

Removal of Zn, Pb, and Ni heavy metals from aqueous system using efficient modified-banana peel adsorbent

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ABSTRACT

Heavy metals contamination of water is a serious and complex environmental problem due to rapid industrialization, bioaccumulation and non-degradability. Therefore, the reuse of agricultural waste in the process of purifying water from pollutants is an attractive and promising method. Almost inexpensive materials are used to purify water, thus achieving the desired economic and environmental goal. In this study banana peel (BP) was used before and after modification by 0.1M sulphuric acid (H₂SO₄) to enhance the removal of Zinc Zn(II), Lead Pb(II) and Nickel Ni(II). The effect of various parameters was studied Such as pH, contact time, adsorbent dosage and initial metal ion concentration at 5 ppm. All these parameters were studied in batch experiments for a comparative study. The removal percentage was found to be 84% Zn (II), 78% Pb (II) and 72% Ni (II) before modification and 92% Zn (II), 94% Pb (II) and 96% Ni (II) after modification at initial concentration of 5 ppm. The data obtained from sorption isotherms were described with Langmuir and Freundlich isotherm models but were found to be well fitted for the Langmuir model. The correlation coefficient values R² for Langmuir were at the range (0.996-0.999) while that for Freundlich were at the range (0.912-0.972). The rate of adsorption follows Pseudo-second-order kinetics. This work proved the high banana peels efficiency as an adsorbent agent for heavy metals removal from aqueous solutions.

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1. Introduction

Heavy metals are one of the important primary pollutants. A major contributor to the extremely release of heavy metals into the environment is the rapid industrialization due to population explosion which became of a global concern now leading to toxicity in the ecosystem¹. According to the World Health Organization (WHO), the permissible limit in drinking water of Zinc, Lead and Nickel are 3, 0.01 and 0.07 mg/L, respectively². There are various sources of heavy metals which are detected as a reason of different processing industries such as mining, paint, pesticide, printing, smelting, petroleum refining, metal plating, electroplating and so on³. All biological systems are potentially affected by the action of heavy metals when they exceed the permissible limit. This is due to non-biodegradability and accumulation of these elements in living tissues causing various diseases so that the need to remove them from the industrial waste water before they are discharged into environment. There are various methods for the removal of different pollutants and heavy metals from industrial waste water have been reported such as chemical precipitation, ion exchange, reverse osmosis, membrane separation, electro-floatation, electro dialysis and solvent extraction⁴. These types of treatment techniques have a disadvantage of being highly cost so that an interest study to produce a cheaper methods using the adsorption phenomena especially in developing countries like Egypt⁵. Activated carbon is a mostly effective an adsorbent with high surface areas

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and can be regenerated by thermal desorption or burning of the toxic agent in air, but it remains very expensive^{5-6,7}. In the light of the above factors, there is an intense need to develop a low cost adsorbents for the treatment of wastewater from heavy metals and are considered as the best adsorbent due to their availability^{8,9}. The untreated plant wastes such as papaya wood, maize leaf, tea leaf powder, lang (*Imperata cylindrica*) leaf powder, rubber (*Hevea brasiliensis*) leaf powder (*Coriandrum sativum*), peanut hull pellets, sago waste, saltbush (*Atriplex canescens*) leaves, tree fern, rice husk ash, neem bark, grape stalk wastes, sugarcane bagasse, etc. are mostly used as an adsorbents for the removal of heavy metals from waste water¹⁰⁻¹³. The paper reported that hydroxyl, carboxyl, phosphate, amino and thio functional groups on the agricultural biomass surface are responsible for the heavy metals binding. This process is done by the metal-functional groups binding through a process of ion exchange of hydrogen ions or through complex formation by sharing electron pair and etc¹⁴. Granular activated carbon showed low adsorption capacities than most of these agricultural materials¹⁵. The application of untreated plant wastes as an adsorbents could develop several problems like high chemical oxygen demand (COD) and biological oxygen demand (BOD) and so a low adsorption capacity. This is due to the soluble organic compounds released from the plant materials^{16,17}. Thus, a treatment of the surface of the adsorbent materials should be carried out before applying of the removal technique by using various modifying agents such as oxidizing agents like hydrogen peroxide, base solutions (e.g. potassium hydroxide) and mineral acids (e.g. hydrochloric acid)¹⁸. The literature is studying the removal of Zinc, Lead and Nickel using the dried banana peel as an adsorbent from their aqueous solutions. Banana is a major consumed fruit worldwide and the peels of banana fruit represent a waste material in large quantity. Banana peels consists of cellulose, hemicelluloses, lignin and pectin which contain several functional groups such as carboxyl, hydroxyl and amine. These functional groups are important for binding of metal ions on the bio-sorbents surface^{19,20}. Our aim of study is to develop a somewhat cheap adsorbent that is able to treat waste water containing non-biodegradable heavy metals through the use of banana peel and 0.1M H₂SO₄ as an activating agent. In this study various parameters are optimized such as pH, contact time, the adsorbent dosage and the initial metal ion concentration in batch experiments. Adsorption isotherms are used to study the maximum adsorption capacity of unmodified (BP) and modified banana peels(BP) using Langmuir isotherm equilibrium. Also the intensity of adsorption was studied by Freundlich adsorption isotherm. Kinetic studies are performed using the Pseudo-first-order and the Pseudo-second-order kinetic models. Fourier Transform Infrared Spectroscopy (FTIR) was used to identify the affinity of functional groups on the adsorbent surface to remove Zinc, Lead and Nickel ions. Also the adsorbent material was characterized by Scanning Electron Microscope (SEM) which of great importance in confirming the tubular structure morphology(shape), and size distribution of adsorbents.

2. Experimental

2.1 Chemicals and reagents

All used reagents and chemicals which of the certified analytical category were ZnSO₄·7H₂O (1000 mg/L), Pb(NO₃)₂·anhydrous (1000 mg/L), NiCl₂·6H₂O(1000 mg/L), murexide indicator, EBT indicator, NaOH, H₂SO₄, HNO₃, NH₄Cl, NH₄OH, "ethylene diamine tetra acetic acid" EDTA, MgCl₂·6H₂O, CaCO₃, HCl, tartaric acid, and NaCl, which were purchased from Fluka chemicals in addition to first distilled water for washing and second distilled water that was used for all solutions preparation.

2.2 Adsorbent

The sample of banana peels (BP) produced and was collected from a shop a fruit selling juice located at darelsalam town, sohag.

2.2.1 Preparation of adsorbent

The collected peels were washed with tap water then washed by first distilled water and naturally dried. The dried BP was grinding into powder then boiling with second distilled water for 10 min. BP was washed with hot second distilled water several times using a magnetic stirrer and was separated by decantation and single filtration. Finally, BP was dried in an oven at 70 °C until reaching a constant mass and was sieved for particle size 125 µm then packing in a clean plastic polypropylene air tightly bottles and as BP.

2.2.2 Chemical treatment of Banana Peels

For this treatment, BP was firstly suspended for 30 min in 0.1M sulphuric acid with a solid–liquid relation of 0.003g/0.1mL at ambient temperature and then was agitated on a shaker at 100 rpm for 2hr. After that, separation and washing of the biomass was performed by decantation with second distilled water until pH 7. After decantation the filtration was discharged then the biomass (H₂SO₄–BP) was dried in oven at 70 °C and then was sieved to the particle size 125µm then was packed in a clean plastic polypropylene air tightly bottles. The adsorbent is designated as mBP.

2.3 Apparatus

Orbital shaker (BTC Model BT4010, made in Egypt), pH meter (Adwa model AD110, Romania), and magnetic stirrer (IDL GMBH model ME1, Germany), drying oven (bender, Germany), shaking standard testing sieves (model: RX-29-10, USA), grinding (food processor) and balance Sartorius (model ED224S, Germany) were used for sample preparation. Infrared spectrometer (FTIR, Nicolet model 7199 (170 SX) TR infrared spectrometer, China) was used to illustrate the functional groups existing in the adsorbents. CHNS/O analyzer (Perkin-Elmer model CHNS/O 2400 II, USA) was used for elemental analysis, SEM (model JEOL JSM-5500 LV, made in Japan), Mortar for grinding, Glassware flasks (Volumetric and Conical), Glassware (beakers, cylinders, Pipettes, Clear glass bottles and funnels), polypropylene bottles and filter paper GVS (made in Italy) were used in working experiments.

2.4 Zinc, Lead and Nickel adsorption study

There were several factors that affect the metal ions sorption of (Zn(II), Pb(II) and Ni(II)) by the active sites on the adsorbent surface such as pH of the solution, contact time, the adsorbent dosage and the initial concentration of the metal ion. These factors were studied at fixed circumstances; room temperature, particle size 125 μm , and agitation speed 100 rpm²¹. Erlenmeyer flasks and orbital shakers were used to carry out the tests. From the results of preliminary experiments; pH, contact time and dosage of adsorbent were selected as 6.5, 60 min and 12 g/L respectively for Zn(II) and, 6, 100 min and 4 g/L respectively for Pb(II) and 6.5, 60 min and 8 g/L respectively for Ni(II) and these data were kept constant throughout the study. After 60, 100 and 60 min of contact time for Zn(II), Pb(II) and Ni(II) respectively, the suspension was filtered, and the concentration of the metal in the filtrate was analyzed by complex-metric "ethylene diamine tetra acetic acid" EDTA titration^{22, 23}. The amount of Zn(II), Pb(II) and Ni(II) adsorbed onto bio-sorbent was calculated using Eq. (1)²⁴:

$$q_t = (C_i - C_f)V/m \quad (1)$$

For calculating the percentage uptake (Removal), the following Eq. (2) is used²⁵:

$$\text{Removal (\%)} = ((C_i - C_f)/C_i) \times 100, \quad (2)$$

where q_e is the amount of the adsorbed metal ion (mg/g), C_i and C_f (mg/L) are the initial and final concentrations of Zn(II), Pb(II) and Ni(II) in the solution respectively, V (L) is the solution volume, and m (g) is the adsorbent mass.

3. Results and Discussion

3.1 Characterization of the adsorbent

3.1.1 Elemental Analysis for BP and mBP

The elemental analysis of BP and mBP in **Table 1** show some similarity in their composition except for the presence of a larger amount of sulfur only in BP than that of mBP and that could be attributed to the role of H_2SO_4 which was basically responsible for creating sulphonic acid groups ($-\text{SO}_3$) onto mBP surface²⁶.

Table 1. The elemental analysis of BP and mBP

Sample	Elemental results(% dry basis)				
	H%	C%	S%	O%	N%
BP	5.14	42.55	10.11	41.06	1.14
mBP	3.94	58.14	0.39	35.78	1.75

3.1.2. FTIR Discussion for BP and mBP

The FTIR provides important information where the surface of BP showed the presence of O–H, N–H, C–H, C=O, C=C, C–N, C–O and C–H vibrations on the surface thereby providing sufficient surface functionality for pollutant interaction. FTIR showed peaks which represents the oxidized carbon materials C–O and/or C–O–C stretching in acids, phenols, alcohols, ethers and/or esters groups and sulphonic acid groups ($-\text{SO}_3$). The IR spectrum in Fig.1 (a, b) show that IR bands for BP were comprised of the stretching bands of CH, CH_2 and CH_3 at (2933 cm^{-1}), the overlapped stretching vibrations of hydroxyl (O–H) and amine (N–H) groups at (3836 cm^{-1}) and the C–O stretching vibrations at (1042 cm^{-1}). IR spectrum of BP that are chemically modified by 9.1 M H_2SO_4 indicate a modulation of functional features where major wave numbers and peaks intensities noticed for untreated BP show alterations where there is a decrease in the broad hydroxyl bands from 3836 cm^{-1} ²⁷ to 3275 cm^{-1} , the decrease of the C–O stretching vibrations from 1042 cm^{-1} to 1037 cm^{-1} and the decrease of CH, CH_2 and CH_3 stretching vibrations from 2933 cm^{-1} to 2917 cm^{-1} which prove the partial oxidation of these functional

group. The modification led to the appearance of the stretching bands of carbonyl groups ($C=O$) at 1644 cm^{-1} that are related to carboxyl groups, ketones, aldehydes and lactones²⁸⁻³⁰.

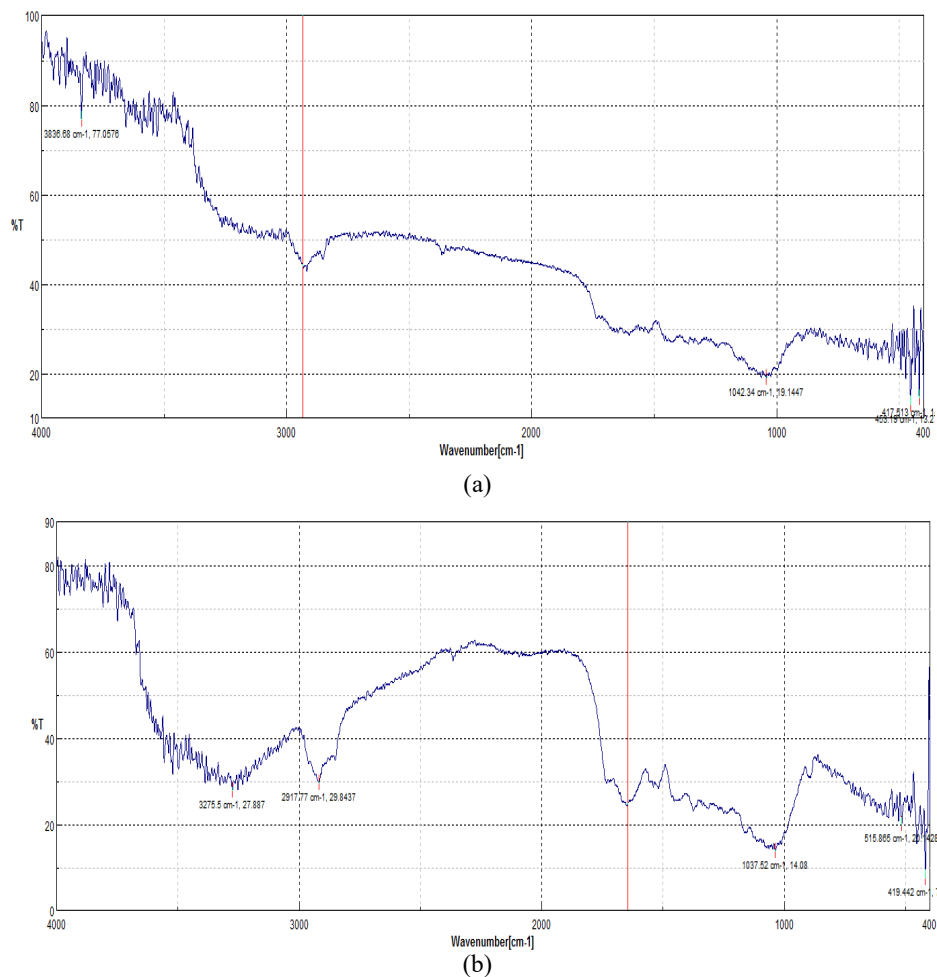
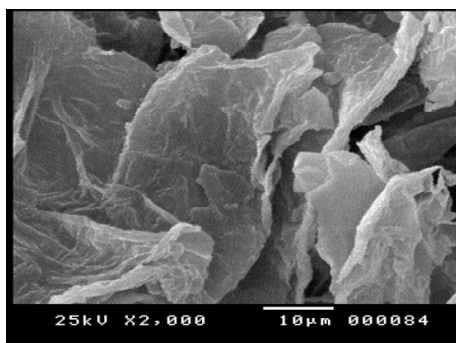


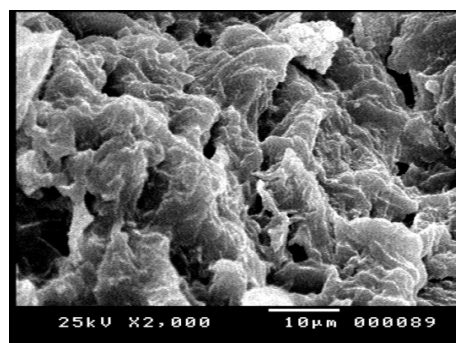
Fig.1. IR spectra analysis (a): BP (b): mBP.

3.1.3 Scanning electron microscopy

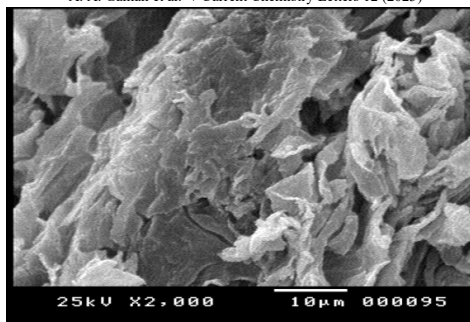
The material was of particle size $125\ \mu\text{m}$ and its surface morphology was analyzed using a Jeol Jsm-5500 LVSEM at an accelerating voltage of 25 kV and a working distance of $10\ \mu\text{m}$. **Fig. 2** shows the SEM of (a) BP, (b) H_2SO_4 -BP and (c) BP-Pb samples. The surface morphology of the samples (a) and (b) are clearly different where the external surface of H_2SO_4 -BP appeared to be highly porous and heterogeneous as a result of the oxidation process. This is because of the splitting of bridging C-O bonds on the BP surface after H_2SO_4 treatment. A difference in the morphology of the sample surface (a) it reveals a rough, irregular and porous surface and (c) where after adsorption, the surface is a uniform, smooth and covered are seen due to the bounding of the lead ions on the BP surface³¹.



(a)



(b)



(c)

Fig. 2. SEM (a) BP, (b) mBP by H₂SO₄ and (c) BP-Pb.

3.2 Effect of pH on adsorption

The effect of pH of the aqueous solution on the removal percentage of Zn(II), Pb(II) and Ni(II) for BP were shown in **Fig. 3**. Results generally showed that the maximum metal adsorption behavior occurring at high pH values. The other parameters were kept constant. The initial pH values of the solutions were detected by adding 0.01M HNO₃ and 0.01M NaOH solutions to reach the desired value. The figure displayed that the removal percentage of BP for Zn(II) and Ni(II) increased with increasing of pH, achieving a somewhat constancy at the range 6.5–10. At the other side, the removal percentage of Pb(II) by BP increased with increasing pH up to 6 and then decreased with more increasing in pH. The increase of removal percentage with increasing pH could be demonstrated due to the degree of ionization and the charge on the adsorbent surface. At low pH, the highly movable H⁺ would vie with the metal ions to bind the active sites. Thus the binding sites becomes protonated resulting in decreasing of the metal sorption on the adsorbent surface. At higher pH, H⁺ concentration and also the solubility of metals were decreased which enhanced the sorption of metals on the adsorbent surface. Any more increase in pH upon 7 caused precipitation of the metal's hydroxides. This precipitation is an preferred as adsorption process will not occur³².

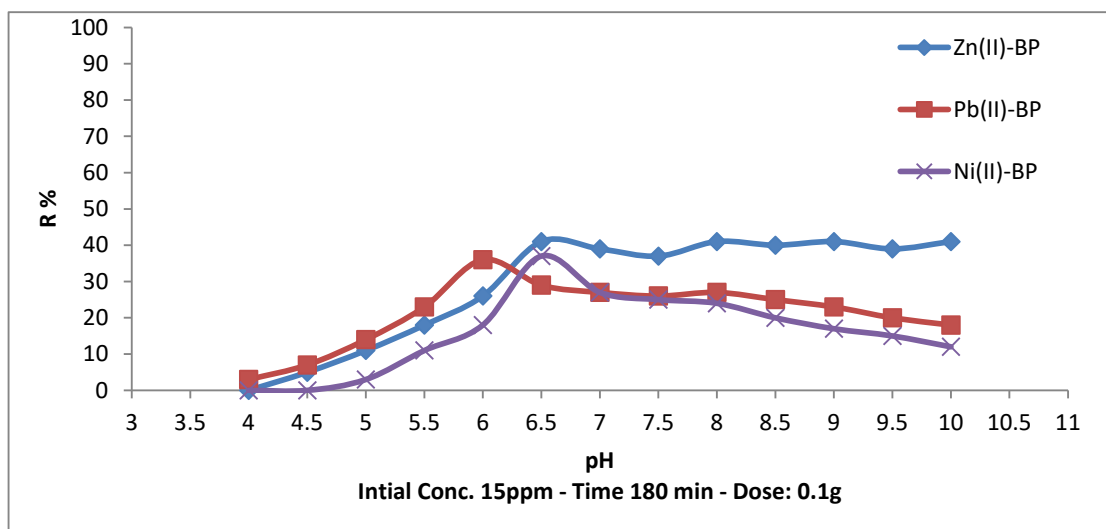


Fig.3. Effect of pH for BP.

3.3. Effect of contact time

The effect of different adsorption times on the removal percentage of Zn(II), Pb(II) and Ni(II) using BP were shown in **Fig.4** where the optimum contact times for the metal ions were 60, 40 and 60 min for Zn(II), Pb(II) and Ni(II) respectively. The other adsorption conditions were kept constant during the study. The removal percentage gradually increased, then slowed down till reaching the equilibrium state with time. This was due to the reaction of functional groups of the BP with the metal ions and thus the adsorption sites became gradually occupied. The removal percentage of the heavy metal ions reached its maximum limit when the adsorption sites and functional groups of BP were close to saturation³³. It was noticed that Pb(II) has a greater affinity to the adsorbent surface than Zn(II) and Ni(II) where the preference of the adsorbents for metals has been related to the hydrated ionic radius of the metals. The values of hydrated ionic radius are 0.40 Å for Pb(II), 0.65 Å for Zn(II) and 0.63 Å for Ni(II). The smaller the hydrated ionic radius the greater will be the affinity to penetrate into smaller pores and, therefore, greater access to active groups of the adsorbent at faster time. Also this relative preference for Pb(II) may be explained by the higher stability of the complex formed by Pb(II) with carboxylate groups in compared with those formed by Zn(II) and Ni(II)^{34, 35}.

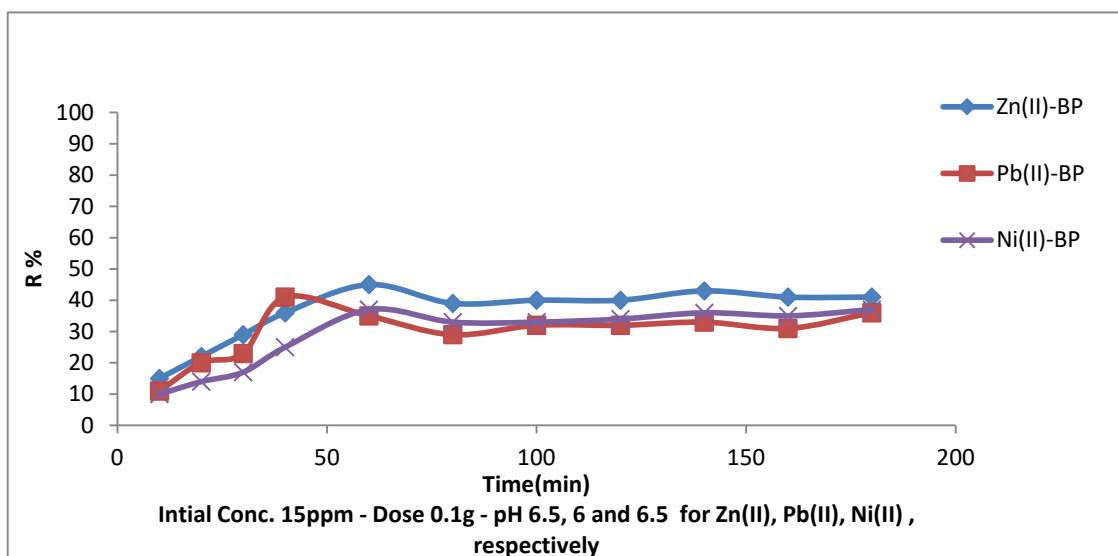


Fig. 4. Effect of contact time For BP.

3.4 Effect of the amount of the adsorbent

The effect of adsorbent dosage on the removal percentage of Zn(II), Pb(II) and Ni(II) metal ions from synthetic wastewater were shown in Fig. 5 where the optimum dose for the metal ions were 0.1, 0.1 and 0.1g for Zn(II), Pb(II) and Ni(II) respectively. It was observed that as the weight of biomass increased, gradual increase in the removal percentage was obtained for metal ions. This referred to the increasing sorptive surface area and the active binding sites was more available on the adsorbent surface with increasing of the adsorbent dose. Further, any increase in the adsorbent dosage will not have any major changes³⁶.

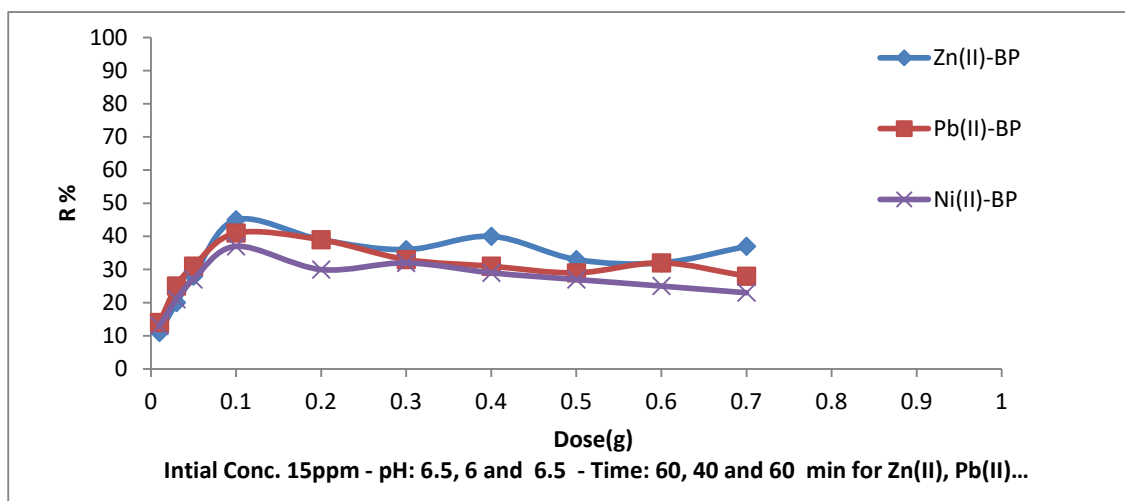


Fig. 5. Effect of dose for BP

3.5 Effect of metal ions concentrations

A comparative sorption study was accomplished with modified and non-modified banana peel to deduce the sorption efficiency of the sorbents. The effect of modification of BP on the biosorption of Zn(II), Pb(II) and Ni(II) were shown in Fig. 6 where the results of Zinc, Lead and Nickel biosorption tests with BP before and after modification with 0.1M H₂SO₄ solution were shown. The metal ions concentrations were explained at the range of 5 to 50 mg/L with a fixed optimum parameters of pH, contact time and dose as illustrated before. Since the concentrations before the 5 ppm make the removal percentage of 100%, which we as researchers cannot confirm a comparison between the different ions for the removal process with a particular adsorbent, so that this concentration was used as a minimum limit for comparison with low economical cost. The removal capacity of the metal ions were decreased by increasing concentrations from 92% to 21% for BP and 96% to 30% for H₂SO₄-BP with Zn(II), 86% to 19% for BP and 92% to 28% for H₂SO₄-BP with Pb(II) and for Ni(II) the removal capacities decreased from 78% to 17% for BP and 90% to 27% for H₂SO₄-BP. Thus, the removal efficiency was decreased by increasing metal ions concentrations in the solutions. By increasing the metal ion concentration, the number of sorption sites in a certain mass of an adsorbent substance became saturated.

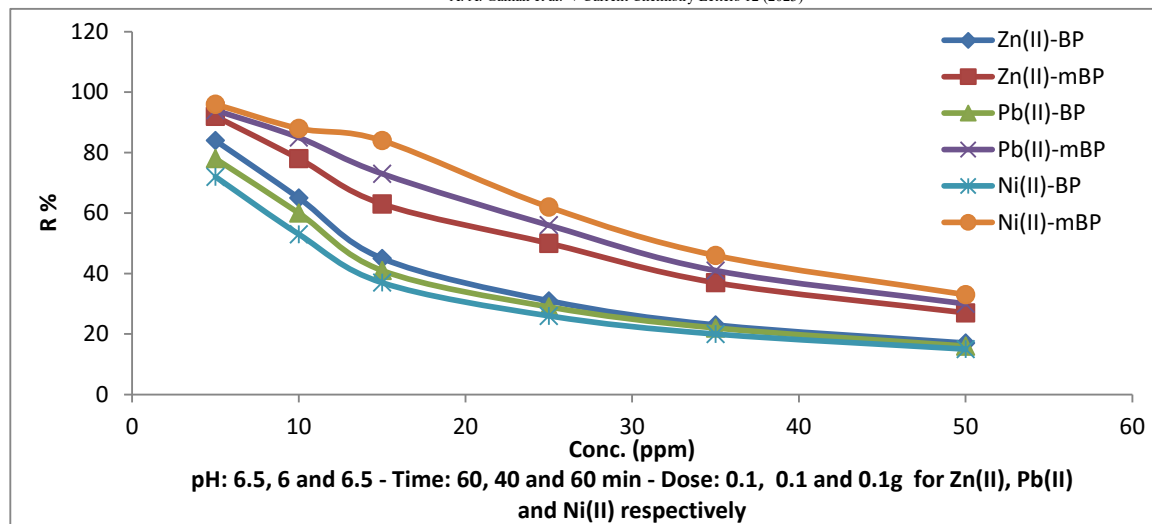


Fig.6. Effect of conc. for BP and mBP.

3.6 Adsorption isotherms

Zinc, Lead and Nickel sorption data were correlated with Langmuir³⁷ and Freundlich³⁸ models [Eqs. (3) and (4)].

$$C_e/q_e = 1/(q_{max} * b) + (1/q_{max}) * C_e \quad \text{Langmuir equation} \quad (3)$$

$$\text{Ln}q_e = \text{Ln}K_f + (1/n_f) \text{Ln}C_e \quad \text{Freundlich equation} \quad (4)$$

where C_e is the metal solution concentration at equilibrium (mg/L), q_e the metal amount sorbed at equilibrium (mg/g), q_{max} the maximum sorption capacity, q_{max} and b is Langmuir constants, K_f and n_f are Freundlich constants.

Langmuir and Freundlich isotherms equilibrium models of the biosorption of Zn(II), Pb(II) and Ni(II) onto unmodified BP and modified BP by H_2SO_4 at $(30 \pm 5)^\circ\text{C}$ were reported in **Table 2**. The correlation coefficient values (R^2) illustrated that the Langmuir isotherm model was best prepared for the biosorption of heavy metal ions on BP and mBP as shown in **Fig.7:(a, b)**³⁹.

Table 2. Langmuir and Freundlich models of the metal ions adsorption on BP and mBP

Metal ion	Adsorbent	Langmuir			Freundlich		
		q_{max}	b	R^2	K_f	n_f	R^2
Zn(II)	BP	2.232	0.546	0.996	1.169	5.714	0.946
	mBP	3.521	0.593	0.998	1.531	4.065	0.972
Pb(II)	BP	2.123	0.445	0.996	1.028	5.181	0.948
	mBP	3.846	0.855	0.999	1.775	4.132	0.948
Ni(II)	BP	1.961	0.363	0.996	0.884	4.808	0.965
	mBP	4.253	1.187	0.999	2.052	4.132	0.912

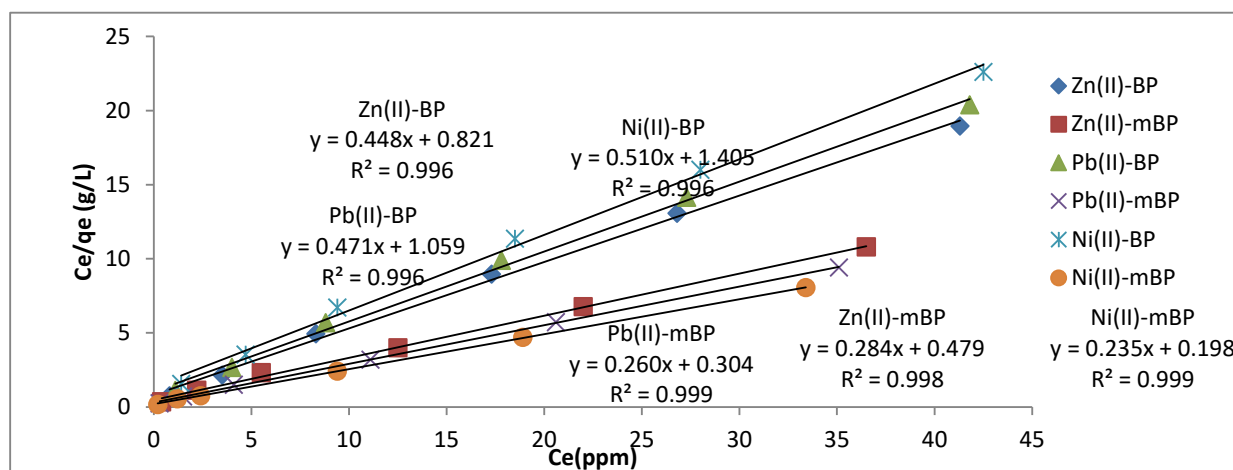


Fig.7(a). Langmuir model for BP and mBP.

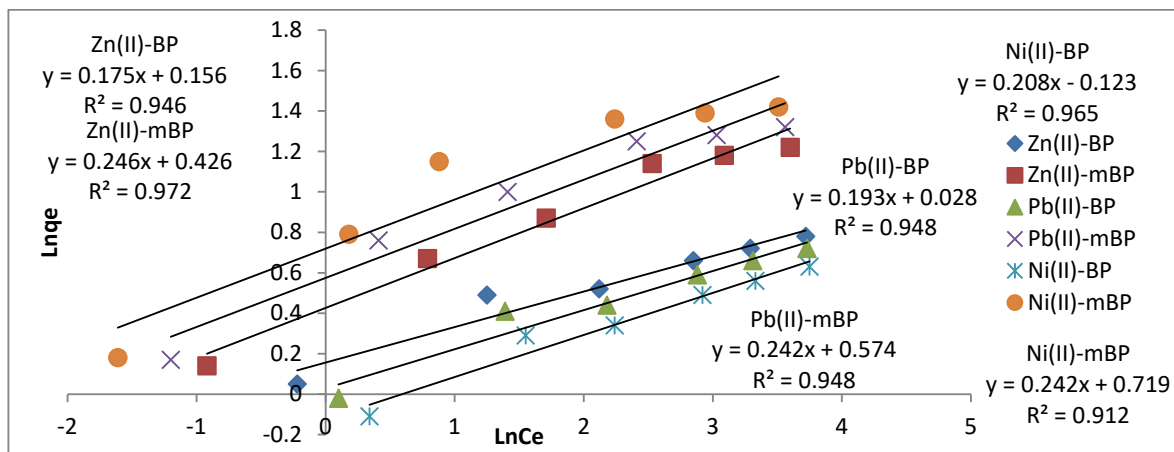


Fig.7(b). Freundlich model for BP and mBP.

3.7 Adsorption kinetics

In this study the Pseudo-first and Pseudo-second order kinetic models were applied to study and describe the adsorption kinetics of the metal ions^{40,41}. The Pseudo-first equation that represented the adsorption of a solute from liquid solution was shown in Eq. (5). In addition, the Pseudo-second-order equation that depended on the adsorption equilibrium capacity could be expressed in Eq. (6).

$$\ln(q_e - q_t) = \ln q_e - K_1 * t \quad (5)$$

$$t/q_t = 1/k_2 q_e^2 + t/q_e \quad (6)$$

where q_e is the adsorbed metal ion mass at equilibrium (mg/g), q_t is the adsorbed metal ion mass at time t (mg/g), K_1 is the pseudo-first order reaction rate constant (1/min) and K_2 is a constant that represents the pseudo second-order reaction rate equilibrium (g/mg min).

The two kinetic models were reported in **Table 3**. The estimated models for Zinc, Lead and Nickel and the related statistic parameters that depended on linear regression data (R^2), the adsorption kinetics of the metal ions onto the adsorbent could be well represented by the Pseudo second-order equation⁴² as shown in **Fig. 8**.

Table 3. Kinetic model's parameters of Zn(II), Pb(II) and Ni(II) adsorption on BP and mBP

Heavy metal	Type of adsorbent	1st order				2nd order			
		$q_{e,exp}$ (m $g g^{-1}$)	$q_{e,cal}$ (m $g g^{-1}$)	R^2	K_1	$q_{e,exp}$ (m $g g^{-1}$)	$q_{e,cal}$ (m $g g^{-1}$)	R^2	K_2
Zn(II)	BP	1.68	0.836	0.839	0.013	1.68	1.72	0.990	0.040
	BP-H ₂ SO ₄	2.38	1.05	0.864	0.018	2.38	2.49	0.996	0.038
Pb(II)	BP	1.55	0.82	0.632	0.007	1.55	1.36	0.971	0.055
	BP-H ₂ SO ₄	2.73	0.72	0.387	0.012	2.73	2.77	0.987	0.038
Ni(II)	BP	1.4	1.1	0.903	0.018	1.4	1.66	0.971	0.018
	BP-H ₂ SO ₄	3.15	1.44	0.865	0.022	3.15	3.32	0.997	0.033

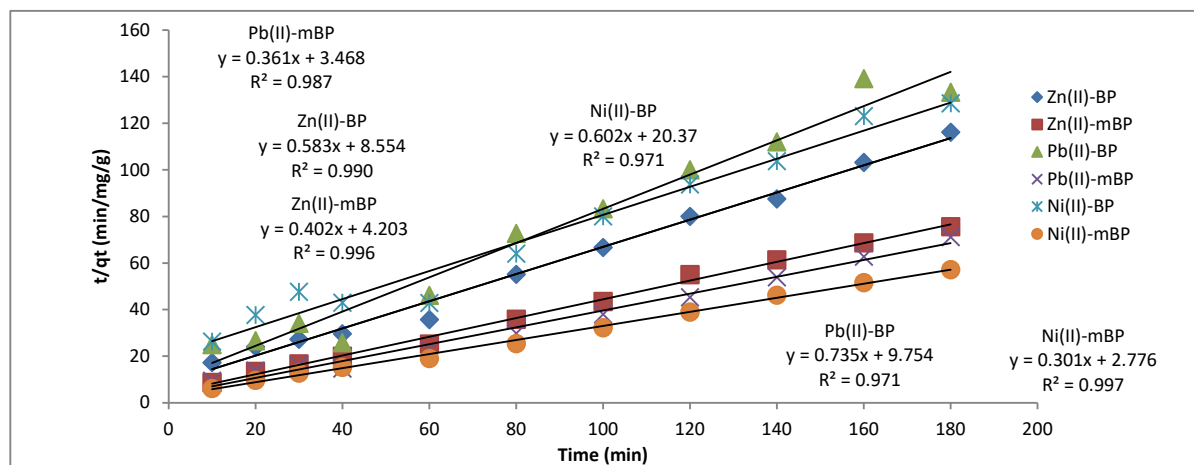


Fig. 8. Pseudo Second Order Model for BP and mBP

4. Conclusions

This work aimed to use the abundantly low-cost agricultural waste banana peel, unmodified and modified by 0.1M sulphuric acid (H_2SO_4), as a biosorbent material by studying its characterization and its removal of Zn(II), Pb(II) and Ni(II) metal ions from their aqueous solutions. The chemical modification increased the surface area of BP which enhanced the adsorbent efficiency for Zn(II), Pb(II) and Ni(II) removal. Parameters such as pH, contact time, dosage of adsorbent and initial ion concentration of the adsorbate were also determined. Through the study, both the Freundlich and Langmuir adsorption isotherms models were tested onto both BP and mBP to describe the adsorption behavior. Langmuir adsorption isotherm model provides the best description of the adsorption behaviour of Zn(II), Pb(II) and Ni(II) metal ions. The experimental data showed that the Pseudo second-order model provides the best description. IR spectra Characterization of the biosorbent was performed that the modified BP supported well for the adsorption capacity efficiency for the metal ions removal. Thus the biomass BP could be enhanced by chemical modification for heavy metals removal from aqueous system.

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