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Adsorption Capacity of Nickel (II) and Cobalt (II) Ions from Aqueous Solutions by Oil Palm Waste and Sawdust

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Abstract. Four types of biomass were characterized to investigate its metal adsorption capacity. The biomass were soaked in with nickel and cobalt solutions to examine the effect of biomass to amount of metal adsorbed. Oil palm mesocarp fibre (OPMF), empty fruit bunch (EFB), palm kernel shell (PKS) and sawdust were used in this study. Among all the biomass studied, oil palm mesocarp fibre shows the highest adsorption capacity with 1.8 mg/g and 1.6 mg/g of nickel and cobalt uptake, respectively. The metals adsorbed on the biomass were found to disperse into nano-size range.

Introduction

Pollution from heavy metals is a major concern in developing countries. The discharge of heavy metals into watercourses is a serious pollution problem which may affect the quality of water supply. Nickel presents in wastewater of a number of industries e.g. batteries manufacture, steel, electroplating, etc [1]. The main contaminant sources of cobalt in wastewater are electroplating, catalytic processes, ceramic and alloys industries [2]. The concentrations of these metals must be brought down to the permissible limit before discharging into watercourses. If the permissible limit is exceeded, it can potentially results in damaging effects of human health and biological systems [3].

Conventional heavy metal removal technologies such as ion exchange, coagulation, flocculation, chemical precipitation, reverse osmosis, etc. are often ineffective or expensive. Adsorption is an alternative method for the removal of heavy metals from aqueous solutions because of its low cost and simple design. Biosorption is a bioremediation process of heavy metals by using agricultural byproducts. This utilizes inactive microbial biomass to bind and concentrate heavy metals from waste stream. A large variety of unconventional adsorbents have been examined for their ability to remove various types of pollutants from water and wastewater and have been reviewed extensively[1].

Malaysia is one of the major suppliers of palm oil. Palm oil mills leave behind a huge amount of biomass, such as as empty fruit bunch (EFB), kernel's shells and oil palm mesocarp fiber (OPMF) are the most abundantly available biomass wastes. Malaysia produces about 80 million tonnes of dry biomass and it is projected to increase to 100 million tonnes by the year 2020 [4]. Biomass from oil palm and wood industry contributes about 86% and 4% of the total biomass available in Malaysia, respectively [5].

In the present study OPMF, EFB, PKS and sawdust was selected as adsorbent. The aim of this paper is to investigate the capacity of different biomass in adsorbing Ni(II) and Co(II) ions from aqueous solutions.

Materials and Methods

Samples of OPMF, PKS and EFB were collected from Sime Darby Plantation Sdn Bhd, Pulau Carey. Sawdust was collected from KPS Plywood Sdn Bhd , Puchong. The biomass were sun dried for two days and further dried in oven for one night at 110°C for 24h to remove the remaining moisture [6]. The resulting material was sieved in the size range of 125-300 μm particle size. The material was placed in airtight container for further use and placed in refrigerator.The stock solution of metal ions was prepared by dissolving their corresponding nitrate salts{$Ni(NO_3)_2.6H_2O$, $Co(NO_3)_2.6H_2O$} in distilled water. All the chemicals used were obtained from Sigma-Aldrich.

Metal adsorption by OPMF, EFB, PKS, and sawdust was evaluated using initial metal concentrations 2018 mg/L and 2025 mg/L for nickel and cobalt ion respectively .200 g of biosorbent was added in 1200 ml aqueous solution. The mixture solutions were stirred by magnetic stirrer in a beaker for 24h. The mixture was filtered and the solid sample was rinsed with distilled water several times until the filtrates have constant pH and no nickel detected using ICP-OES (iCAP 6000 Series).

The solid samples were digested by using acid digestion method. It was prepared by mixing 2 ml H_2O_2 (30%) and 6 ml HNO_3 (65%). The digested samples were then being analyzed by ICP-OES. The capacity of different biomass in adsorbing metal ions was computed using the equation:

$$q = \frac{(Ci - Cref)V}{W} \qquad (1)$$

where q is the adsorption capacity (mg/g), Ci is the concentration of metal in solution after the biosorbent have been digested (mg/L), $Cref$ is the concentration of metal in solution after the biosorbent have been digested (blank sample)(mg/L), V is the volume of metal ion solution (L) and W is the weight of the adsorbent used to digest (g). Analysis of the biosorbent were made using Fourier Transform Infrared (Perkin –Elmer 2000) and X-ray Diffractometer (Rigaku Model Ultima IV).

Results and Discussion

Adsorption Capacity of Ni(II) and Co(II) Ions OPMF was found to be the most efficient in adsorbing nickel and cobalt ions from its aqueous solution among all the biosorbent tested (Fig. 1). The order of metal adsorption is as followed OPMF > Sawdust > EFB > PKS for both nickel and cobalt ions.

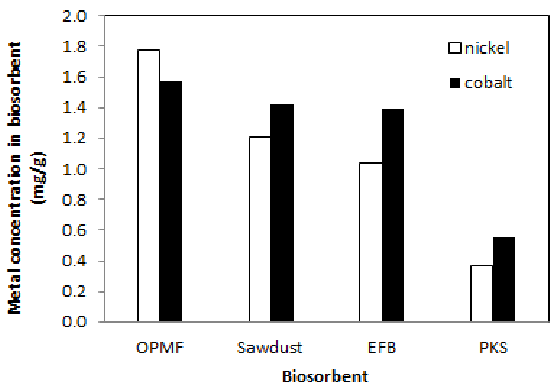

Figure 1: Capacity of Ni(II) and Co(II) by different biosorbent.

Characterization of Biomass

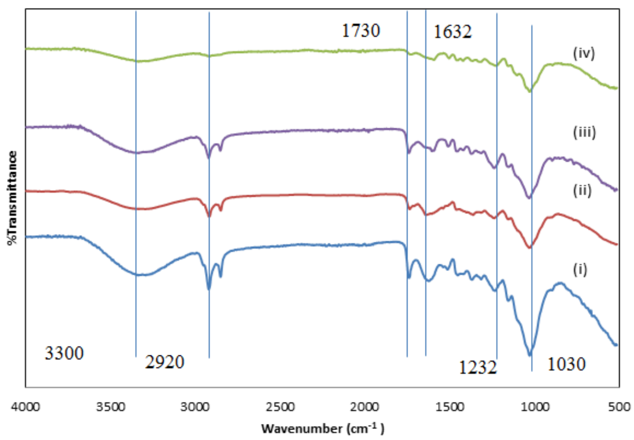

Figure 2: FTIR spectra of raw biomass (i) OPMF (ii) EFB (iii) PKS (iv) sawdust.

Table 1: Main functional groups of four biosorbent.

Wavenumbers (cm^{-1})	Vibration	Functional group
3600-3100	O-H	phenol
2860-2970	$C\text{-}H_n$	alkyl,aliphatic, aromatics
1700-1730	C=O	ketone and carbonyl
1632	C=C	benzene stretching ring
1232	$COOH^-$	carboxyl group
1030	C-O	ethanol

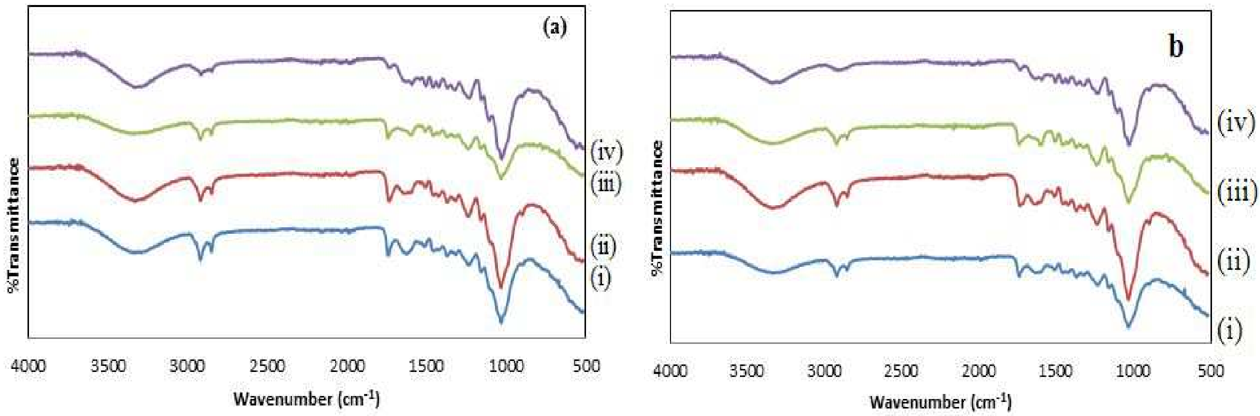

Figure 3: a FTIR spectra of nickel loaded biomass (i) OPMF (ii) EFB (iii)PKS (iv) sawdust. b Spectra of cobalt loaded biomass (i) OPMF (ii) EFB (iii) PKS (iv) sawdust.

FTIR Spectral Analysis FTIR spectra for raw OPMF, EFB, PKS and sawdust are shown in Fig 2. The typical functional groups and the IR signals are listed in Table 1, along with a list for each signal as a preference. The spectra of raw OPMF, EFB and PKS are similar to their intensities . The infrared spectra of oil palm mesocarp fibre exhibited broader bands at 3300 cm^{-1} and 1030 cm^{-1} than other biomass [6]. These broader bands show high frequency of the functional group.The high frequency of the functional group in turn suggests that exists abundant sites for metal adsorption [7]. FTIR spectra of loaded biomass with nickel and cobalt in Fig. 3 a and b respectively.

No significant band shifts were observed among nickel and cobalt loaded biomass. However, the above functional groups are slightly affected in their position and intensity. Exposure of Ni^{2+} and Co^{2+} causing minor shift in the O-H band, which is associated with the stretch of phenol group as shown in Table 2.

Table 2: FTIR spectral O-H band in raw and metal loaded adsorbent.

	OPMF (cm^{-1})	EFB(cm^{-1})	PKS(cm^{-1})	Sawdust(cm^{-1})
Raw adsorbent	3326	3341	3341	3334
Nickel	3341	3336	3330	3335
Cobalt	3340	3340	3335	3336

The phenol group is suggested to adsorb at the surface of the biomass by ion exchange mechanism with the functional groups present in the biomass or by hydrogen bonding as shown below.

$$2(\text{-ROH})+M^{2+} \rightarrow 2(\text{RO})M+2H^+ \quad \text{ion exchange} \tag{2}$$

$$\text{-ROH} + M(OH)^+ \rightarrow (\text{-RO})M(OH)+ H^+ \quad \text{ion exchange} \tag{3}$$

$$2(\text{-ROH})+M(OH)_2 \rightarrow (\text{-ROH})_2 +M(OH)_2 \quad \text{H –bonding} \tag{4}$$

Where M represents the metal ions and R represents the matrix of biomass, respectively. A similar theory was proposed by several earlier workers for metal sorption on different adsorbents [7,8].

XRD Analysis The XRD results of the nickel and cobalt loaded biomass are shown in Fig 4 a and b respectively.It was observed as $Ni(NO_3)_2$ at 2θ =15.45, 15.77, 22.07, 22.41, 22.64, 22. 84. For

$Co(NO_3)_2$ at 2θ = 15.62, 16.05, 21.82, 21.97, 22.83 and 26.29. The crystalline size was calculated using Scherer equation. It was observed that the crystalline size of $Ni(NO_3)_2$ and $Co(NO_3)_2$ was between 18-30 nm.

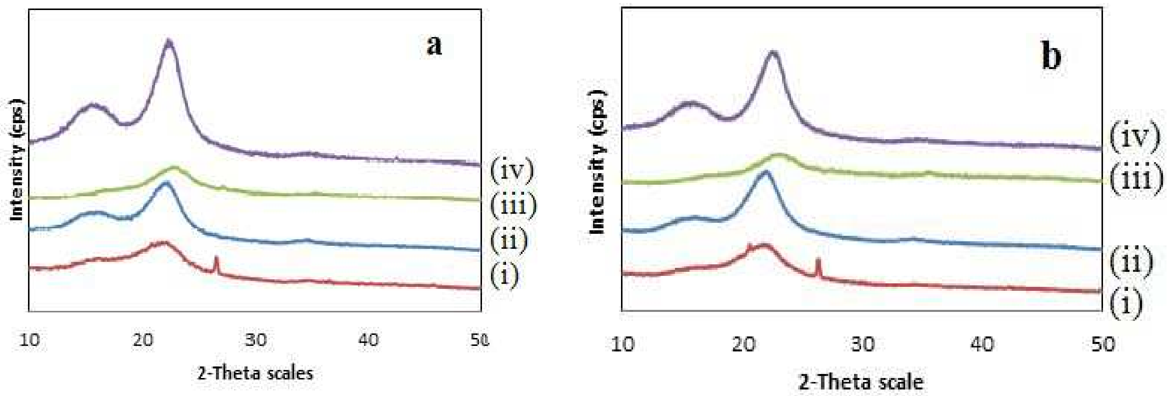

Figure 4: a XRD diffraction pattern of nickel loaded biomass (i) OPMF (ii) EFB (iii)PKS (iv) sawdust. b XRD diffraction pattern of cobalt loaded biomass (i)OPMF (ii) EFB (iii) PKS (iv) sawdust.

Conclusions

The results obtained in this study demonstrated the potential use of OPMF, EFB, PKS and sawdust for the adsorbtion of Ni(II) and Co(II) ions from aqueous solutions. Oil palm mesocarp fibre (OPMF) showed the highest metal adsorption capacity among other biomass because of the the high concentration of the functional group. The order of metal adsorption is as followed; OPMF> Sawdust> EFB> PKS. The metal adsorb on the biomass were found to disperse into nano-size range.

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