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Research Article

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Biosorption of Copper (II), Lead (II), Cadmium (II) and Zinc (II) ions from aqueous solution by *Nypa fruticans* Merr Shell on batch method

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ABSTRACT

The Nypa fruticansMerr shell was used for removal of Cu (II), Pb(II), Cd(II) and Zn (II) ions from aqueous solution by batch adsorption method. Several variables such as effect of pH, contact time, concentration of toxic metal, stirring time and agitation speed on the absorption capacity of metals ion has been investigated. The optimum condition was achieved for Cu(II), Pb(II), Cd(II) and Zn(II) on pH 6, contact time 60s, concentration 50 mg/L. The Agitation speed of Cd(II), Cu(II), Pb(II) were 200 rpm and Zn(II) was 150 rpm.All metals ion concentration has been measured by using atomic absorption spectrometry. On te other hand functional groups present on the shell was measured using Fourier Transform Infra Red spectroscopy.

Keywords: Biosorption, Heavy metal, *Nypa fruticans*Merr shell, FTIR.

INTRODUCTION

Environmental pollution with heavy metals has become a global phenomenon as a consequence of industrial and metallurgical process which introduce majority of toxic chemicals into the environment [1-5]. The heavy metals of widespread concern to human health are lead, copper, mercury, cadmium, arsenic, chromium, as well as zinc [6].

These are stable metals that cannot be destroyed or degraded in the environment and get passed up in the food chains to humans. At present, these toxic metals have polluted our atmosphere, our water, our soil and our food chain, and have been reported to be slightly toxic even at low concentration [7,8]. For instance, exposure to Lead causes anaemia, disease of the liver and kidney, brain damage and ultimately death, while, prolonged inhalation of Cu(II) spray is claimed to cause an increase in the risk of lung cancer [9]. However, extensive research has been conducted on the discharge of metal ion contained in industrial effluents because of the presence and accumulation of toxic effects on living species.

Recently, biosorption has emerged as a treatment methods as an alternative tecnology to the conventional used ones for the wastewater treatment. There are various secondary and tertiary treatment techiques for the removal of heavy metals from aquaeous solution [10]. However, these processes are having technical and or economical constraits [11]. Biosorption has emerged as an alternative to these methods with the major advantage such as low cost, high efficiency, minimization of chemical and or biological sludge, regeneration of biosorbent and possibility of metal recovery [12,13].

Various biosorbents such as agricultural by products and microorganisms such as rice husk, algae, citrus peels, grape stalks, cocoa shell, mangostana fruit shell, have been reported for the removal of toxic metal from enviromental water [13]. Biosorption refers to different modes of non-active metal binding, where metal sequestration by cell wall can take palce through adsorption, ion exchange and complexation. Numerous functional groups namely,

sulphydryl, carbonyl, hydroxide amino, thiol, carboxyl and amide moieties are possible for the binding metal ions [13]. *Nypa fruticans*Merr shell has eralier been reported fir its biosorption properties for a number of metal ions including mechanism prediction by using artificial neural network [14].

The present study is focused to explore the ability of enviromentally friendly agricultular by product such as Nipah palm fruit shell for the removal of Cu, Cd, Pb, and Zn from aqueous solutions under batch method. Experimental parameters affecting the biosorption process such as pH, contact time, stirring speed, particle size, concentration has been investigated to calculate the biosorption capacity of the *Nypa fruticans*Merr shell.

EXPERIMENTAL SECTION

2.1. Preperation of biosorben

*Nypa fruticans*Merr shell were taken in Surantih, Painan, cleared of mud that sticks, then washed with water and dried in the open air. Once dried and then crushed with pastle and sieved with particle size to be used is 160µm. The *Nypa fruticans*Merr shell in a solution of 0,1 M HNO_3 for 2 hours while stirring occasionally. Results filtered then washed with distilled water. After that, it was soaked with ethanol for 2 hours, then dried again.

2.2. Chemical

$CuSO_4$ (Merck), $Pb(NO_3)_2$ (Merck), $CdCl_2$ (Merck), $ZnCl_2$ (Merck), HNO_3 65% (Merck), NaOH (Merck), ethanol distillation and the distilled water.

2.3. Experimental procedure

The experiment was conducted in two phases. The first is the creation of adsorbent the *Nypa fruticans*Merr shell. The second is testing the ability of the metal ion uptake of Cu (IV), Pb (II), Cd (II) and Zn (II) with agitation speed variation of metal ion solution, time varying stirring, concentration, particle size and pH to determine the optimum conditions using batch sorption method.

2.3.1. Determination of Optimum Conditions

Determination of optimum conditions performed for each metal ion Cu, Pb, Cd (II), and Zn (II). For each treatment using 0,5 g of biomaterial.

2.3.2. Effect of pH

*Nypa fruticans*Merr shell put into a flask with a particle size of 160 µm was then added 10 mL of metal ion 50 mg/L at pH variation 3,4,5,6 and 8, then those are shaked for 60 minutes with a rotation speed of 150 rpm. Equal treatment for solution Cu, Pb, Cd and Zn has been done. The resulting filtrate was analyzed by atomic absorption spectrophotometer.

2.3.3. Effect of Particle Size

Biomaterial put into each flask with a size of 160, 250 and 425 µm, then added with 10 ml of metal ion 50 mg/L at pH variation 3,4,5,6 and 8, then those are shaked for 60 minutes with a rotation speed of 150 rpm. Equal treatment for solution Cu, Pb, Cd and Zn has been done. The resulting filtrate was analyzed by atomic absorption spectrophotometer.

2.3.4. Effect of Concentration

*Nypa fruticans*Merr shell put into a flask with optimum particle size, then added 10 mL of metal ion, respectively 10, 20, 30, 40 and 50 mg/L with pH optimum. The solution then are shaked for 60 minutes with rotation speed of 150 rpm. Equal treatment for solution of Cu, Pb, Cd and Zn (II) has been done. The resulting filtrate was analyzed by atomic absorption spectrophotometer.

2.3.5. Effect of Contact Time

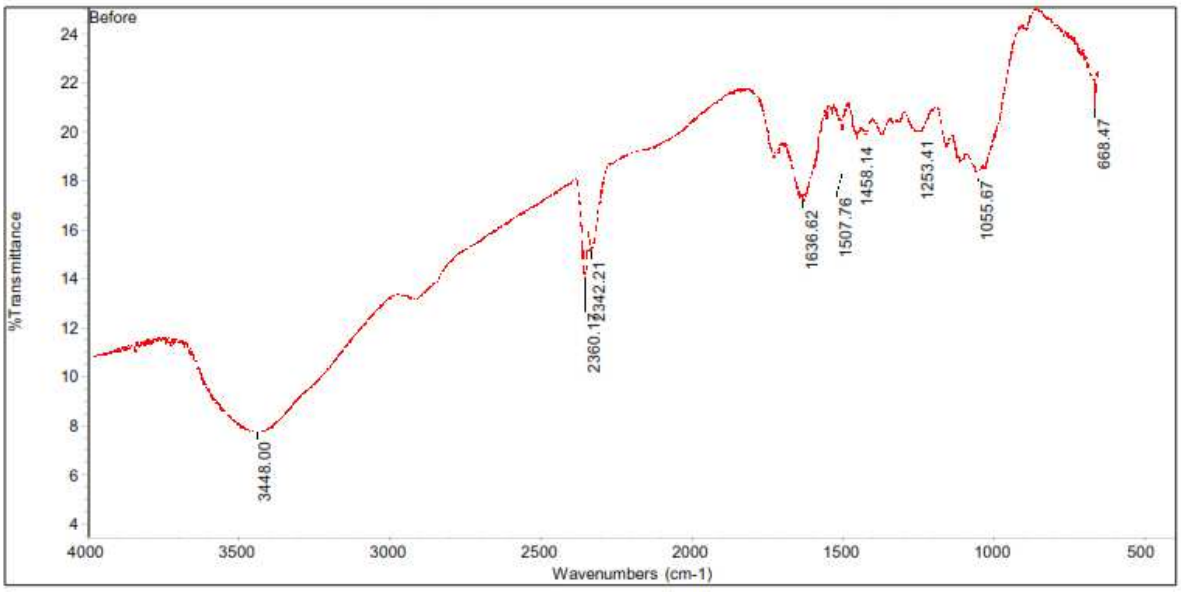
Biomaterial with particle size 160 µm wighed 0,50 grams. Then added a solution of 10 mL of metal ion was shaked for 5, 10, 20, 30, 40, 50 and 60 minutes with rotation speed of 150 rpm. After it was filtered and the resulting filtrate is collected and analyzed by atomic absorption spectrophoptometer.

2.3.6. Effect of Agitation Speed

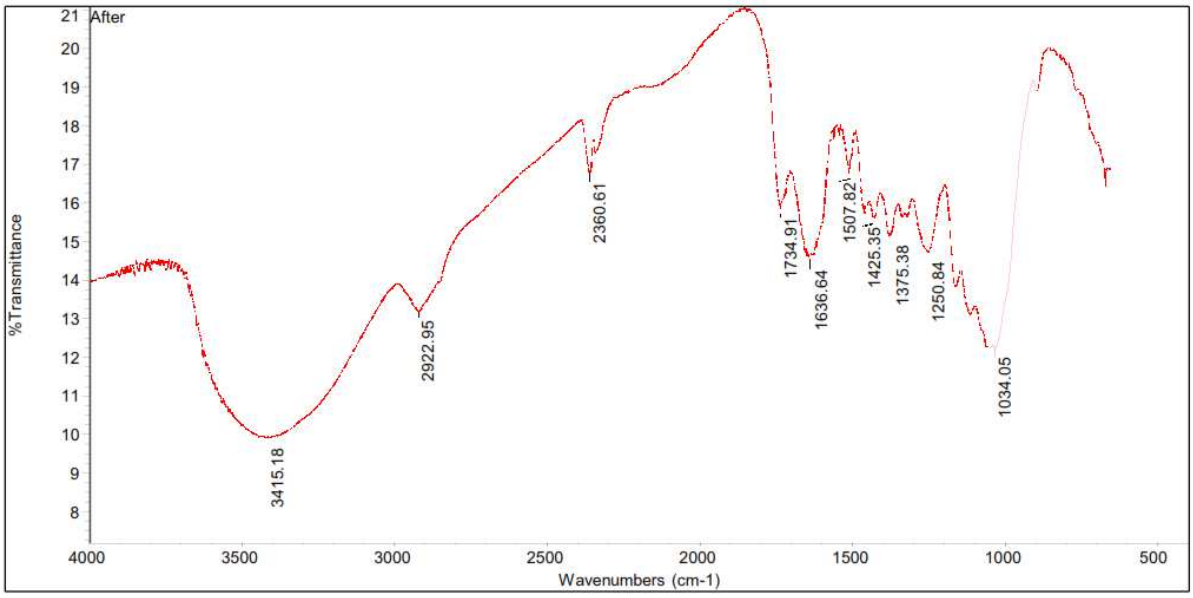
Adsorbent with a particle size of 160 µm wighed 0,50 grams. Then added a solution of 10 mL of metal ion and it was shakaed for 30 and 60 minutes with an agitation speed of 50, 100, 150 and 200 rpm. After it was filtered and the resulting filtrate is collected and analyzed by atomic absorption spectrophotometer.

RESULTS AND DISCUSSION

FTIR is an important analytical technique, which detects the vibration characteristics of chemical functional groups existing on the surface of adsorbent. Some characteristic peaks obtained from the functional groups proteins and polysaccharides. Functional groups contained in *Nypa fruticans* Merr shell be shown in Fig. 1a-1b.



(a)



(b)

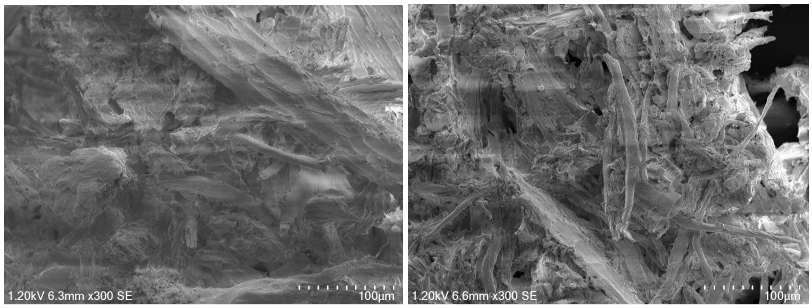
Fig.1. FTIR of *Nypa fruticans* Merr shell before (a) and after(b) uptake of metalions

The spectrum can be seen in the shift of the transmittance values of functional groups contained in the *Nypa fruticans* Merr shell. The spectrum having characteristic peaks in the range of 4,000 to 2,500, according to the absorption peak due toNH, CH and OH single bond.

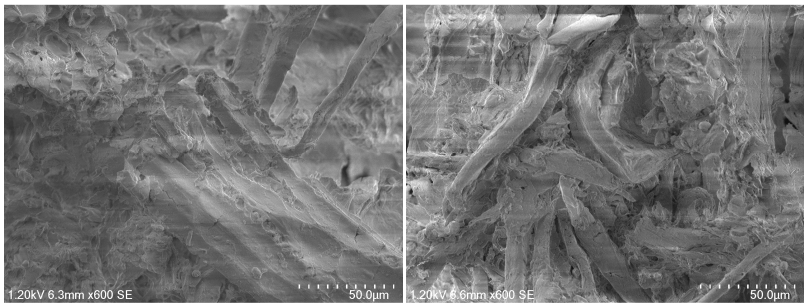
3.1 Scanning Electron Microscopy

FE-SEM (Field Emission Scanning Electron Miscroscope) is used to see whether the metal ions already bound to the surface of the *Nypa fruticans* Merr shell. At 300X magnification circumstances before absorption of functional groups on the roof of the *Nypa fruticans* Merr shell indicated the presence of light. Mean while, after the absorption of light is reduced which indicates that the functional groups have been bonded to heavy metal. Fig. 2 presents the SEM of the samples. 1000X magnification FE-SEM of the bioamterial surface after absorption. Where surface such

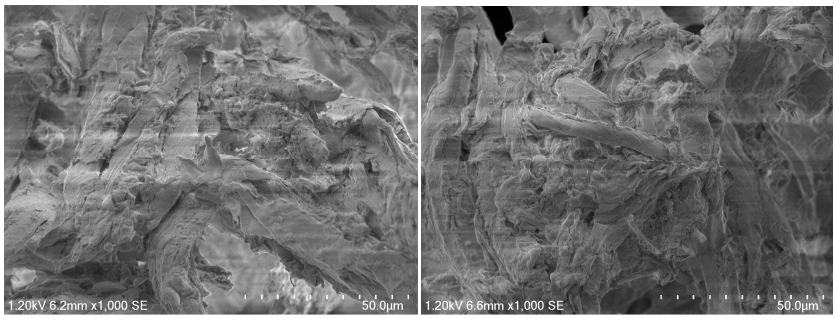
as coated by heavy metals. Fig. 2 is a photograph of FE-SEM *Nypa fruticans* Merr shell that interact with a solution of ion metal.



A



B



C

Fig2. FE-SEM of the *Nypa fruticans* Merr shell 300X magnification(A), 600X(B) and after absorption of Cu(II) at 1000X magnification(C)

3.2 Effect of pH

Among all other parameters, pH of solution has been found to be the most important one. It not only influences the speciation of metal ions but also the charges on the sorption sites of *Nypa fruticans*Merr. So, it is very important to consider the ionic states of the functional groups of the biosorbent as well as the metal solution chemistry at different pH values. With the change in pH of solution, the behaviour of each of these functional group changes.

The removal of all the four ions under consideration was affected by changes in pH as observed from Fig.3. Their removal was high under acidic conditions were removed at pH 6; further increase in pH above 6 led to decreased adsorption of metal ion up take. At pH>7, removal of all the ions remained almost constant. Generally, metal ions are more soluble at lower pH values and this enhances their adsorption.

3.3 Effect of Contact Time

Fig. 4 shown that the absorption capacity of the largest found in metal ion Zn and Cu with stirring time of 5 minutes and 6 minutes. At the time of 6 minutes for Pb and Cd minutes for interaction between metal ions and active groups biosorben the more and the greater the possibility of absorption capacity. When metal ions mixed with the material in the flask will be an interaction between the metal ions with active the *Nypa fruticans*Merr shell, the length of time the interaction will affect the amount of metal ions adsorbedon the surface of the skin off the *Nypa fruticans* Merr shell. Attime >7 minutes, removal of all the ions remained almost constant. Absorption increases with the

length of time to interact and reach equilibrium at the optimum time. It also occurs on the metal ion Zn, Cu, Pb and Cd.

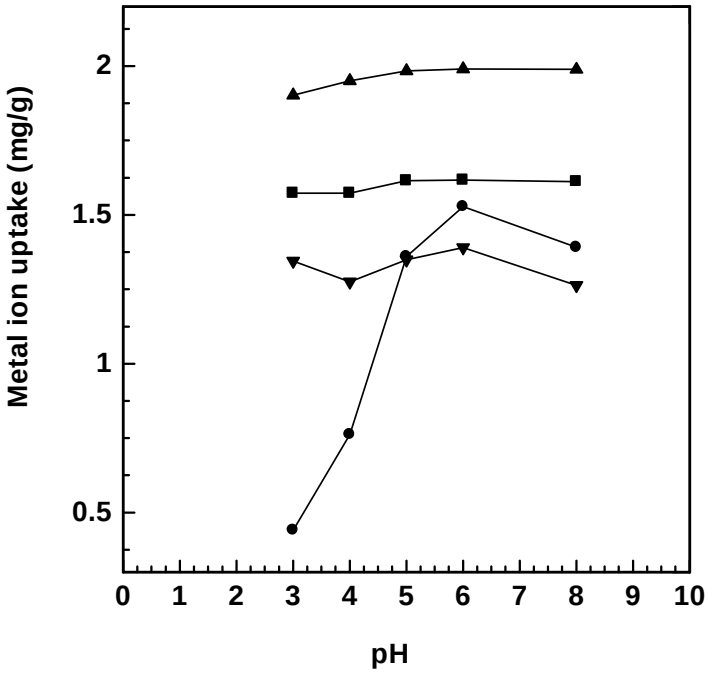


Fig.3 Effect of pH between metal ions and biomaterial on Cu (●), Pb (▲), Cd (■) and Zn (▼) adsorbtion by *Nypa fruticans* shell

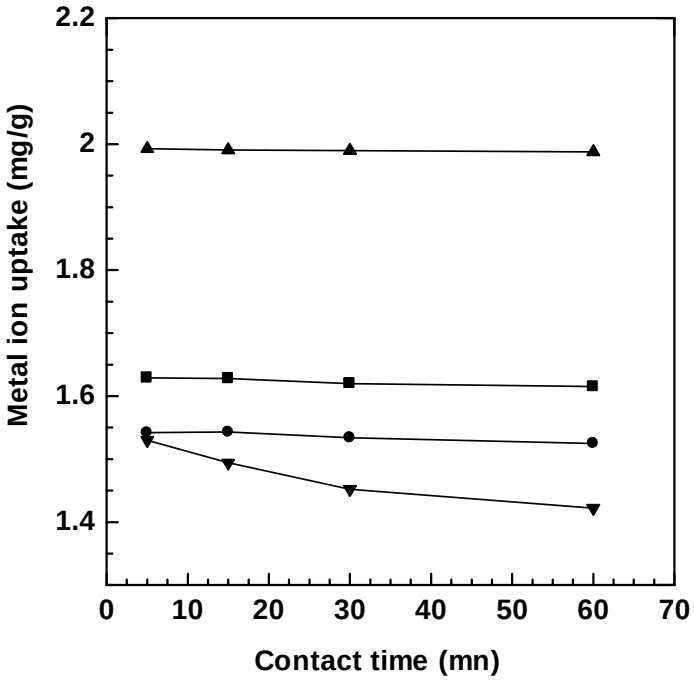


Fig. 4. Effect of contact time between metal ions and biomaterial on Cu (●), Pb (▲), Cd (■) and Zn (▼) adsorbtion by *Nypa fruticans* shell

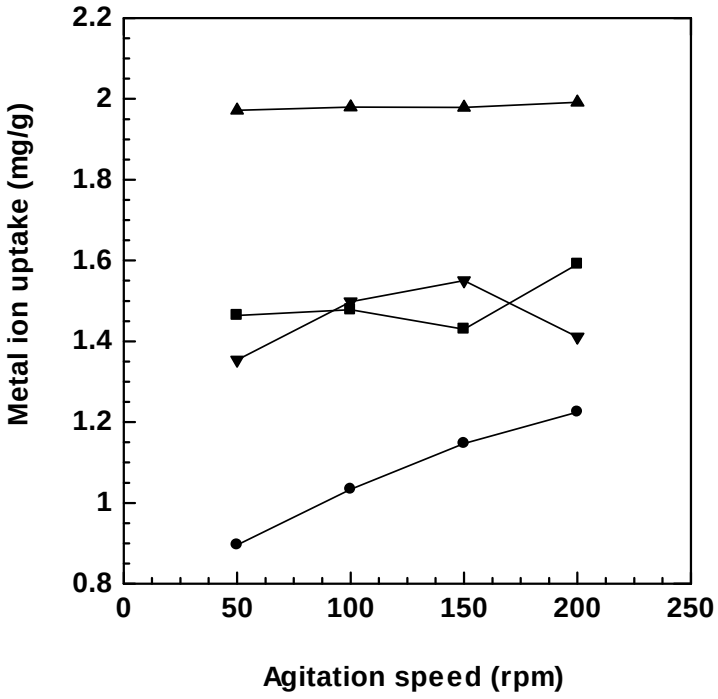


Fig. 5. Effect of agitation speed between metal ions and biomaterial on Cu (●), Pb (▲), Cd (■) and Zn (▼) adsorbtion by *Nypa fruticans* shell

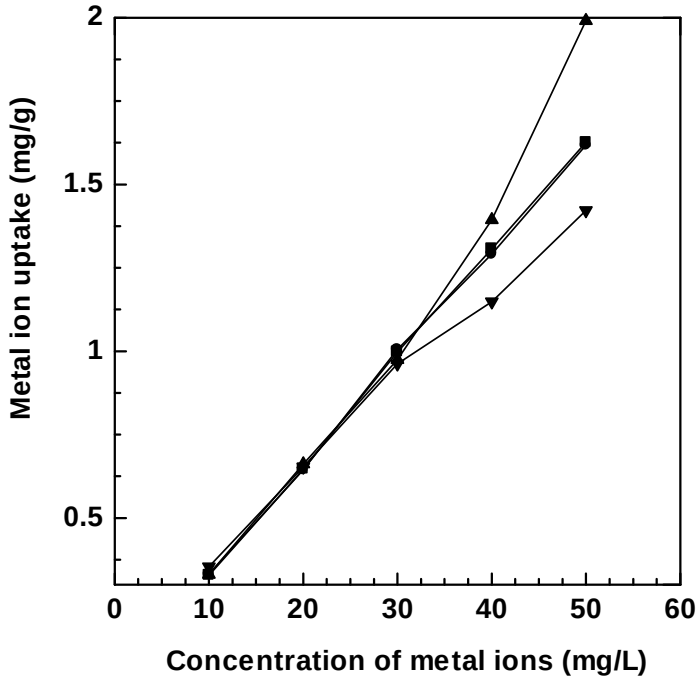


Fig 6. Effect of concentration between metal ions and biomaterial on Cu (●), Pb (▲), Cd (■) and Zn (▼) adsorbtion by *Nypa fruticans* shell

3.4 Effect of Agitation Speed

The boundary layer which surrounds the biosorbent contains important active site for biosorption process. This boundary layer became an external mass transfer between two phases of biosorbent and heavy metals ion solution. Since the biosorption rate was dependent on the external film diffusion, appropriate agitation speed is

important to minimize mass transfer resistance. Fig.5. shows that the biosorption increased with increasing agitation speed from 50 to150rpm but it decreased at 200rpm for Zn and Pb.Absorption was maximum at 200 rpm for Cd and Cu.

However, lowest biosorption was determined at 50rpm for Cu, Pb Cd and Zn. It was believed that at 150 and 200rpm, all active binding sites on the biosorbent surface were sufficient enough for metal ions biosorption, thus, it made more binding to occur. At the agitation speed of 200 rpm, a lower efficiency in biosorption.

3.5 Effect of Concentration

Varying concentration of Cu, Pb, Cd and Zn have any effecton its adsorption from solution as could be observed in Figure 6, as 90% of the ions was removed at 50mg/L. 70% of Cu, Pb, Cd and Zn were removed at 30 mg/L of solution.

CONCLUSION

FE-SEM (Field Emission Scanning Electron Miscroscope) is used to see whether the metalions already bound to the surface of the *Nypa fruticans* Merr shell. Mean while, after the absorption of light is reduced which indicates that the functional groups have been bonded to heavy metal.

The pH of solution has been found to be the most important one. It not only influences the speciation of metal ions but also the charges on the sorption. So, it is very important to consider the ionic states of the functional groups of the biosorbent as well as the metal solution chemistry at different pH values. With the change in pH of solution, the behaviour of each of these functional group changes.

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