chemical processes [4].

### 3.7. Adsorption Thermodynamic

Thermodynamic parameters such as enthalpy change ( $\Delta H^\theta$ ), entropy change ( $\Delta S^\theta$ ) and free energy ( $\Delta G^\theta$ ) are important in order to determine the spontaneity of the adsorption process. Those parameters can be

calculated from experimental data at various temperatures (298, 323, 348 K) using Van't Hoff equation as below

$$\ln K_D = \Delta S^\theta / R - \Delta H^\theta / RT \quad (8)$$

where  $K_D$  is distribution coefficient ( $\text{mL} \cdot \text{g}^{-1}$ ),  $\Delta S^\theta$  is standard entropy,  $\Delta H^\theta$  is standard enthalpy,  $T$  is absolute temperature (K) and  $R$  is gas constant. The distribution coefficient,  $K_D$  is obtained from  $q_e/C_e$  where  $q_e$  is the adsorption capacity and  $C_e$  is the concentration at equilibrium.

The enthalpy  $\Delta H^\theta$  and entropy  $\Delta S^\theta$  values can be obtained from the slopes and intercepts of linear regression of the plot  $\ln K_D$  versus  $1/T$  whereas the free energy was determined using the following equation

$$\Delta G^\theta = \Delta H^\theta - T \cdot \Delta S^\theta \quad (9)$$

Thermodynamic parameters for Ni(II) adsorption onto peh-g-opefb are tabulated in Table 2 below.

**Table 2.** Thermodynamic parameters of nickel (II) adsorption onto peh-g-opefb.

| Temperature<br>(K) | Enthalpy, $\Delta H^\theta$<br>(kJ·mol <sup>-1</sup> ) | Entropy, $\Delta S^\theta$<br>(J·mol <sup>-1</sup> ·K <sup>-1</sup> ) | Free energy, $-\Delta G^\theta$<br>(kJ·mol <sup>-1</sup> ) |
|--------------------|--|---|--|
| 298                |  |   | 6.83   |
| 323                | 51.38  | 195.31  | 11.71  |
| 348                |  |   | 16.60  |

The negative values of free energy,  $\Delta G^\theta$  indicates the spontaneous nature of the adsorption process. The  $\Delta G^\theta$  for Ni(II) adsorption increase as the temperature increase which leads to an increase in the feasibility of the adsorption at higher temperature [31,32]. In other words, more negative values reflect a more energetically favorable adsorption process [7].

The positive value of entropy,  $\Delta S^\theta$  indicates that the system becomes more disordered at the solid-solution interface during adsorption [33], resulting in the irreversibility of the process [34]. The positive value of enthalpy  $\Delta H^\theta$  shows that an endothermic process occurred during adsorption of Ni(II) onto peh-g-opefb.

#### 4. Conclusions

Poly(ethyl hydrazide) grafted opefb (peh-g-opefb) was successfully prepared via refluxing poly(methyl acrylate) grafted opefb (pma-g-opefb) with 15% (v/v) hydrazine hydrate in ethanol for 4 h. The pma-g-opefb obtained with percentage grafting ( $P_g$ ) of 117.24%. The modified fiber was characterized using FTIR shows two absorption bands were observed in peh-g-opefb at about 3300 and 3100  $\text{cm}^{-1}$  indicating the N–H stretching for amine group. pH study indicates that nickel adsorption occurred at pH 6 with maximum adsorption capacity of 42.19  $\text{mg} \cdot \text{g}^{-1}$  at 25 °C. The isotherm data indicates Ni(II) adsorption fit with Langmuir model and it follow pseudo-second-order kinetic model. This study reveals that peh-g-opefb has a great future potential as biosorbent for heavy metal removal from agricultural waste which is abundant in Malaysia.

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## Conflict of Interest

The authors declare no conflict of interest.

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