

Removal of Some Heavy Metals From Aqueous Solution Using Biosorbent Materials and Nanoparticles

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ABSTRACT: A batch sorption experiments were carried out to study the role of biosorbent and nano-particles on removal of some heavy metals from aqueous solution. The rice straw waste was used as biosorbent material(by-product of agricultural activity). In addition, Nano-Hydroxyapatite (60 nm) and nano-Zero Valent Iron (25 nm) were used as nanoparticles. The batch sorption was done using rice straw waste (RSW) with three sizes as 0.125, 0.25 and 0.5 mm with Pb²⁺ and Ni²⁺ with concentrations up to 28.14 and 100 mg/l, respectively. Also, the sorption experiment was conducted using nano-particles (n-HAP and n-ZVI) and phosphate rock for Pb²⁺ and Ni²⁺ with concentration up to 20 mg/l for Ni and 18.0 mg/l for Pb. The results indicated that RSW (0.250 mm) was best size for heavy metals removal. The rice straw waste has more ability for retention of heavy metals such as Ni and Pb according to linear and Freundlich sorption models. Also, the results indicated that maximum sorption capacity of heavy metals was occurred on Nano-Hydroxyapatite (n-HAP) for both Pb and Ni. These results may be due to the functional groups found in Nano-Hydroxyapatite. When RSW mixed with n-HAP, the results indicated maximum removal percentage of heavy metals. The removal percentage of Pb (99.70%) was more than Ni (38.25%) indicated that the ability of Pb to bind with RSW or n-HAP more than Ni. The current results are very useful in the treatment of wastewaters for the removal of heavy metals, making them suitable for agricultural purposes. The present study recommends a future studies to understand the role of nanomaterials on removal the different heavy metals under different conditions.

Keywords: heavy metals, batch sorption, biosorbents, biosorption, nano-particles, n-HAP, n-ZVI, phosphate rock.

INTRODUCTION

The presence of high levels of heavy metals in the environment may cause long-term health risks to humans and ecosystems. It is therefore mandatory that their levels in drinking water, wastewater and water used for agricultural and recreational purposes must be reduced to within the allowable concentrations recommended by national and international health authorities such as the World Health Organization. Adsorption is an effective physicochemical purification and separation technique used in water and wastewater treatments. It is considered as preferred method for removal, recovery and recycling of toxic heavy metals. Cost is an important parameter for comparing the sorbent materials. Biosorbent or biomaterials able for adsorption of heavy metals on their active surfaces and can be used with safe for removal of heavy metals from wastewaters up to concentration of 200 mg/l.

Treatment of metal bearing industrial wastewater is of height ended interest (Pakshirajan and Swaminathan, 2009; Acheampong *et al.*, 2013). This is mainly because heavy metals are toxic even at a very low concentration to human, animal and plant species.

Natural wastes such as agricultural solid wastes have surface active materials can be able to remove or reduce the concentration of heavy metals from polluted ground and surface water. Natural clay and hydroxyapatite will be used also for heavy metals adsorption then; the treated water can be used for irrigation purposes.

Amongst the different known techniques to remove heavy metals from wastewater, biosorption seems to be cost effective as it involves only a passive process for heavy metal sequestration by using mostly dead/inactive and cheap biomass (Nadeem *et al.*, 2014). Also, among the different biomass types available for heavy metal removal, the cyanobacterial biomass is particularly attractive owing to its complex biomass structure, minimum nutrient requirement, abundant growth within a short time period, ability to grow well under environmentally stressed conditions etc. The use of dead cyanobacterial biomass is also advantageous because it doesn't require any kind of special media for its growth (Gupta and Rastogi, 2008). Further, it has been reported that chemical pretreatment of such biosorbents show a large ability to form complex with metal ions, thus aiding in their efficient removal from aqueous solution (Afkhami *et al.*, 2007).

Industrial heavy metal pollution has become a serious environmental and sanitary problem all over the world in recent years. Heavy metals can not only have toxic and harmful effects on organisms living in water, but also accumulate throughout the food chain and may also affect human beings (Martins *et al.*, 2004; Sari and Tuzen, 2008). Heavy metals such as cadmium, lead and nickel among others, are commonly detected in industrial effluents. A variety of syndromes, renal function hypertension, hepatic injury, lung damage and teratogenic effects may result from cadmium toxicity (Sari *et al.*, 2008). Lead may cause mental disturbance, retardation, and semi-permanent brain damage (Paulino *et al.*, 2008). The occurrence of heavy metals especially cadmium and nickel in industrial effluents beyond permissible limits brings serious environmental pollution, threatening human health and ecosystem. Therefore, these pollutions must be removed to an acceptable level before being released into water ecosystem.

Many techniques, such as ion exchange, precipitation, adsorption, membrane processes, reverse osmosis, sedimentation, electro-dialysis, etc., have been employed for separation of heavy metals from wastewater (Perez-Quintanillo *et al.*, 2007; Amini *et al.*, 2009). With the increase in environmental pollution, there is a growing demand to develop new adsorbents of higher efficiency for heavy metal ions removal from aqueous media than those commercially available (Matlock *et al.*, 2002).

The present study adopts a non-expensive and safe technology for removal of heavy metals from industrial wastewater using biosorbents and nanoparticles.

MATERIALS AND METHODS

Biosorbent

Rice straw waste (RSW) was collected from an agricultural farm in Damnhour, El-Beharia Governorate. The RSW was ground to powder and was sieved with three different sized meshes to obtain three different grade particle sizes namely; 0.125 mm, 0.125-0.25 mm, and 0.25-0.5 mm. The properties of the used rice straw are presented in Table (1).

Nanoparticles

Zero valent Iron nanoparticle (n-ZVI), consisting of Fe (0) surface stabilized nanoparticles, 98% Pure, APS: 25 nm and hydroxyapatite nanoparticles (n-HAP), $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$, Calcium phosphate tribasic, 96% Pure, APS: 60 nm were used. Morphology: Needle like. The materials were purchased from M K Impex Corp. Division: MKnano 6382 Lisgar Drive, Mississauga, Ontario L5N 6X1, Canada. The properties of the used Zero Valent Iron nanoparticle and hydroxyapatite nanoparticles.

Phosphate Rock

The Phosphate rock crushed and passed through an 0.063 mm sieve. Analysis of phosphate rock was carried out according the methods described in Safi *et al* (2006), Hassan *et al.* (2013) and Aissa *et al.* (2014). The properties of the phosphate rock are illustrated in Table (2).

Table (1). Some chemical properties of the rice straw waste (RSW)

Parameters	Unit	Value
pH	-	7.73
EC	dS/m	7.2
Ni	mg/ kg	0.35
Co	mg/ kg	0
Cd	mg/ kg	0
Pb	mg/ kg	3.05
B	mg/ kg	21.45
Cu	mg/ kg	1.45
Zn	mg/ kg	9.75
Mn	mg/ kg	9.9
Fe	mg/ kg	87.6
Ca	%	0.12
Mg	%	0.05
K	%	0.59
P	%	0.04
N	%	0.6
OM	%	79.5
Cellulose	%	38.3
Hemi cellulose	%	29.7
Lignin	%	10.2
Ash	%	4.8

Table (2). Some chemical properties of the phosphate rock (PR)

Parameters	Unit	Soluble	Total
N	%	0.059	2.10
P ₂ O ₅	%	0.11	8.24
K ₂ O	%	0.02	0.02
Ca	%	0.62	19.30
Mg	%	0.03	0.60
Fe	%	0.00	1.10
Mn	%	0.07	0.55
Zn	%	0.013	0.35
Cu	mg/kg	0.0	9.0
Ni	mg/kg	2.5	23.0
Cd	mg/kg	1.0	4.5
Pb	mg/kg	3.7	330
Co	mg/kg	0.0	0.0

Batch experiments**Batch biosorption of RSW**

The stock solutions of the Pb²⁺ and Ni²⁺ used in this study was (1000 mg/l). Subsequent dilutions of (2.94, 3.53, 6.81, 11.92, 20.88 and 28.14 mg/l) and (2, 5, 10, 20, 50 and 100 mg/l), respectively were prepared by suitably diluting the stock solution with double distilled water. The experiments were performed in 100 ml flasks containing 25 ml of Pb²⁺ or Ni²⁺ of different concentration plus 0.5 g rice straw waste with three different sizes, and with three replicates for each experiment. The mixture was shaken in a rotary shaker at 50 rpm for one hour followed by filtration using Whatman filter paper (No.1). The filtrate containing the residual concentration of Pb or Ni was stored for analysis.

Batch nanoparticle and phosphate rock sorption

The stock solutions of the Pb²⁺ and Ni²⁺ used in this study was (1000 mg/l). Subsequent dilutions of (1.25, 2, 5, 11.97, 13.53 and 18) and (1, 2, 5, 10, 15 and 20 mg/l), respectively were prepared by suitably diluting stock solution with double distilled water. The experiments were performed in 100 ml flasks containing 25 ml of Pb²⁺ or Ni²⁺ of different concentration plus 0.1 g of Zero Valent Iron nanoparticle (n-ZVI), hydroxyapatite nanoparticles(n-HAP) or 0.2 g of phosphate rock, and with three replicates for each experiment. The mixture was shaken in a rotary shaker at 50 rpm for one hour followed by filtration using Whatman filter paper (No.1). The filtrate containing the residual concentration of Pb or Ni was saved for analysis.

Batch sorption of hydroxyapatite nanoparticles and rice straw waste mixture

Batch equilibrium experiments were performed at room temperature in 100 ml Erlenmeyer flasks containing 25 ml of either Pb^{2+} or Ni^{2+} of known concentration, 20 mg/l. An accurately weighed 1g of rice straw, size of 0.25 mm and 0.1g of hydroxyapatite nanoparticles was added to each flask with three replicates. The mixture was shaken in a rotary shaker at 50 rpm for 30 minutes followed by filtration using Whatman filter paper (No.1). The filtrate containing the residual concentration of Pb or Ni was saved for analysis.

Heavy metal sorption models

According to Sethuraman and Balasubramanian (2010), the percentage of Pb^{2+} and Ni^{2+} removal was calculated using the following equation:

$$\text{Removal of } Pb^{2+} \text{ or } Ni^{2+} (\%) = \frac{C_0 - C_e}{C_0} * 100$$

Where, C_0 and C_e represent initial and equilibrium concentrations of Pb^{2+} and Ni^{2+} .

According to (Vieira and Volesky, 2003; Vijayaraghavan *et al.*, 2006) the equilibrium sorption capacity of Pb^{2+} or Ni^{2+} was calculated using the following equation:

$$S = \frac{(C_0 - C_e) \times V}{m}$$

Where;

S = equilibrium Pb^{2+} or Ni^{2+} ions capacity (mg/g),

V = suspension volume (l),

m = mass of pomelo material (g),

C_e = Pb^{2+} or Ni^{2+} ions concentration at equilibrium (mg/l), and

C_0 = initial ions concentration (mg/l)

To study and compare the sorption of aqueous Ni and Pb on rice straw waste, n-HAP, n-ZVI and phosphate rock, the sorption data were fitted to some sorption models such as linear and Freundlich isotherm models using software IsoFit (Matott, 2007).

Linear isotherm model

$$S = K_d \times C_e$$

Freundlich Isotherm model

$$S = K_f \times C_e^{1/n}$$

Where:

K_d : partition parameter (L/kg),

C_e : equilibrium concentration (mg/l)

K_f : Freundlich isotherm parameter, ((mg/kg)/(mg/l))^(1/n), and

1/n: Freundlich exponent (no units).

RESULTS AND DISCUSSION

1. Characteristics of sorbents

The rice straw waste (RSW), nanomaterials (n-HAP and n-ZVI) and natural material (phosphate rock, PR) were subjected to analysis by Scanning electron microscopy (SEM), Fourier Transform Infrared (FTIR) and thermal analysis (TA) to study its surface texture and surface functional groups. The SEM graphs of the all materials are presented in Figures (1 to 4).

1.1. Scanning Electron Microscopy

SEM Images of n-HAP is presented in Figure (1), Surface morphology and the size distribution of the particles was investigated with the Scanning Electron Microscope (SU 1510) operated at 20kV, magnification x20,000. The solid samples were sprinkled on the adhesive carbon tape which is supported on a metallic disk. The sample surface images were taken at different magnifications. The scale was about 60 nm.

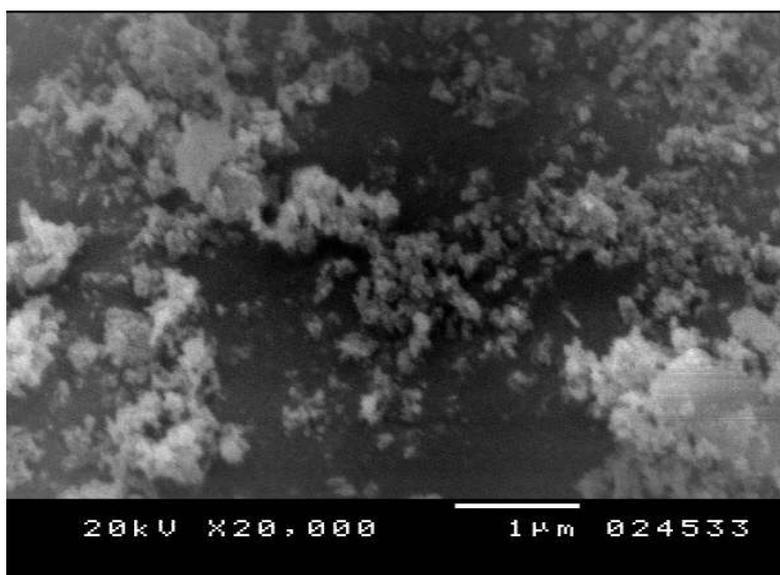


Figure (1). SEM micrograph of n-HAP particles (60 nm)

Figure 2 shows the SEM image of freshly synthesized zero valent iron nanoparticles. It can be observed that the zero valent iron nanoparticles are in the form of nanospheres, which exist in contact with each other and form chains having diameters of 25 nm.

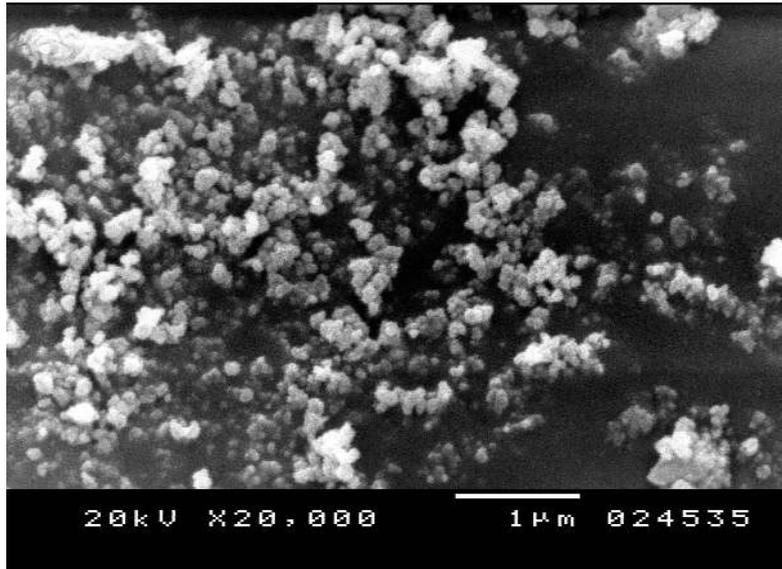


Figure (2). SEM micrograph of n-ZVI particles (25 nm)

SEM Images of phosphate rock particles is presented in Figure (3). The spheres having diameters of around 0.063 mm can be distinguished from each other and is in agreement with SEM results.

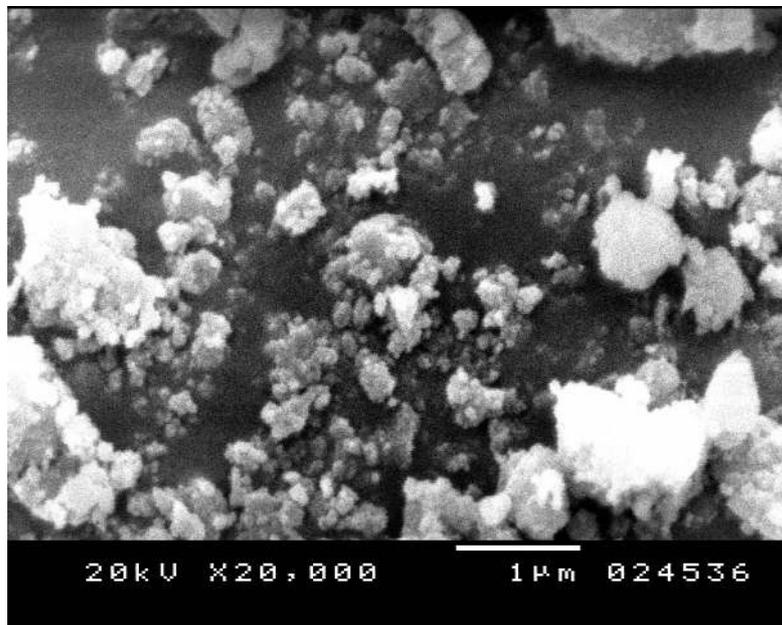


Figure (3). SEM micrograph of phosphate rock particles (0.063 mm)

SEM Images of rice straw waste powder is presented in Figure (4). The spheres having diameters of around 0.25 mm can be distinguished from each other and is in agreement with SEM results.

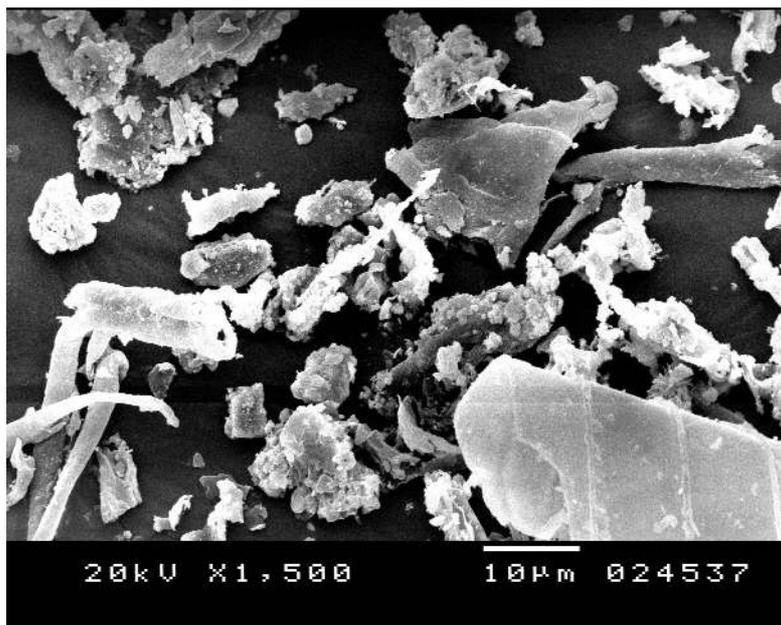


Figure (4). SEM micrograph of rice straw waste powder (0.25 mm)

1. 2. The Fourier Transform Infrared (FTIR)

The Fourier Transform Infrared spectra (FTIR) of rice straw waste (RSW), nanomaterials (n-HAP and n-ZVI) and natural material (phosphate rock, PR) are presented in Figures (5 to 7). Firstly, FTIR spectra of n-HAP, n-HAP particles after the sorption of aqueous Ni and Pb are illustrated in Figures (5, 6 and 7), respectively.

As interpreted from the data of FTIR analysis, the data show the function group of n-HAP type according to wave number. The main peaks are seen in the n-HAP. The functional groups were identified using the peak assignments. A strong peak at 1638.66 cm^{-1} was assigned to the $\text{R-C}^{\text{=O}}\text{-NR}_2$ stretching in N-monosubstituted amides in solid state group.

The strong band at 1038.837 cm^{-1} was assigned to P-O-Alkyl stretching alkane group. The alkyl halide stretching C-Br at 567.759 cm^{-1} was also observed. However, adsorption cases about Ni and Pb documented decrease in transmittance and more a symmetric stretching. It is obvious that the intensity of the peaks has increased after adsorption of Ni and Pb. The intensity of the peaks has increased after adsorption of Ni and Pb in stretching vibrations of the $\text{R-C}^{\text{=O}}\text{-NR}_2$ at 1640.475 and 1639.336 cm^{-1} , respectively.

The intensity of the peaks has increased after adsorption of Ni and Pb in stretching vibrations of the P-O-Alkyl at 1043.22 and 1039.899 cm^{-1} , respectively, and stretching vibrations of the C-Br at $568,203$ and 567.927 cm^{-1} , respectively.

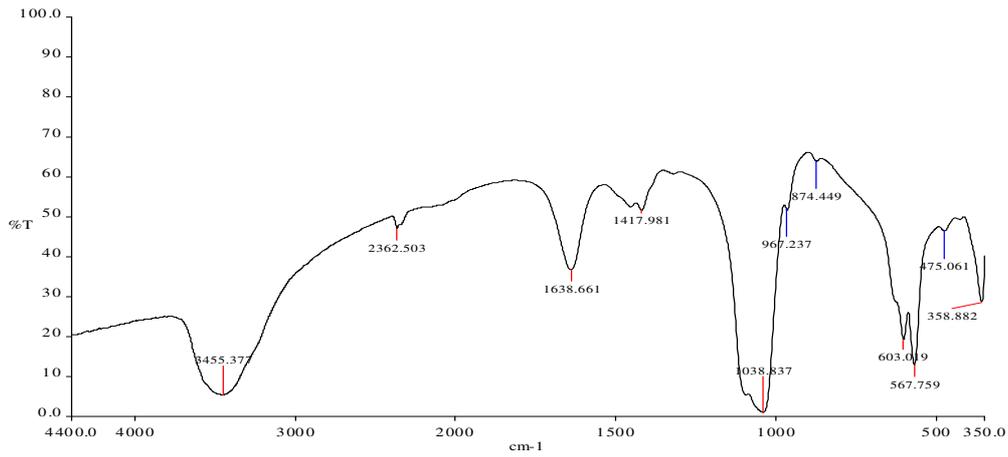


Figure (5). FTIR Spectra of n-HAP particles

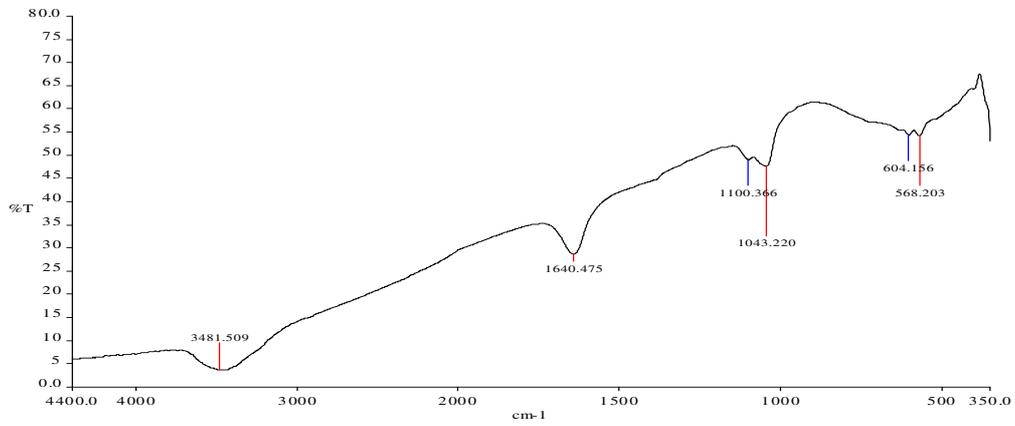


Figure (6). FTIR Spectra of n-HAP particles after the sorption of aqueous Ni

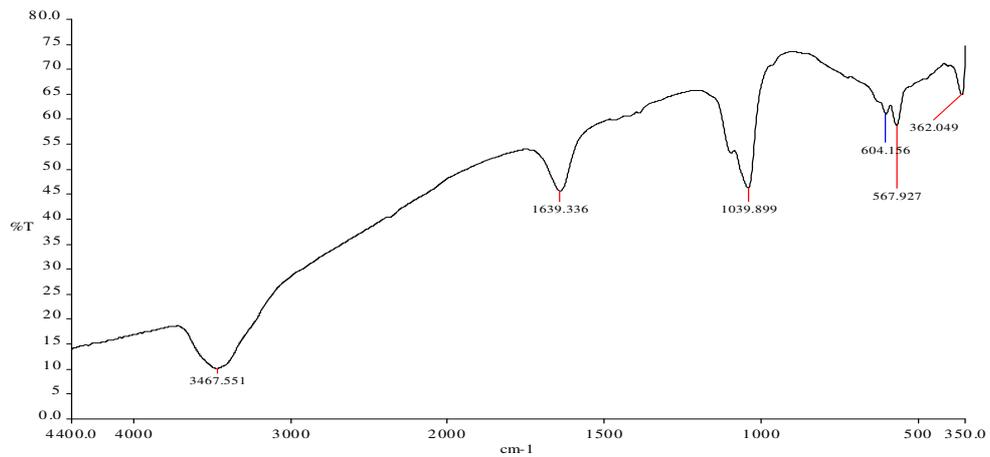


Figure (7). FTIR Spectra of n-HAP particles after the sorption of aqueous Pb

The FTIR spectra of n-ZVI, n-ZVI particles after the sorption of aqueous Ni and n-ZVI particles after the sorption of aqueous Pb, respectively are shown in in Figures (8, 9 and 10). As interpreted from the data of FTIR analysis, the function group of n-ZVI type according to wave number. The sorption peaks at 3458.407 and 1636.48 cm^{-1} are ascribed to stretching vibrations of $-\text{CONH}-$ groups and the $\text{R}-\text{C}^{\text{=O}}-\text{NR}_2$ stretching in N-monosubstituted amides in solid state, stretching in N-N disubstituted amides, respectively. By comparing the FTIR spectra of n-ZVI before and after adsorption, there were remarkable shifts in some bands. These bands are the function groups of n-ZVI participate in Ni and Pb biosorption. It is obvious that the intensity of the peaks has increased after adsorption. Moreover, the wave number of the $-\text{CONH}-$ was shifted from 3458.407 to 3467.397 cm^{-1} after the sorption of Ni. The wave number of the $-\text{CONH}-$ was shifted from 3458.407 to 3476.189 cm^{-1} after the sorption of Pb. The intensity of the peaks has increased after sorption of Ni or Pb in stretching vibrations of the $\text{R}-\text{C}^{\text{=O}}-\text{NR}_2$ at 1638.022 and 1637.352 cm^{-1} , respectively.

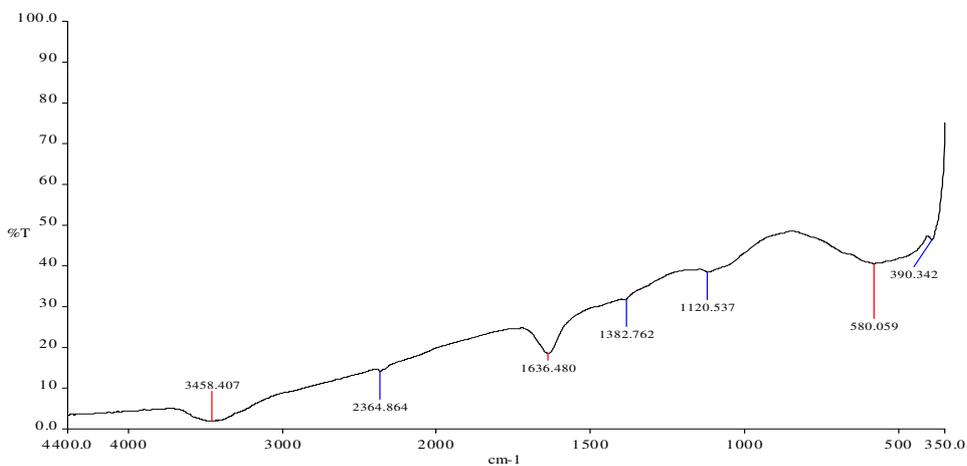


Figure (8). FTIR Spectra of n-ZVI particles

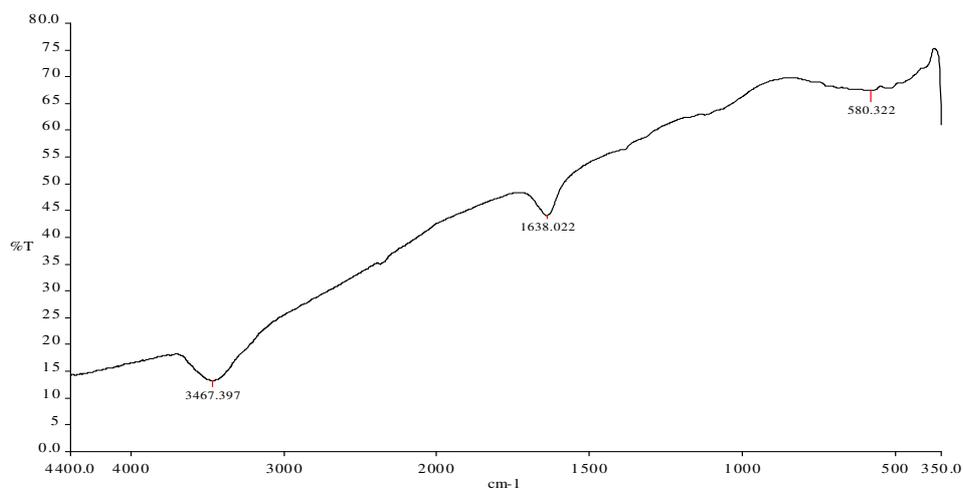


Figure (9). FTIR Spectra of n-ZVI particles after the sorption of aqueous Ni

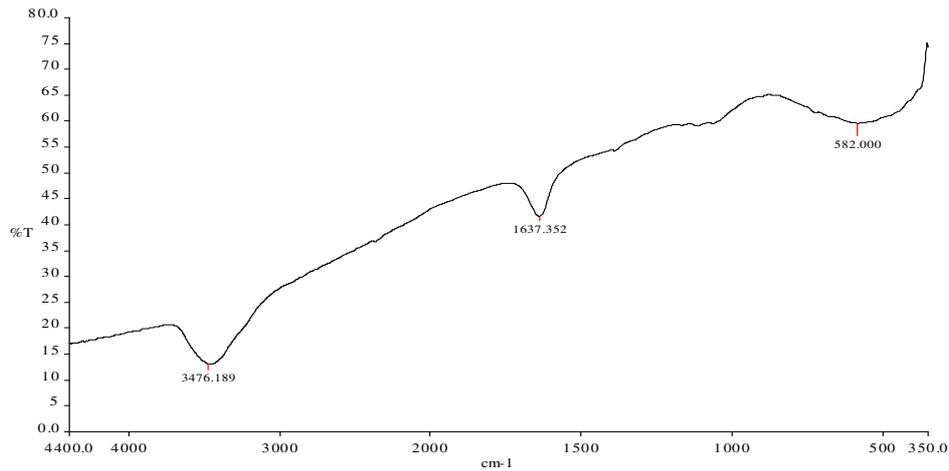


Figure (10). FTIR Spectra of n-ZVI particles after the sorption of aqueous Pb

FTIR spectra of phosphate rock particles, phosphate rock particles after the sorption of aqueous Ni and phosphate rock particles after the sorption of aqueous Pb are illustrated in Figures (11 to 13), respectively. As interpreted from the data of FTIR analysis, the function group of n-HAP type according to wave number, the main peaks are noticed in the phosphate rock particles. The strong bands at 3463.04, 1428.878 and 1049.536 cm^{-1} are due to symmetric stretching mode of $-\text{CONH}-$, $\text{RO}-\text{SO}_4-\text{OR}$ and $-\text{C}-\text{O}-\text{H}$, respectively. The wave number of the $-\text{CONH}-$ was shifted from 3463.04 to 3451.547 cm^{-1} after the sorption of Ni, and from 3463.04 to 3455 cm^{-1} after the sorption Pb. The wave number of the $\text{RO}-\text{SO}_4-\text{OR}$ was shifted from 1428.878 to 1427.139 cm^{-1} after the sorption of Ni, and from 1428.878 to 1423.105 cm^{-1} after the sorption Pb. The wave number of the $-\text{C}-\text{O}-\text{H}$ was shifted from 1049.536 to 1054.342 cm^{-1} after the sorption of Ni, and from 1049.536 to 1048.541 cm^{-1} after the sorption Pb.

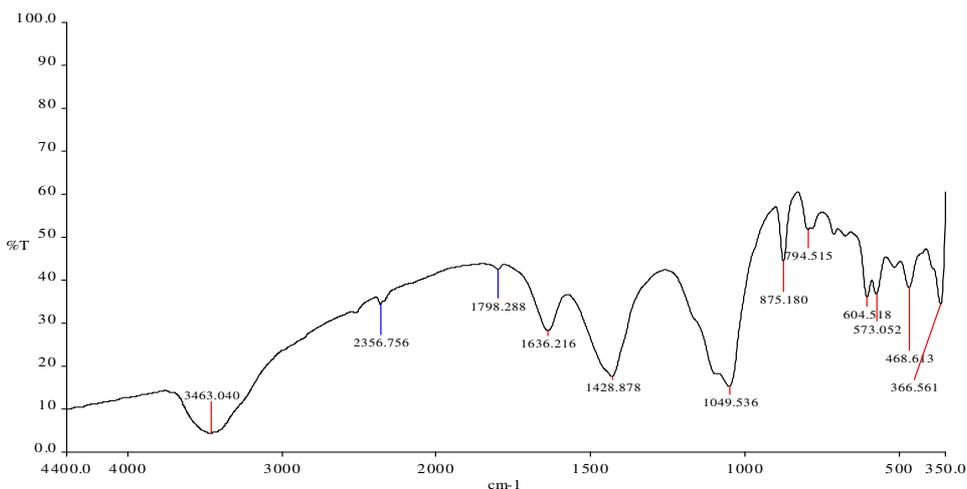


Figure (11). FTIR Spectra of phosphate rock particles

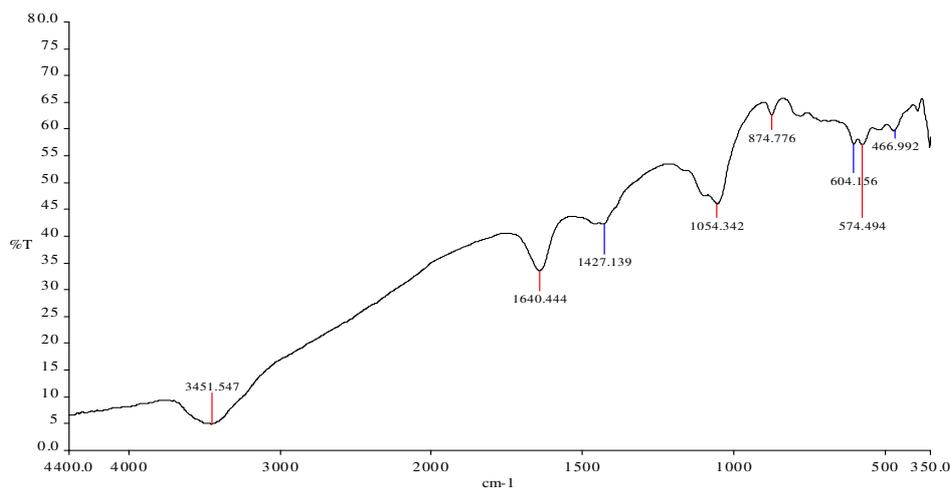


Figure (12). FTIR Spectra of phosphate rock particles after the sorption of aqueous Ni

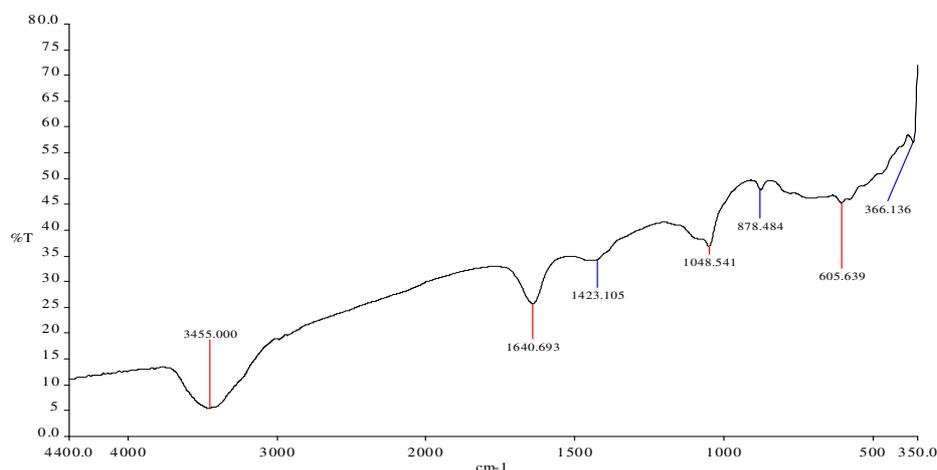


Figure (13). FTIR Spectra of phosphate rock particles after the sorption of aqueous Pb

The Figures (14 to 16) show the FTIR spectra of rice straw waste (RSW) powder, RSW powder after the sorption of aqueous Ni and RSW powder particles after the sorption of aqueous Pb, respectively. As interpreted from the data of FTIR analysis, the functional groups of RSW powder were sorted according to wave number. The main peaks are noticed in the RSW powder. A strong peak at 1639.189 cm^{-1} was assigned to the O-amino – stretching in hydroxyarylketones groups, $\text{R}-\text{C}^{\text{O}}-\text{NR}_2$ stretching in primary amides in solid state, the $\text{R}-\text{C}^{\text{O}}-\text{NR}_2$ stretching in N-mono-substituted amides in solid state, stretching in N-N di-substituted Amides, $-\text{C}=\text{C}^{\text{C}=\text{O}}$ and $-\text{O}-\text{NO}_2$. By comparing the FTIR spectra of RSW powder before and after sorption, there were remarkable shifts in some bands. These bands are the function groups of RSW powder in Ni and Pb biosorption. It is obvious that the intensity of the peaks has increased after sorption. Moreover, the wave number was increased from 1639.189 cm^{-1} to 1641.451 cm^{-1} after the sorption Ni. Also. the wave number of the $-\text{CONH}-$ was shifted from 1639.189 to 1640.27 cm^{-1} after the sorption of Pb.

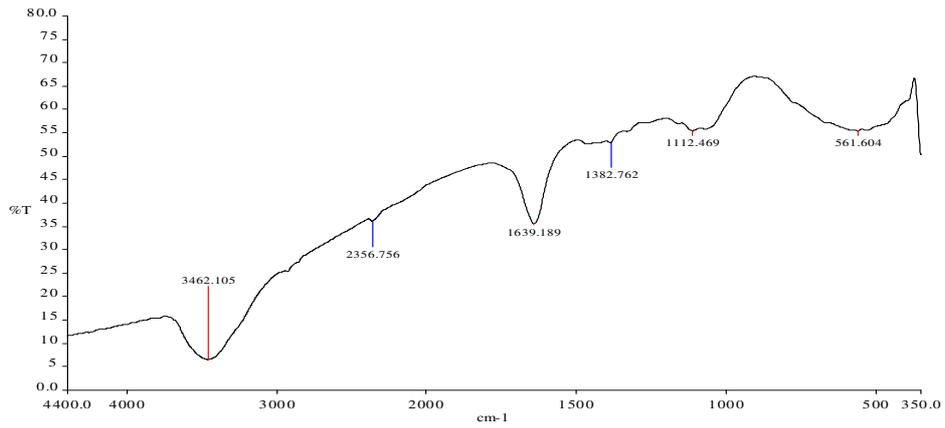


Figure (14). FTIR Spectra of rice straw waste (RSW) powder

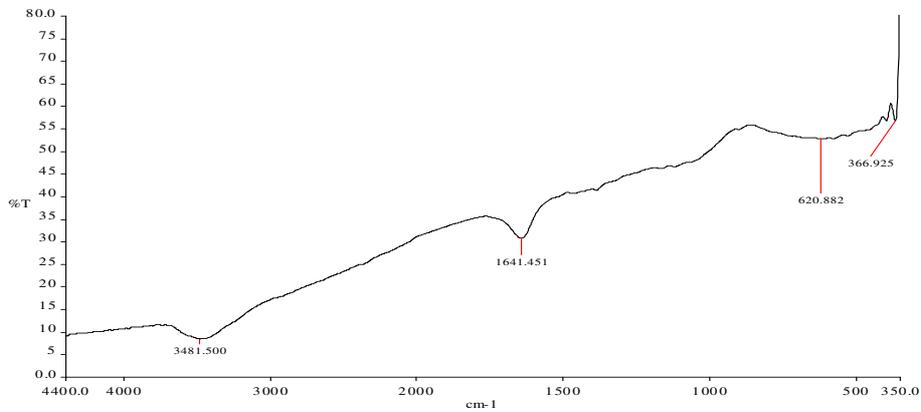


Figure (15). FTIR Spectra of rice straw waste particles after the sorption of aqueous Ni

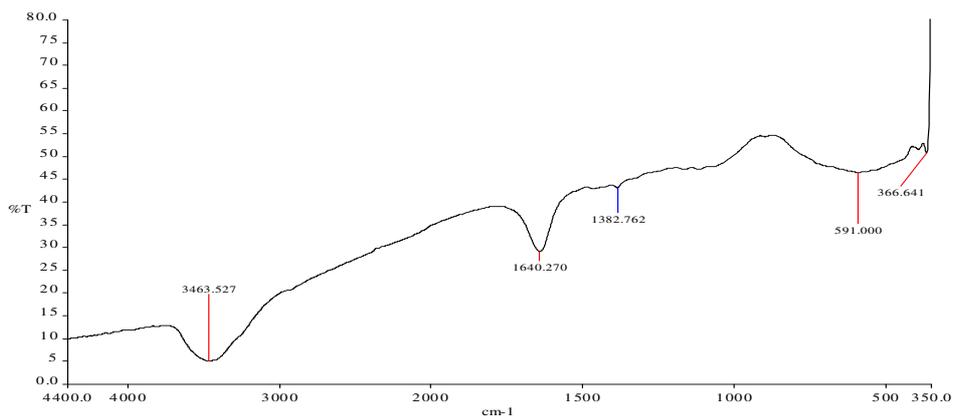


Figure (16). FTIR Spectra of rice straw waste particles after the sorption of aqueous Pb

1.4. X-ray analysis

X-ray analysis graphs of the n-HAP are presented in Figure (17). A broad single peak was observed in the X-Ray diffraction spectrum of raw bone at 2θ of 32.7° , confirming that the n-HAP is amorphous.

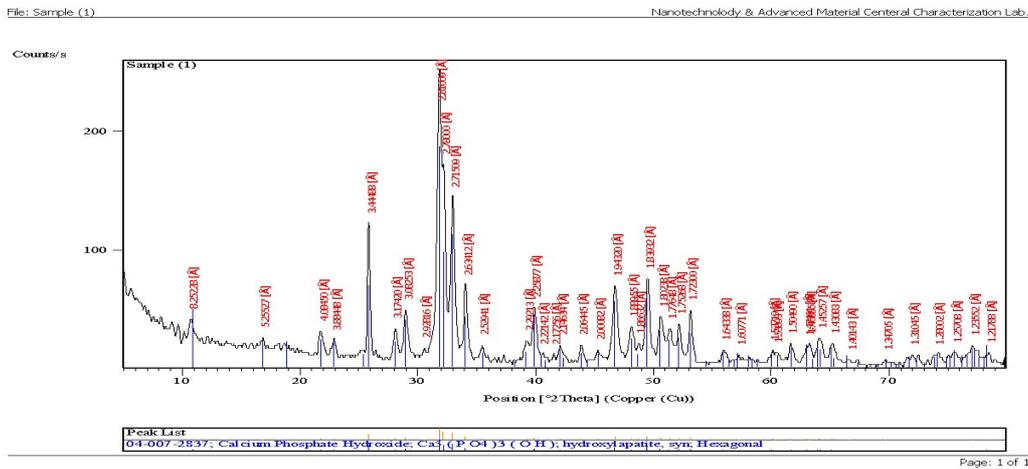


Figure (17). X-ray analysis graph of n-HAP particles

X-ray analysis graphs of the n-ZVI are presented in Figure (18). The peak at 2θ of 44.25° indicates the presence of n-ZVI nanoparticles.

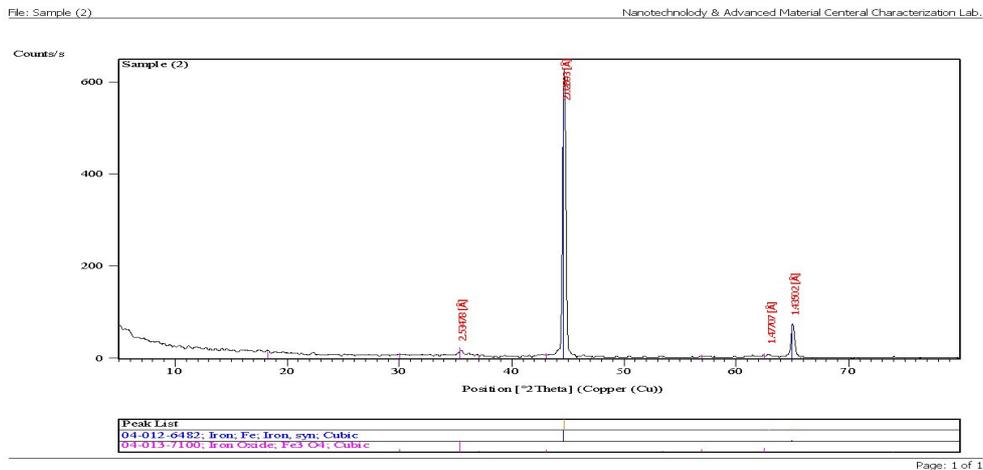


Figure 18. X-ray analysis graph of n-ZVI particles

The diffractogram, presented in Figure 19, shows that phosphate rock was composed of different phases with different intensities. For each sample, the quantitative analysis of its diffractogram using MATCH program reveals the presence of the following phases: calcium carbonate phosphate $Ca_5(PO_4)_3(CO_3)$ (2θ : 32.10° ; 33.24° ; 33.87° ; 46.96° ; 49.57°), calcite $CaCO_3$ (2θ : 29.42° ; 35.99° ; 39.43°), dolomite $CaMg(CO_3)_2$ (2θ : 30.96° ; 41.17°) and quartz SiO_2 (2θ : 26.65° ; 40.17°). It appears that the recorded dolomite, calcite and quartz phases due to their nature exogangue, while the interference of these phases with fluorapatite are due to their natural endogangue.

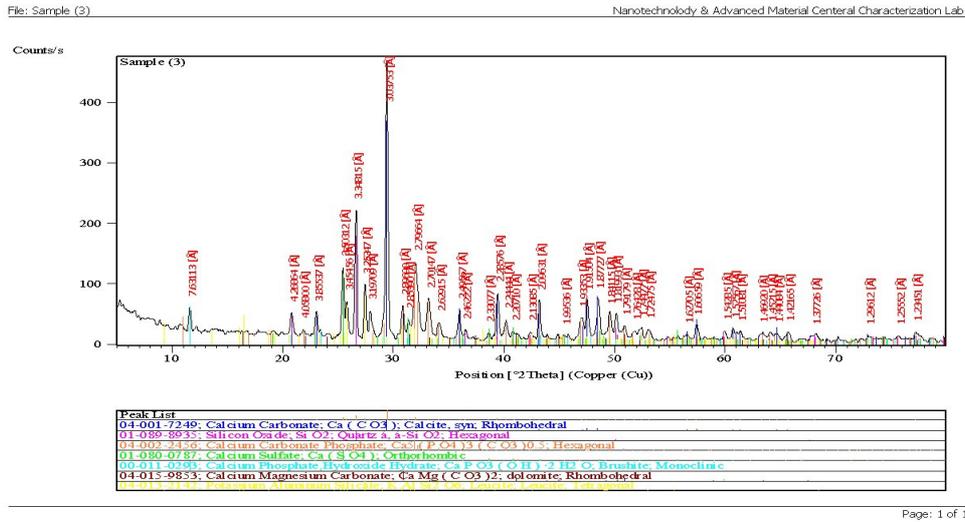


Figure (19). X-ray analysis graph of phosphate rock (PR) particles

2. Batch sorption of rice straw waste (RSW)

Biosorption capacity of rice straw waste (RSW) with three different sizes (0.125, 0.25 and 0.5 mm) increased with an increase in the initial concentration of Pb and Ni as shown in Tables (3 and 4). It suggested that the biosorption capacity of Ni (at 100 mg/l) increased with decreasing the particle size of RSW (0.125, 0.25 and 0.5 mm). It is account as 2840.5, 2826.0 and 2749.5 mg/kg, respectively. The biosorption capacity (S) of Pb (at 28.14 mg/l) in rice straw with three different sizes (0.125, 0.25 and 0.5 mm) were 1160.3, 1179.75 and 1157.0 mg/kg, respectively. The results indicated that optimum size of rice straw waste is 0.25 mm for maximum sorption of both Pb and Ni. These results may be due to the functional groups present on their cell wall offer certain forces of attractions for the metal ions and provide a high efficiency for their removal in RSW.

Similar results have been reported by Suemitsu *et al.* (1986); Wong *et al.* (2003) and El-Sayed *et al.* (2010). Rice straw waste possesses high oxygen; which is largely fixed in hydroxyl group of polysaccharides. These groups help in biosorption process by making a complex between metal ions (present in aqueous solutions) and oxygen of hydroxyl group (Hafiza *et al.*, 2010). The low particle size, have more surface area which plays an important role in the sorption process (Hayam, 2015). The adsorption capacity and the heavy metal efficiency are enhanced with the increase in the surface area because of the functional groups carboxylic groups responsible for the chelation of heavy metals.

Table (3). Equilibrium concentration (mg/l) of Ni at different sizes of RSW

Concentration (C ₀) mg/l	0.5 mm		0.25 mm		0.125 mm	
	Ce mg/l	S mg/kg	Ce mg/l	S mg/kg	Ce mg/l	S mg/kg
0.0	0.0	0.0	0.0	0.0	0.0	0.0
2.0	1.5	25.6	1.3	33.6	1.1	44.3
5.0	2.5	125.6	2.4	131.5	3.0	102.5
10.0	5.6	220.8	5.3	237.4	4.2	290.6
20.0	11.0	450.0	10.9	398.5	10.8	461.0
50.0	28.4	1079.3	20.0	1075.5	22.8	1494.0
100.0	45.0	2749.5	43.5	2826.0	40.0	2840.5
Average removal %	43.86		49.29		49.69	

Table (4). Equilibrium concentration (mg/l) of Pb at different sizes of RSW

Concentration (C ₀) mg/l	0.5 mm		0.25 mm		0.125 mm	
	Ce mg/l	S mg/kg	Ce mg/l	S mg/kg	Ce mg/l	S mg/kg
0.00	0.00	0.00	0.00	0.00	0.00	0.00
2.94	0.34	130.09	0.31	131.79	0.37	128.85
3.53	0.45	153.95	0.58	147.51	0.67	143.13
6.81	0.76	302.35	0.90	295.35	0.90	295.35
11.92	1.65	513.50	1.60	516.00	1.65	513.50
20.88	3.55	866.50	3.10	888.85	3.06	891.10
28.14	5.00	1157.00	4.55	1179.75	4.93	1160.30
Average removal %	85.98		85.92		84.91	

The experimental data (sorption isotherm) of heavy metals sorption on rice straw waste were modeled using various simple adsorption models such as linear and Freundlich models and the equation parameters are presented in Table (5).

Table (5). Parameters of some sorption isotherm models of Ni and Pb on rice straw waste

Sorption model	Size of rice straw waste	Parameters	Ni ²⁺	Pb ²⁺
Linear	0.125 mm	K _d	59.20	299.84
		R ²	0.9987	0.9306
	0.250 mm	K _d	66.50	322.61
		R ²	0.9927	0.9571
	0.5 mm	K _d	58.13	276.04
		R ²	0.9830	0.9926
Freundlich	0.125 mm	K _f	55.47	302.31
		1/n	1.02	0.937
		R ²	0.9988	0.9955
	0.250 mm	K _f	65.82	309.11
		1/n	1.00	0.896
		R ²	0.9928	0.9966
	0.500 mm	K _f	20.33	287.33
		1/n	1.29	0.967
		R ²	0.9991	0.9929

The results indicated that the optimum size of rice straw waste is 0.25 mm; it has maximum sorption of both Ni and Pb. The rice straw waste has more ability for retention of heavy metals such as Ni and Pb according to linear and Freundlich models (Table 5). The ability of RSW for removing heavy metals such as Ni and Pb ranging from 46.86 to 49.69% for Ni related to 0.125, 0.25 and 0.5 mm RSW.

Effective sorption of heavy metals using agricultural products and by-products may be documented such as modified rice husk (Lee *et al.*, 1998 and Kumar and Bandyopadhyay, 2006), rice husk activated carbon (Guo *et al.*, 2002) and maize husk (Jogi and Ansari, 2003). In general, an adsorbent can be termed as a low cost adsorbent if it requires little processing, is abundant in nature, or is a by-product or waste material from another industry (Khan *et al.*, 2004).

The present results are in agreement with Aqeel *et al.* (2011). The removal efficiencies of lead, copper and zinc after applying low cost agricultural by-product as an adsorbent, increase as their initial concentrations in the polluted solution decrease. Khan *et al.* (2004) mentioned that the sorption capacity is depended on the type of the investigated period of contact adsorbent and the nature of the wastewater.

Also, natural low cost material that have been studied for the removal of heavy metals by adsorption include rice straw (Hui *et al.*, 2008), black gram husk (Holan and Volesky, 1994), sugarcane bagasse (Volesky and Holan, 2008) and wheat bran. Rice straws proved to be the best biosorbent for Pb (II) and Ni(II) in aqueous solution. The biosorption characteristics fit well with Langmuir and Freundlich isotherm (Khalid *et al.*, 2010). Also, Mathew (2008) stated that rice husk showed a maximum removal efficiency of 99.5% for Ni (II), 80.0 % for Cd (II), 72.8% for Cr (VI), 56.2% for Cr (III) and 40.0% for Cu (II).

Rice straw and sugarcane bagasse are abundant agro-residues. The sugarcane bagasse is currently used as a biofuel and in the manufacture of pulp and building materials. On the other hand, open field burning of rice straw frequently causes serious air pollution (Nelson *et al.*, 1980). Thus a new technology for utilization of these agro-residues to a more value added material should be developed. Many researchers proposed the use of lignocellulosic waste as biosorbents for the removal of heavy metal ions in waste water (Lee and Rowell, 2004).

Rice straw possesses high oxygen; which is largely fixed in hydroxyl group of polysaccharides. These groups help in biosorption process by making a complex between metal ions present in aqueous solution and oxygen of hydroxyl group().

Biosorption has been demonstrated as an efficient and economical method for the removal of heavy metals in wastewaters (Benguella and Benaissa, 2002). Several naturally available biomasses, such as seaweeds and wheat straw, can be used as biosorbents. Non-living microorganisms, seaweeds, crab shells and other waste biomasses have also been tested and shown as promising sources of biosorbents (Gadd, 1992; Vieira and Volesky, 2003). The availability of a biomass at a low cost is a key factor dictating its selection for a biosorption process. Biosorption was earlier considered to follow a mechanism similar to that of adsorption (Wagner, and Jula, 1981). Several governing mechanisms of metal uptake by a biomaterial have been proposed, including chemisorption, complexation, chelation of metals, ion exchange, adsorption and micro-precipitation (Volesky, 2000). The metal binding depends on the biosorbent type, the metal ion species and concentration, temperature, pH, and ionic interference by other metal ions in the solution

3. Batch sorption of nanoparticles and phosphate rock

The effect of initial metal concentration (Pb^{+2} and Ni^{+2}) on adsorption onto biosorbents (Nano- hydroxyapatite, Nano- Zero Valente Iron and phosphate rock) are illustrated in Tables (6 and 7). The increase in biosorption capacity of Nano- Hydroxyapatite, Nano-Zero Valente Iron and phosphate rock was corresponded with increasing in the concentrations of Pb and Ni (up to 18 and 20 mg/l, respectively). The maximum Biosorption capacities of Pb by these ingredients were 4496.3, 4017.5 and 2152.5 mg/kg, respectively. The maximum Biosorption capacity of Ni^{+2} were 1283.5, 1026.8 and 757.1 mg/kg, respectively. The results indicated that maximum sorption capacity of heavy metals was occurred on Nano-hydroxyapatite for both Pb and Ni. These results may be due to the functional groups found in Nano-Hydroxyapatite. Similar results have been reported by Chen *et al.* (2010) and Yuan *et al.* (2010).

The experimental data (sorption isotherm) of heavy metals sorption on nanoparticles were modeled using various simple adsorption models such as linear and Freundlich models (Table 8). The nanoparticles used in the present study were hydroxyapatite nano-powder and Zero Valente Iron nano-powder, besides phosphate rock.

Table (6). Equilibrium concentration (mg/l) of Pb at nanoparticles and phosphate rock

Concentration (C ₀) mg/l	Nano- Hydroxyapatite		Nano- Zero Valente Iron		phosphate rock	
	Ce	S	Ce	S	Ce	S
	mg/l	mg/kg	mg/l	mg/kg	mg/l	mg/kg
0.00	0.00	0.0	0.00	0.0	0.00	0.0
1.25	0.02	308.3	0.06	297.0	0.12	141.3
2.09	0.02	517.8	0.13	491.3	0.17	240.4
5.01	0.04	1243.8	0.40	1152.5	0.30	588.8
11.97	0.06	2977.9	1.10	2717.5	0.62	1418.8
13.53	0.06	3367.1	1.32	3052.5	0.65	1610.0
18.07	0.09	4496.3	2.00	4017.5	0.85	2152.5

Table (7). Equilibrium concentration (mg/l) of Ni at nanoparticles and phosphate rock

Concentration (C ₀) mg/l	Nano- Hydroxyapatite		Nano- Zero Valente Iron		phosphate rock	
	Ce	S	Ce	S	Ce	S
	mg/l	mg/kg	mg/l	mg/kg	mg/l	mg/kg
0.0	0.0	0.0	0.0	0.0	0.0	0.0
1	0.8	55.8	1.0	0.5	0.6	51.0
2	1.5	132.1	1.9	31.5	1.4	80.9
5	4.0	250.0	4.3	166.0	3.2	223.9
10	7.6	605.3	8.0	500.0	6.9	385.3
15	11.5	876.0	12.0	750.0	10.7	535.0
20	14.9	1283.5	15.9	1026.8	13.9	757.1

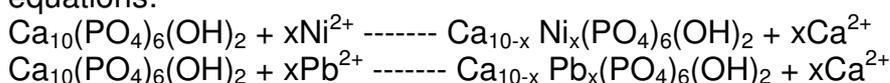
Table (8). Parameters of some sorption isotherm models of heavy metals on nanoparticles and phosphate rock

Sorption model	Nanoparticles	Parameters	Pb	Ni
Linear	Nano-Hydroxyapatite (n-HAP)	K _d	51361.15	81.89
		R ²	0.9355	0.9903
	Nano-Zero Valente Iron (n-ZVI)	K _d	2151.16	62.97
		R ²	0.9787	0.9767
	Phosphate Rock (PR)	K _d	2421.58	53.86
		R ²	0.9791	0.9916
Freundlich	Nano-Hydroxyapatite (n-HAP)	K _f	55257.6	94.89
		1/n	1.41	0.95
	Nano-Zero Valente Iron (n-ZVI)	R ²	0.9857	0.9849
		K _f	2439.9	32.22
	Phosphate Rock (PR)	1/n	0.75	1.26
		R ²	0.9985	0.9929
		K _f	2421.58	67.83
		1/n	0.90	0.903
		R ²	0.9791	0.9939

The results show the sorption parameters of heavy metals (Pb^{2+} and Ni^{2+}) on different nanoparticles indicated that maximum sorption of heavy metals was occurred on Nano- hydroxyapatite for both Pb and Ni according to linear and Freundlich sorption models (Table 8). The Nano-hydroxyapatite has more ability for retention of heavy metals such as Pb and Ni. The partition coefficient was 81.89 L/kg for Ni and 51361.15L/kg for Pb, indicated that Pb is more binding on such materials than Ni. The values for n-ZVI were 62.97 and 2151.2 L/kg, respectively. For phosphate rock the values were 53.86 and 2421.6 L/kg, respectively. The more ability of n-HAP to retain the Pb than Ni reflected in high value of partition coefficient.

As reported by Mavropoulos *et al.* (2002); Nzihou and Sharrock (2002) and Mobasherpour *et al.* (2011), calcium hydroxyapatite (CaHAP), $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$, is used for the removal of heavy metals from contaminated soils, wastewater and fly ashes. The most important properties related to various surface characteristics of HAP, e.g., surface functional groups, acidity and basicity, surface charge, hydrophilicity, and porosity. It has been found that HAP surface possesses 2.6 groups nm^{-2} of P-OH groups acting as sorption sites (Tanaka *et al.*, 2005). The sorption properties of HAP are of great importance for both environmental processes and industrial purposes.

In general, HAP selectivity towards divalent metal cations is a result of the ion-exchange process with Ca^{2+} ions (Monteil Rivera and Fedoroff, 2002). Ionic radius of Ni^{2+} (0.72 \AA) slightly differ from that of Ca^{2+} (0.99 \AA), and it can substitute Ca^{2+} in the HAP crystal lattice. No structural changes of nano- HAP were detected by the powder X-ray diffraction analysis and FTIR of the solid residue with maximum amount of uptake capacity of Ni^{2+} and Pb^{2+} . Monteil Rivera and Fedoroff (2002) reported that the reaction mechanism corresponds to equimolar exchange of nickel or lead and calcium yielding $\text{Ca}_{10-x}\text{Ni}_x(\text{PO}_4)_6(\text{OH})_2$, where x can vary from 0 to 10 depending on the reaction time and experimental conditions Ni^{2+} or Pb^{2+} ions are first adsorbed on the nano-HAP surface and substitution with Ca^{2+} ion occurs as described by the following equations:



The n-HAP is an effective adsorbent for the removal Ni^{2+} or Pb^{2+} from aqueous solutions. The results of XRD analysis and FTIR strongly support the ion exchange as a main mechanism for Ni^{2+} and Pb^{2+} removal by n-HAP. The results show that the Ni^{2+} or Pb^{2+} sorption by nanohydroxyapatite proceeds with a rapid surface complexation of the Ni^{2+} or Pb^{2+} on the -POH site before the formation of a compound of formula $\text{Ca}_{10-x}\text{Ni}_x(\text{PO}_4)_6(\text{OH})_2$.

Sorption of heavy metals on HAP has been extensively studied. It has previously shown by researchers that HAP had the greatest sorption capacity for Pb compared to other heavy metals and it could effectively immobilize Pb ions existing in the contaminated soils and waters (Lee *et al.*, 2005; Smiciklas *et al.*, 2008). High sorption capacity of HAP for Pb is due to the different dominant sorption mechanism for Pb, dissolution– precipitation, whose driving force is rapid dissolution of HAP followed by precipitation of less soluble

hydroxypyromorphite (HPy) (Mavropoulos *et al.*, 2002; Zhang *et al.*, 2010; Googerdchian *et al.*, 2012).

In recent years, iron nanoparticles (INP), amongst other metallic nanoparticles; have received much attention for their potential application to the treatment of contaminated soils and waters. Their high surface area to volume ratio and high surface energy (Zhang *et al.*, 1998) means that INP offer a greater reactivity than the surfaces of bulk scrap metal or iron filings/granules commonly used for remediation purposes in permeable reactive barriers, injection, etc., Tratnyek (1996) and Bigg and Judd (2000) for reviews. The remediation mechanism depends on the nature of the contaminant but in all cases is driven by the oxidation of Fe (0) (Miehr *et al.*, 2004).

To date, iron nanoparticles have been shown to be effective remediators of a range of contaminants including chlorinated organics (Nurmi *et al.*, 2005; Kanel *et al.*, 2005) and inorganic anions (Ponder *et al.* 2000; Zhu, 2010; Wijesinghe *et al.*, 2014). In addition, INP have also been shown to successfully remediate solutions contaminated with a range of metals, including Pb, Cr, Cu, As, Ni, Zn, Cd and Ag (Li and Zhang, 2007).

As the present results, n-ZVI has high reactivity with contaminants such as Pb and Ni due to their high surface volume (Cantrell, and Kaplan, 1997 and Saleh *et al.*, 2005). However, high reactivity alone is not enough to appoint this promising technology as a good in-situ remediation tool. Simultaneously, n-ZVI needs to be properly dispersed in water (Saleh *et al.*, 2005).

4. Batch sorption of Nano- hydroxyapatite and rice straw waste mixture

The effect of rice straw waste and nano-hydroxyapatite as alone, and their mixture on removal percentage of Pb and Ni are presented in Table (9). Data showed that removal percentage of Pb increased as 21.48, 25.67 and 38.25 % for rice straw waste (RSW), nano-hydroxyapatite (n-HAP), and their mixture (RSW+ n-HAP), respectively. The trend of Pb removal was 94.41, 99.67 and 99.69%, respectively.

The results indicated maximum percentage removal of heavy metals was occurred on their mixture of nano- hydroxyapatite with rice straw waste for both Pb and Ni. These results may be due to the many functional groups in RSW and n-HAP.

The removal percentage of Pb was more than of Ni indicated that the ability of Pb to bind with RSW or n-HAP more than Ni. Explanation for this phenomenon may be due to the properties of the metal according to Marilen *et al.* (2007). Which could be due to larger ions might better binding site with two distinct active groups according to Figueiral *et al* (2000).

Table (9). Effect of RSW, n-HAP and mixtures of n-HAP and RSW on percentage of Ni and Pb removal

Treatment	Percentage Removal	
	Ni ⁺²	Pb ⁺²
Rice straw waste	21.48	94.41
Nano-hydroxyapatite	25.67	99.67
Rice straw waste + Nano-hydroxyapatite	38.25	99.69

Hannah and Thompson (2008) stated that the recent revolution of nanoscience and the advanced sophistication in the tools of characterization, shrinking the particle size of the sorbents is expected to influence the sorption capacity and further assist in developing commercial nanosorbents for wastewater treatment. In fact, nanotechnology has a significant impact to deal with legacy environmental pollution and to predict and prevent future environmental problems.

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الملخص العربي

إزالة بعض العناصر الثقيلة باستخدام مواد الاممصااص الحيوى والحبيبات النانوية

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أجريت تجارب الاممصااص لدراسة دور مواد الاممصااص الحيوى والحبيبات النانوية لازالة بعض العناصر الثقيلة (الرصاص والنيكل) من المحاليل المائية . استخدم قش الارز كمادة ادمصااص حيوية (نواتج العمليات الزراعية) . بالاضافة لذلك استخدمت مواد نانوية مثل نانو هيدروكسي اباتيت (٦٠ نانوميتر) ونانو الحديد غير المشحون (٢٥ نانوميتر). وقد استخدم قش الارز باحجام ٠,١٢٥ و ٠,٢٥ و ٠,٥٠ مم لتجارب ادمصااص بعض العناصر الثقيلة بتركيزات تصل الى ١٠٠ مجم/لتر في حالة عنصر النيكل و ٢٨.١٤ مجم/لتر في حالة عنصر الرصاص . مع المواد النانوية وكذلك مسحوق صخر الفوسفات (٠.٠٦٣ مم)، أوضحت النتائج ان قش الارز بحجم ٠,٢٥ مم كان الانسب في ازالة العناصر الثقيلة (الرصاص والنيكل) بتركيزات حتى ٢٠ مجم/لتر في حالة النيكل و ١٨ مجم/لتر في حالة الرصاص وهذا يرجع الى القابلية العالية للمواد النانوية لادمصااص العناصر الثقيلة كما أوضحت نماذج ادمصااص الخطي ونموذج فريندليش. كذلك اوضحت النتائج القدرة العالية لحبيبات الهيدروكسي اباتيت النانوية مع قش الأرز لادمصااص الرصاص والنيكل وهذا قد يعود الى المجاميع الفعالة في قش الارز والحبيبات النانوية . كما ان خليط قش الارز وحبيبات الهيدروكسي اباتيت النانوية كانت ذات قدرة عالية لادمصااص العناصر الثقيلة. اوضحت النتائج ان نسبة ازالة الرصاص وصلت الى ٩٩.٧٠ % وللنيكل ٣٨.٢٥ % وهذا يوضح قدرة الرصاص العالية للارتباط بقش الارز وحبيبات الهيدروكسي اباتيت النانوية . النتائج الحالية مفيدة جدا في معالجة المياه العادمة (مثل مياه الصرف الصناعي ومياه الصرف الزراعي) وازالة العناصر الثقيلة وجعلها صالحة للاستخدام الزراعي. كما تلقى الدراسة الحالية الضور على فاعلية حبيبات الهيدروكسي اباتيت النانوية في ازالة أيونات الرصاص والنيكل من المحاليل المائية ومعالجة المياه العادمة. وتوصى الدراسة بعمل دراسات مستقبلية لمعرفة دور المواد النانوية في ازالة العناصر الثقيلة المختلفة من المياه العادمة مختلفة المصدر .

