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A Comparative Study of Cadmium, Nickel and Chromium Adsorption using Residual Biomass from *Elaeisguineensis* Modified with Al_2O_3 Nanoparticles

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Abstract

Background: The biosorption technology has been recognized as an attractive alternative for heavy metal ions uptake due to its several advantages as low cost and environmental friendly. **Objectives:** In this work, a biosorbent was synthesized from African oil palm bagasse biomass and alumina nanoparticles in order to use it for removing cadmium, nickel and chromium from aqueous solution. **Methods/Analysis:** The synthesis of Al_2O_3 was performed according to sol-gel methodology. The nanoparticles were loaded into biomass using an organic solvent. The resulting material was characterized by FT-IR, SEM and EDX analyses. The point of zero charges as well as ultimate analysis were also carried out for biomass. **Findings:** The FT-IR analysis revealed absorption bands characteristic of lignocellulosic biomass attributed to carboxyl, hydroxyl and amides functional groups. The presence of O-Al-O and Al-C=O suggested the successful synthesis of biosorbent. The morphology was identified as porous which enhances adsorption process. The EDX analysis confirms that carbon is the major constituent of biosorbent, similar to the results of ultimate analysis of African oil palm bagasse. In addition, removal yield values for cadmium, nickel and chromium of 92.02, 87.06 and 4%, respectively, were achieved at pH=6. **Novelty/Improvement:** This biosorbent exhibited excellent adsorption properties and could be used efficiently for removing cadmium and nickel water pollutants.

Keywords: Biosorption, Heavy Metals, Removal Yields, Uptake

1. Introduction

The increasing development of industries has led to discharge hazardous wastes into the environment including heavy metal ions[1]. Heavy metal water pollutants have been recognized of major concern worldwide due to its non-biodegradability, non-thermodegradability, persistence and bioaccumulation in living organism[2]. Several conventional technologies have been applied in chromium, nickel and cadmium removal as chemical precipitation, evaporation, biosorption, ion exchange and membrane separation[3]. Among these, biosorption process has emerged as a cost-effective and efficient alternative for water and wastewater treatment[4]. Different novel approaches are being proposed to prepare biosorbents from residual lignocellulosic biomass, which consists of three basic macromolecular components: cellulose, hemicellulose and lignin[5]. African oil palm (*Elaeisguineensis)* is a perennial crop widely used for producing oil generating a huge amount of biomass wastes mainly in plantation and milling activities[6]. The use of residual biomass offers many advantages including low cost of biosorbent, solution of disposal problems, and decrease of vector-borne disease. Additionally, modifications of residual biomasses have been recently studied using compounds such as calcium chloride, citric acid and nanoparticles[7,8]. The load of nanoparticles onto biomass increases mass transport because of the high surface area of the resulting biosorbent[9]. The aim of this work is to compare removal yield of different heavy metal ions using a biosorbent prepared from African oil palm bagasse chemically modified with Al_2O_3 nanoparticles.

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2. Material and Methods

2.1 Biomass Preparation

The bagasse of African oil palm (*Elaeisguineensis*) was purchased from a local market and used for preparing biosorbent. The raw biomass was cut into small pieces and washed with distillate water several times to remove surface-adhered particles. After drying for 24 hours at 80°C, the dried biomass was grounded and sieve-meshed to obtain homogenous-size particles (0.355, 0.5 and 1 mm)[10,11].

2.2 Synthesis of Nanoparticles

The synthesis of alumna nanoparticles (Al_2O_3) was carried out according to sol-gel method reported by[12]. In brief, 0.5 M ($Al(NO_3)_3 \cdot 9H_2O$) solution was added to 0.5 moles of citric acid ($C_6H_8O_7$) and stirred continuously under a temperature of 60°C. After observing a yellow color, the temperature was increased to 80°C and a gel was formed. In order to obtain a power, the resulting gel was heated at 750°C for 2 hours.

2.3 Biomass Modification with Alumina Nanoparticles

Dimethyl sulfoxide (DMSO), Tetra ethyl-o-silicate (TEOS) and ethanol (C_2H_5OH) were used as starting materials for loading Al_2O_3 nanoparticles into African oil palm bagasse biomass. It was prepared a suspension of DMSO with 0.5 g of biomass and kept under stirring for 24 hours at 120 rpm. The TEOS solution was added and stirred for 48 hours at 100 rpm. It is well known that TEOS molecules hydrolyzed and condensed during this procedure. Then, 0.3 of nanoparticles powder was mixed with the suspension of biomass and stirred for 12 hours. Finally, the resulting biosorbent was washed thoroughly with ethanol[13,14].

2.4 Characterization Techniques

The prepared biomass was characterized by ultimate analysis in order to determine contents of main elements as carbon, hydrogen and nitrogen. Fourier Transform Infrared Spectroscopy (FT-IR) was also carried out to identify functional groups. The presence of lactonic, phenolic and carboxylic components was determined by Boehmtitration. Table 1 summarizes analytical methods applied to African oil palm bagasse biomass.

Table 1. Analytical methods for chemical characterization of biomass

Parameter	Method
Carbon (%)	AOAC 949.14
Hydrogen (%)	AOAC 949.14
Nitrogen (%)	AOAC 984.13 KJELDAHL
Ashes (%)	Thermogravimetry
Pectin (%)	Digestion-thermogravimetry
Lignin (%)	Photocalorimetry
Cellulose (%)	Digestion-thermogravimetry
Hemicellulose (%)	Digestion-thermogravimetry
Functional groups	FT-IR
Lactonic, phenolic and carboxylic components	Böehm titration

The Boehm method is limited to quantify phenol, lactones and carboxyl components and is based on a neutralization of acid groups in biomass surface by sodium etoxide, sodium hydroxide, sodium carbonate and sodium bicarbonate[15]. The methodology for Boehmtitration is described as follows: 50 mL of 0.05 M $NaHCO_3$, Na_2CO_3 and NaOH solutions were prepared. Afterward, 1.5 g of biomass was added to this solution and stirred for 24 hours at 180 rpm. Filtration was required to separate solids from aqueous sample and an aliquot of 10 mL was extracted. Standardized HCl and NaOH were added dropwise and final pH was measured.

The average crystalline size of alumina nanoparticles was determined according to the results provided by powder X-ray Diffraction (XRD) analysis. Scanning Electron Microscopy (SEM) technique was carried out in an EOL JSM-6490LV microscope coupled to an EDS for biomass modified with Al_2O_3 nanoparticles in order to study morphology of these nanomaterials and identify its elemental composition. The effects of alumina nanoparticles on biomass were observed by variations of functional groups in FT-IR spectrum.

2.5 Determination of Point of Zero Charges

The point of zero charges corresponds to the pH value in which the net charge of biomass surface is neutral reaching dissociation and association equilibriums[15]. This pH value is widely calculated for materials used in adsorption process because of the changes of surface charge after adsorbing H^+ or OH^- ions[16]. In this work, the point of zero charges (pH_{PZC}) was determined by mixing 0.5 g of biomass with 50 mL of distillate water previously pH adjusted. The mixture was kept in continuous stirring for 48 hours and pH solution was measured.

2.6 Biosorption Study

The adsorption experiments were carried out on a stirrer plate at room temperature (28°C) for 2 hours. The stock solutions of Ni (II), Cd (II) and Cr (VI) ions were obtained by dissolving nickel sulfate ($NiSO_4$), cadmium sulfate ($CdSO_4$) and potassium dichromate ($K_2Cr_2O_7$) in deionized water. The pH was adjusted to 6 by adding HCl and NaOH solutions. The remaining heavy metal ions concentration was determined by diphenylcarbazide acid solution with an UV/Vis Shimdzu UV 1700 spectrometer. The removal yield was calculated by Equation 1.

$$\text{Removal yield}(\%) = \frac{(C_o - C_e)}{C_o} 100\% \qquad (1)$$

3. Results and Discussion

3.1 Characterization of Residual Biomass

Ultimate Analysis: (Table 2) the ultimate analysis results revealed the presence of characteristic elements in organic materials as carbon, which most contributes to biomass composition with 38 %. In addition, the composition of cellulose, pectin, lignin and hemicellulose was 19.90, 4.88, 17.11 and 7.00 (wt. %), respectively.

Table 2. Composition of African oil palm bagasse biomass

Parameter	Value
Carbon (%)	38.27 ± 0.45
Hydrogen (%)	4.71 ± 0.05
Nitrogen (%)	2.03 ± 0.11
Sulfur (ppm)	0.18 ± 0.04
Ashes (%)	4.23 ± 0.14
Pectin (%)	4.88 ± 0.17
Lignin (%)	17.11 ± 0.27
Cellulose (%)	19.90 ± 0.35
Hemicellulose (%)	7.00 ± 0.12

FT-IR Analysis: The biomass from African oil palm bagasse is mainly made up of lignin and cellulose that content functional groups as hydroxyl, alcohol, aldehydes, ketones, phenolic acids and ethers identified as chemical bonding agent with heavy metal ions[17]. In order to determine functional groups contributing to adsorption of cadmium, nickel and chromium onto the surface of biomass, FT-IR analysis was carried out to African oil palm bagasse before and after loading the nanoparticles. Figure 1 revealed the presence of absorption band around 3367.08 cm^{-1} attributed to hydroxyl stretching vibrations. The peak at 1716.73 cm^{-1} is assigned to carboxyl group, which is widely observed in lignocellulosic biomass. The sharp peak identified at 1034.32 cm^{-1} corresponds to primary alcohols and suggests the presence of C-OH bonding[17]. Other functional groups were

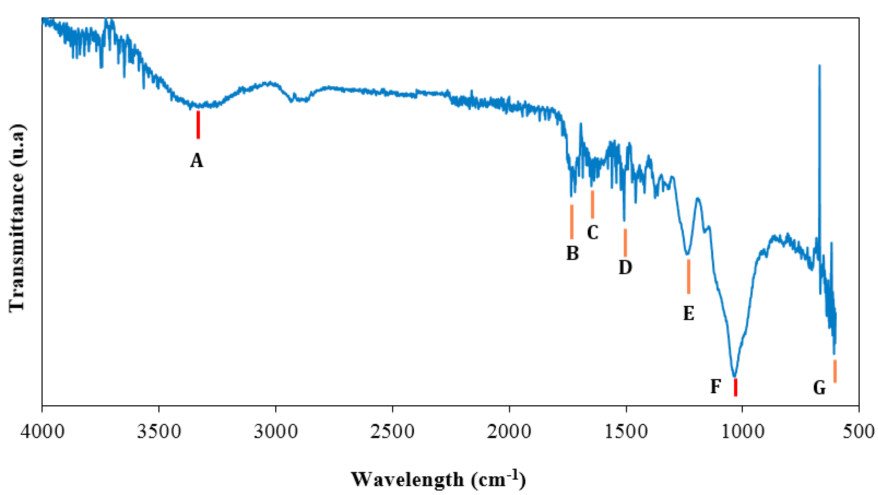

Figure 1. FT-IR spectrum of biomass from African oil palm bagasse.

identified and summarized in Table 3 according to that reported by[18].

Table 3. Characteristic absorption bands in FT-IR spectrum of biomass

Band	Wavelength (cm-1)	Functional group	Bond
A	3367. 08	Alcohol and phenols	O–H
B	1716.73	Aldehydes, ketones and carboxylic acid	C=O
C	1647.04	Alkenes	C=C
D	1507.38	Amides	–NH–
E	1236.21	Secondary alcohol	C–OH
F	1034.32	Primary alcohol	C–OH
G	703.85	Mono and di substituted amine	N–H

Skoog et al.[18]

The FT-IR spectrum of chemically modified biomass with alumina nanoparticles is shown in Figure 2. It can be observed the presence of absorption peaks corresponding to aluminum oxide: the bandsat 650 and 700 cm^{-1} are attributed to Al-O-Al stretching vibrations[19]. In addition, characteristic peak around 950-1200 cm^{-1} corresponds to Al-O-Si and Si-O-Si bonds. These vibrations appeared in frequencies similar to Al-O-Al due to the atomic mass[20]. The stretching vibrations of Al-C=O were identified at 1500-1700 cm^{-1} and the frequencies between 2600-3800 cm^{-1} are assigned to Al-COOH[19], which indicated an effective incorporation if aluminum and oxygen to residual biomass structure. Other bonds with aluminum identified in this spectrum are listed in Table 4.

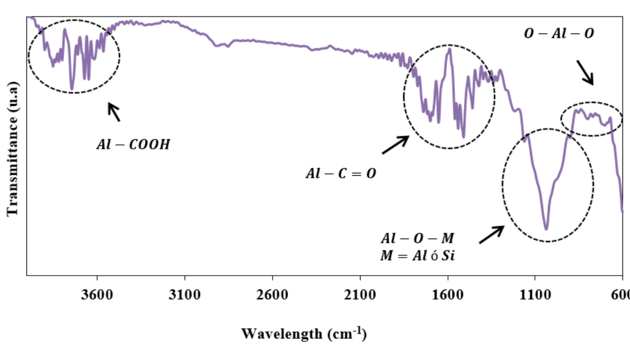

Figure 2. FT-IR spectrum of chemically modified biomass with alumina nanoparticles.

Table 4. Characteristic absorption bands in FT-IR spectrum of chemically modified biomass

Functional groups	Wavelength (cm^{-1})
O-Al-O	650-700
Al-O-M M=Al ó Si	950-1200
Al-C=O	1500-1700
Al-COOH	2600-3800

Carmona[19]

Boehm Titration: The amount of carboxylic, lactonic and phenolic groups were measured by Boehm titration and it was found values of 2362, 18890 and 0 µmoles, respectively. Hence, it can be inferred that African oil palm bagasse exhibits active functional groups related to interactions with metallic species as cadmium and nickel[17,21]. Figure 3 shows pH curve used to determine the equivalent point and the amount of sodium hydroxide required to carry out Boehm procedure[22].

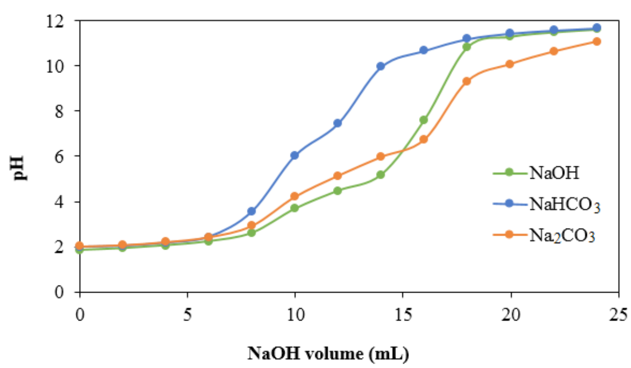

Figure 3. Behavior of pH during titration procedure of African palm bagasse biomass.

XRD Analysis: The particle size of alumina nanoparticles plays an important role to develop adsorbents from biomasses due to it is associated to the surface area of nanomaterials. Hence, a reduction in particle size increases the surface area and the number of active sites in the crystalline surface, which enhances adsorption process and allows to uptake heavy metals ions[23]. XRD analysis was performed in order to determine the particle size of Al_2O_3 nanoparticles using Scherrer method. As is shown in Figure 4 the sharp peaks in XRD pattern suggested the formation of alumina nanoparticles in amorphous phase[24]. The Scherrer equation is described by Equation 2, where is (1.45 Å) and s the line broadening at half the maximum intensity. It was calculated an average particle size of 56 ± 12 nm, similar to that reported by[24] who pointed out particle sizes of alumina nanoparticles synthesized by sol-gel methodology ranged in 15-80 nm.

$$d = \frac{0,89\,\lambda}{\beta Cos\theta} \qquad (2)$$

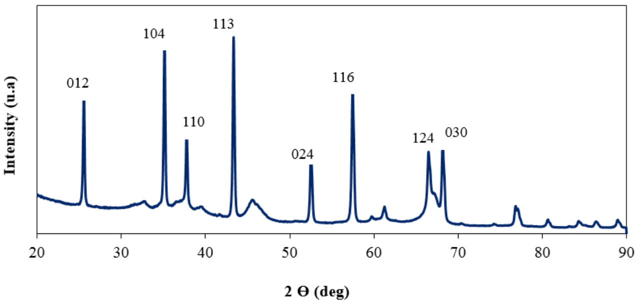

Figure 4. XRD pattern of alumina nanoparticles.

SEM and EDX Analysis: As can be observed in Figure 5, the resulting biomaterial after loading alumina nanoparticles revealed a porous surface, which conforms the presence of alumina amorphous phase. This kind of morphology offers a high surface area recommended for biosorbent-sorbate contact. The SEM micrograph also verified that particle size existed in the nanoscale range[25]. The EDX spectrum of modified biomasses with alumina nanoparticles exhibited characteristic peaks attributed mainly to C and O elements as shown in Figure 6. The elemental composition was identified as follows: C (wt%) 46.92, O (wt%) 48.32, Al (wt%) 2.27 and Si (wt%) 2.48.

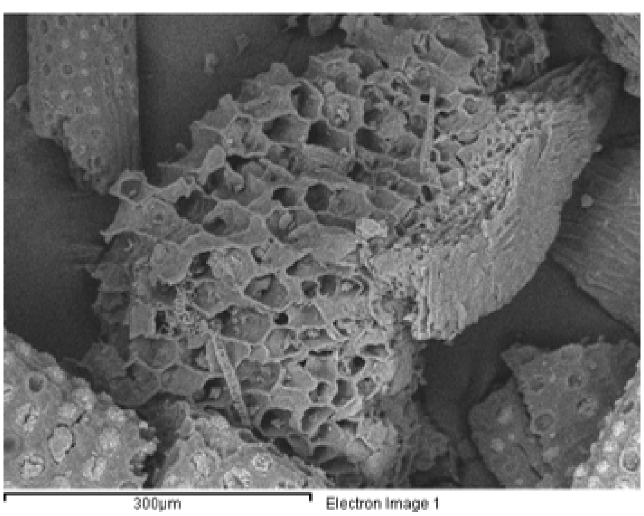

Figure 5. SEM micrographs of chemically modified biomass with alumina nanoparticles.

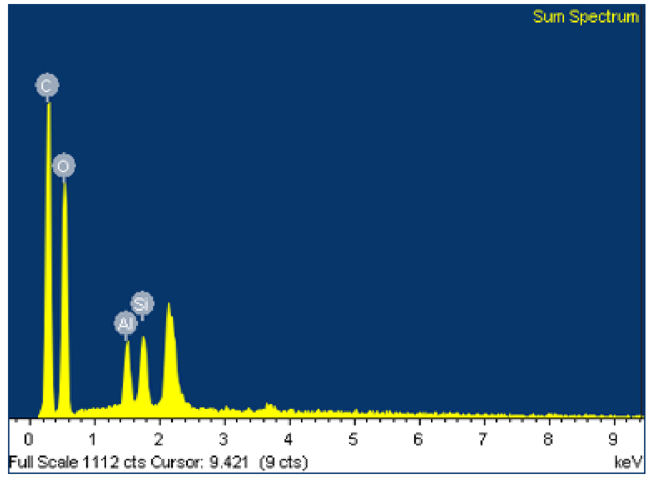

Figure 6. EDX spectrum of chemically modified biomass with alumina nanoparticles.

3.2 Determination of Point of Zero Charges

It is well known that pH solution higher than pH_{pzc} enhances adsorption of cations due to the presence of negative charges onto biosorbent surface. For pH values lower than the point of zero charges, the biomass surface is positively charged affecting the adsorption of cations because of electrostatic repulsion. According to the results shown in Figure 7 it was calculated the value of pH at point of zero charges in 4.29, which suggested that there are more acid sites in biomass than basic sites.

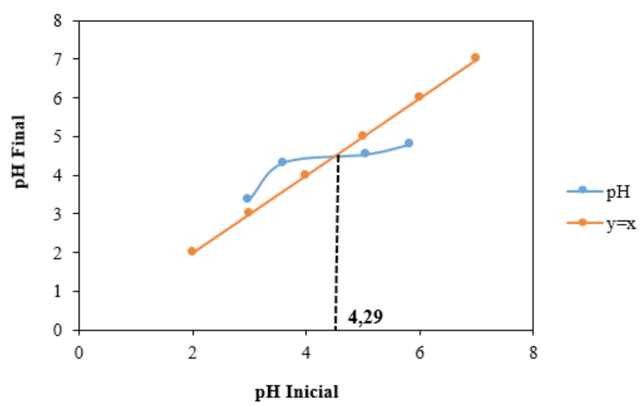

Figure 7. Point of zero charges for African oil palm bagasse biomass.

3.3 Biosorption Study

The batch experiments were performed at fixed operating condition (pH=6 and particle size=0.355 mm) and removal yields results are shown in Figure 8. As can be observed, cadmium and nickel ions were efficiently adsorbed using the biosorbent with removal yields of 92.02 and 87.06%, respectively. However, the removal yield for Cr (IV) ions was 4%, which was attributed to the selected pH value. Other authors reported that high removal yield of chromium is achieved under acid pH value due to the strong electrostatic attraction between highly protonated biosorbent surface and $Cr_2O_7^{2-}$ and $HCrO_4^-$ anions[26]. Hence, it is purpose to evaluate the effect of pH on adsorption process of chromium ions onto this biosorbent in further experiments. The important role of pH on bisorption of heavy metal ions was studied by[27] who used Cocoa shells for removing cadmium and obtained the highest Cd(II) removal yield (93%) at pH=6. For chromium[28] reported highest removal yield (30.6 %) using orange peel biomass at pH=2. Tejada-Tovar also studied adsorption of nickel using African oil palm bagasse obtaining the highest removal yield (81%) at pH=6[29].

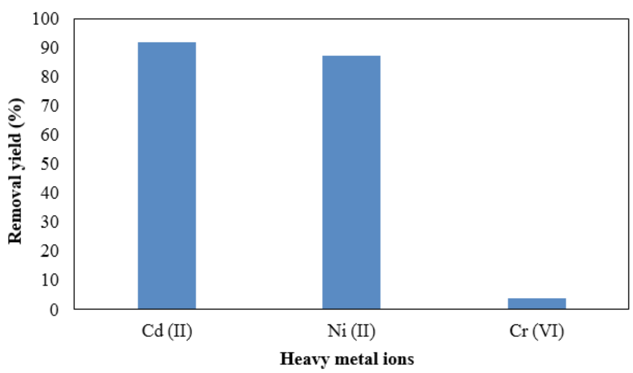

Figure 8. Removal yield of cadmium, nickel and chromium using chemically modified biomass.

4. Conclusions

A biosorbent from African oil palm bagasse biomass and alumina nanoparticles was prepared using DMSO as organic solvent. The alumina nanoparticles were synthesized based on a sol-gel methodology widely implemented for this purpose. The resulting biomaterial was characterized by FT-IR, SEM and EDX analyses. The point of zero charges as well as particle size was also calculated for biomass and alumina nanoparticles, respectively. It was identified from FT-IR analysis of biomass and its modification the presence of characteristic functional groups of lignocellulosic biomasses as carboxyl and hydroxyl, which are recognized for enhancing adsorption process. The characteristic absorption peaks attributed to bonds with Al and O suggested the successful synthesis of biosorbent. Ultimate analysis of biomass and EDX analysis of chemically modified biomass with Al_2O_3 nanoparticles confirm that carbon element most contributes to its composition due to the organic nature of African oil palm bagasse. In addition, the SEM analysis revealed a porous and amorphous surface that can enhance adsorption process because of the high active surface area. The point of zero charges was calculated in 4.29 suggesting the acid tendency of biomass. For alumina nanoparticles, its particle size was calculated in 56 ± 12 nm, value in the range reported by other authors. It was found high removal yield values for cadmium and nickel of 92.02 and 87.06% under pH=6, which suggested that this biosorbent can be efficiently used for removing both heavy metal ions. It is not recommended to use chemically modified biosorbent to remove chromium at pH=6 due to the low removal yield reached.

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