Investigation on the potential of Phyllanthus Niruri powder in removing Cu(II) ions

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Abstract

The Cu(II) adsorption efficiency of Phyllanthus Niruri powder was analyzed in this work. The Response Surface Methodology(RSM) using Central Composite Design (CCD) was employed to find out the optimum parameters for Cu(II) removal using Phyllanthus Niruri powder(PNP). Metal uptake(q_e) was chosen as the response function. The optimized results showed that, P. Niruri works best at pH 2, temperature 63^{o}C and an adsorbent dosage 0.5g/l. The optimum contact time was 15 minutes. The optimum conditions were verified with synthetic Cu(II) solution. The outcome is 68% Cu(II) adsorption. This value is 10% below the RSM predicted percentage. Then, it was tested on industrial waste containing a mix of heavy metals including Cu(II). The Cu(II) adsorption was 39%. This low adsorption capacity could be due to competitiveness amongst other metals present in the sludge sample. The experimental results for industrial sludge solution fitted Langmuir isotherm indicating that single layer adsorption occurred. The study concludes that P. Niruri powder can be used as a cheap biosorbent for Cu(II) present in trace amount.

Keywords—*Phyllanthus Niruri; Wastewater; Biosorption; Heavy metals, Cu(II)*

I. Introduction

Wastewater from various industries such as electroplating, batteries manufacture, mining, metal finishing, brewery and pharmaceutical contains toxic heavy metals such as Cr(VI), Cu(II), Zn(II) and Ni(II) [Rosca, M. et al 2015]. Industrial wastewater can cause serious water pollution problems if not disposed properly [Adaikalam, S. & Malairajan, S. 2015; Rao et al, 2015]. Thus, it is mandatory to treat the industry effluent and dispose in an environmental friendly manner. The present waste water treatment using coagulation, flocculation, sedimentation and filtration process removes both organic and inorganic constituents in waste water in the form of sludge. With the treatment, the treated water qualifies National Water Quality Standard B for Malaysia and is let into the river. The sludge produced from the water treatment poses another disposal issue. At the present solid sludge are disposed into a landfill. Some of the sludge contains valuable heavy metals that can be recovered and reused. One of the heavy metals that are discharged by the industrial wastes from mining and metal industries, electroplating, dye, and brass plating industries is copper ions. The undesired amounts of Cu(II) that are released to the environment can have negative impacts on living organisms. In humans, it causes nose, mouth and eye irritation, headache, chest pain dizziness, nausea and diarrhea. In the environment, it is poisonous for aquatic life and micro-organisms in soil [Rao, P.S. et al 2007]. Therefore, it is important to find an effective way of removing Cu(II) from wastewater. This study focuses on recovering Cu(II) from an industrial sludge that has a mix of heavy metals.

Many studies are conducted to recover Cu(II) from sludge. Recovery methods used were ion-exchange, electrodeposition, chemical and electrochemical precipitation, reverse osmosis, membrane filtration and adsorption [Rosca, M. et al 2015; Vinodhini & Das, 2010; Moussavi & Barikbin, 2010]. These processes do exhibit plausible metal recovery percentage. The recovery process becomes more energy intensive when the ions to be removed are in infinitesimal amounts [Wang & Chen, 2006]. Another popular recovery method amongst researchers is adsorption. Adsorption is the mass transfer and collection of liquid or gaseous molecules from its bulk to a solid surface. Ajenifuja, E. et al

(2017) reported 97.5% Cu(II) removal using photocatalytically modified diatomaceous ceramic adsorbents from an initial concentration of 200mg/l. In another study, Moradi, O. et al (2012) removed 74.5% Cu(II) using polymer based adsorbent. In the recent past, the research interest is being focused towards biosorbents as a cheaper and renewable adsorbent option [Febriana et al 2010].

Biosorption is regarded as an eco-friendly process since the biomass used is bio-degradable and therefore does not accumulate and contaminate the environment. These biosorbents can be any biosolids ranging from industrial organic wastes, such as ash, and living or non-living biomass/biomaterials which have adsorbing capacity [Hansda, A. et al, 2015]. Advantages of choosing biosorption over the conventional adsorption is high efficiency, minimum release of chemical sludge, capable of regeneration, ability to adsorb low metal concentration and ease of operation [Di Caprio, F. et al 2014]. Researchers have been trying to find optimal inexpensive biosorbent with very good adsorptive characteristics since some processes tend to lose its efficiency once the metal concentration becomes low. A study that focused on finding low cost agro-based adsorbent was carried out by Hegazi, H.A. (2013) using rice husk and fly ash to find removal capacity of the heavy metals from wastewater. It was noted that metals with concentration from 20-60mg/l could be successfully removed using these biosorbents with pH of 6-7. Rice husk absorbed Fe, Pb and Ni whereas fly ash absorbed Cu and Cd. Increasing the Cu(II) concentration from 20mg/l to 60mg/l increased the percentage adsorption from 24.49% to 98.177% in the case of rice husk and 37.38% to 98.545% for fly ash. Therefore, fly ash can be used to effectively remove Cu(II) from sludge. In the case of a study by Maheshwari, U. et al (2015), nano-porous activated neem bark was used to remove Cu(II), Zn(II) and Cr(VI) from individual solution as well as mixed solutions. For an initial metal concentration of 200mg/l, the optimum conditions were found to be pH of 1.2, 35^{o}C, contact time of 48hour, adsorbent dosage of 6g/l, maximum adsorption capacity of 21.23mg/g and Cu(II) removal of 63.7%. Modified corn silk has been used in a study by Yu, K. et al (2016) to remove Cu(II), Co(III) & Ni(II) from wastewater. This experiment was carried out in batch biosorption method. For an initial metal concentration of 450mg/L, the optimal parameters were a pH of 6, adsorbent dosage of 0.8g/l, contact time of 20 minutes and maximum adsorption capacity of 96.15mg/g, 90.09mg/g and 76.92mg/g for Cu(II), Co(III) and Ni(II) respectively. A study on algae inhabiting rice paddies was done by Tran, H.T. (2016). Jelly-like batch of algae were obtained from rice paddies (AL-VN) to study their biosorption capacity of Cu(II), Cd(II) and Pb(II) from aqueous solutions in batch mode. The optimum conditions to remove heavy metals using AL-VN at the maximum adsorption capacities Cu(II) 27.78mg/g, Cd(II) 28.57mg/g, and Pb(II) 76.92mg/g are pH of 4 [Cu(II)], 7[Cd(II)] and 5[Pb(II)], temperature of 30^{o}C, initial metal concentration of 5mg/L [Cu(II) and Cd(II)] and 50mg/l [Pb(II)] and contact time of 60 minutes.In another study by Adaikalam, S. & Malairajan, S (2015), Phyllanthus Niruri powder was used as the bio sorbent to remove Cu(II) in a prepared solution. In this study, 89% of Cu(II) was removed at 30^{o}C, pH 4.4, 150min contact time and adsorbent dosage of 2.5g/100ml with an initial concentration of 100mg/l. Phyllanthus Niruri powder is a potential biosorbent due to the low cost and high efficiency of Cu(II) removal from aqueous solution even when present in trace amount. However, P. Niruri is yet not an established biosorbent since the research is still in infancy. Phyllanthus Niruri is a herb that comes from the Euphorbiaceae family and grows up to 60cm. This rainy season weed is found in tropical and subtropical regions of both hemispheres including Asia, America, India and China. The whole plant is very well-known in the pharmaceutical industry due to its remedial effects. It contains active phytochemicals, flavonoids, alkaloids, terpenoids, lignans, polyphenols, tannins, coumarins and saponins. The weed has proven its beneficial characters in healing of dysentery, influenza, vaginitis, tumors, diabetes, diuretics, jaundice, kidney stone, dyspepsia, antihepatotoxic, antihepatitis-B, and antihyperglycemic [Paithankar et al 2011]. The plant extracts are being used to make tablets. The leftover from the extracts has no significant use and can be used as effective biosorbents for heavy metals removal.

The objective of this study is to investigate the potential of Phyllanthus Niruri powder in removing Cu(II) ions from synthetic copper ion solution. The effect of pH, temperature and adsorbent dosage will be discussed. This biosorption experiment parameter ranges are pH (2-8), temperature range of 20-80^{o}C and adsorbent dosage range of 0.5-3.5g/l to identify the optimum conditions for removing Cu(II) using Phyllanthus Niruri powder. The optimal biosorption condition is applied to the real copper containing industrial sludge and the outcome is compared with the synthetic solution performance.

I. MATERIALS AND METHODS

A. Preparation of Phyllanthus Niruri Powder (PNP)

Fresh, well-grown Phyllanthus Niruri leaves were plucked from around University Malaya, Malaysia campus. The leaves were separated from the stems and cleansed with deionized water to remove any impurities. The leaves were sun-dried for 6 hours followed by oven-drying of 24 hours at 60^{o}C. This temperature was chosen so that the leaves become crispy and the functional groups stay active. PNP were obtained by grinding the leaves and sieving using 100µm mesh. Powder form provides larger surface area to enhance adsorption activity during the experiment.

B. Preparation of Cu(II) synthetic solution

Cu (II) stock solution of 100mg/l were prepared by taking 0.378 g of the Copper (II) nitrate trihydrate crystals in a 1l volumetric flask and adding deionized distilled water up to the mark. This concentration of synthetic solution was selected to match the industrial solution concentration. Standard samples of 0.2mg/l, 0.5mg/l, 1mg/l, 2mg/l and 4mg/l were made in 50ml volumetric flask with the required amount of Cu(II) solution, 25ml of 2% HNO3 and finally leveled up to the mark with deionized distilled water. The purpose of adding nitric acid is to make the standards more stable by ensuring most of the metal ions stay dissolved in the solution [Wiel, 2003]. These standard solutions were used to calibrate the intensity results obtained by the Inductively Coupled Plasma Spectrometer (Optima 7000 DV ICP-OES by Perkin Elmer).

C. Acid digestion of the industrial sludge

The sludge obtained from the industry was in a dried form. It was mandatory to carry out acid digestion for dry sludge to extract maximum possible metal ions and ensure most accurate Cu(II) content is obtained during the ICP analysis. Nitric acid digestion method was implicated on the dry sludge. 2g of dry sludge were mixed with 20ml of 55% HNO3 acid and heated at 90^{o}C for 45 minutes followed by further heating at 150^{o}C for 10 minutes. Extra 10ml of 55% HNO3 were added with a dropper at equal intervals during the heating process to sustain the liquid level. Then, the solution was cooled to room temperature and pressure. After cooling down, the solution was filtered in 100ml volumetric flask using Whatman filter paper. The filtrate was diluted by pouring deionized distilled water up to the mark [Hseu, 2004; Da Silva, Y. et al, 2014]. The filtrate was tested for metals contents.

D. Biosorption of Synthetic solutions

Adsorption experiments were carried out in batch mode, on the Cu(II) synthetic solution to evaluate the PNP in adsorbing Cu(II). The DOE (Design of Experiment) software, Design Expert was used to get a list of 20 runs in different conditions that are needed to find the optimum conditions of the biosorption process. A pH range of 2-8, temperature of 20^{o}C - 80^{o}C and adsorbent dosage of 0.5 to 3.5mg/l were chosen to carry out the analysis on 100ml solution containing about 3.5mg/l of Cu(II). The range was determined from preliminary experimental runs. The Cu(II) content was set to be 3.5mg/l to keep resemblance with the copper content in the industrial wastewater used in this study.

The pH of the 100ml samples were first altered by adding drops of HCl (0.1N or 2N) or NaOH (0.1N or 1N) to attain an acidic or alkaline condition respectively. Once the pH had been set, the experiment was carried out on a magnetic stirrer which comes with temperature control. The solution, with a magnetic stirring bar inside, was first allowed to heat up to the required temperature at 200rpm, and then 5ml of the sample were collected using a syringe. Then, PNP was added into solution. 5ml of samples were again collected after 15minutes and 30minutes. Before transferring these 5ml samples into three separate centrifuge tubes, they were filtered using Nylon syringe filters with membrane porosity of 0.25µm and membrane diameter of 13mm. These filters ensured that the samples to be tested by ICP-OES contained no solid particles since it could damage the testing equipment. It should also be noted that the syringe filters were for one-time use only. The 5ml samples that were taken into three individual centrifuge tubes were then topped up with 5ml of 2% HNO_3 acid each. Once again, this was done to dissolve all the Cu(II) ions the sample contained.

E. Biosorption of industrial sludge

50ml of the acid digested sludge solution were transferred into a 100ml volumetric flask and deionized distilled water was added up to the mark. The diluted solution was then transferred to a beaker in which 1N NaOH was added slowly to bring the pH up to 2. The beaker was then heated up to 63^{o}C with magnetic stirring for uniform heating of the system at 200rpm. 0.05g of PNP was added to the 100ml solution to initialize the adsorption experiment. 5ml samples were collected at 0min, 15min and 30min and tested in the same way as described in section D.

F. Adsorption Calculations

The amount of metal adsorbed by the PNP was evaluated using the equation below:

$$qt = \frac{(Co-Ct)V}{m} \qquad \text{[Equation 1]}$$

Where,

q_t = adsorption ability of PNP at time t (mg/g)
V = volume of solution (l)
m = mass of PNP (g)
C_o = initial metal concentration (mg/l)
C_t = metal concentration at time t (mg/l)

G. Adsorption isotherms

Adsorption isotherms are graphs that depict the correlation of adsorbate and adsorbent at a fixed temperature thereby enabling to find the maximum possible metal uptake by any biosorbent [Amirnia et al 2015]. Langmuir and Freundlich isotherms were plotted to find out which best fits the plot and thus evaluate the efficacy of PNP in removing Cu(II) ions.
Langmuir isotherms are useful when the adsorption occurs on a single layer of the adsorbent's surface. The equation for Langmuir isotherm is given below:

$$\frac{1}{qe} = \frac{1}{qm} + \frac{1}{bl.qm.Ce} \qquad \text{[Equation 2]}$$

Where,

q_e = equilibrium adsorption capacity of adsorbent (mg/g)
q_m = maximum adsorption capacity (mg/g)
b_l = Langmuir sorption equilibrium constant (L/mg)
Ce = equilibrium metal concentration (mg/l)

Freundlich isotherms are useful when the adsorption occurs on more than one layer of the adsorbent's surface. The equation for Freundlich isotherm is given below:

$$\log qe = \log KF + nF \log Ce \quad \text{[Equation 3]}$$

Where,
q_e = equilibrium adsorption capacity of adsorbent (mg/g)
n_F = dimensionless Freundlich adsorption affinity
K_F = Freundlich sorption equilibrium constant (l/mg)
Ce = equilibrium metal concentration (mg/l)

II. RESULTS AND DISCUSSION

A. RSM model development

The factors used as the independent variables for the CCD were pH (A), temperature (B) and adsorbent dosage (C) and the metal uptake (qe) was set as the response function. As suggested by the Design Expert software, 20 experiments with different conditions were run for analyzing the model through RSM. The number of runs and the experiment results are summarized below in Table 1.

Table 1: Design of Experiment and its responses

Run	Factors			Response
	pH(A)	Temperature (B)	Adsorbent Dosage (C)	Metal Uptake
1	8	20	3.5	4.90
2	5	80	2.0	0.45
3	5	50	2.0	1.71
4	5	50	0.5	2.01
5	5	50	2.0	0.32
6	2	20	3.5	-0.05
7	5	50	2.0	2.23
8	5	50	2.0	2.04
9	2	50	2.0	8.03
10	8	80	0.5	0.10
11	5	20	2.0	0.12
12	2	20	0.5	1.96
13	5	50	3.5	1.19
14	2	80	3.5	0.35
15	8	50	2.0	2.06
16	8	80	3.5	1.71
17	5	50	2.0	1.28
18	8	20	0.5	0.85
19	2	80	0.5	6.01
20	5	50	2.0	2.85

The above responses were then used in the Design Expert software to produce a model equation. Analysis of variance (ANOVA) was done to check the reliability of the model. The equation below shows the final second-order polynomial equation in terms of coded factors:

qe = 1.95 – 0.62A + 0.018B – 0.33C +2.77A2 -2.11B2 – 0.67C2 -0.99AB + 1.78AC – 0.82BC [Equation 4]

B. Statistical Analysis

Analysis of Variance (ANOVA) was utilized to assess how significant the model is. This type of statistical method works by subdividing the total variation in a data series into elemental parts linked with exact sources of discrepancy in order to inspect the significance of the model. The Fisher's F-test, one of the factors in ANOVA, was used to determine if each term of the quadratic model equation was significant. Table 2 depicted the complete ANOVA analysis for metal uptake. The terms in the model were considered significant if their Prob > F were less than 0.05. Having a Prob > F value of 0.001 indicated that the term was strongly significant, whereas, a value greater than 0.1 would imply that the terms were not significant. In this case, A2, B2 and AC were significant model terms. Furthermore, it was crucial for the lack of fit value to be insignificant to ensure the usability of the model. The 'Lack-of-Fit F-value' of 4.16 implied that there is a chance of 7.19% that a 'Lack-of-Fit F-value' this big could originate from noise. Hence, it is insignificant in this case. A negative predicted R2 value implies that the overall mean is an improved predictor of this response than the present model. Adeq precision is used to determine the signal to noise ratio, for which a value greater than 4 is preferred. Since the response had an Adeq Precision of 6.856, the model could be used to navigate the design space. The final quadratic model equation in terms of the significant terms can be rewritten as:

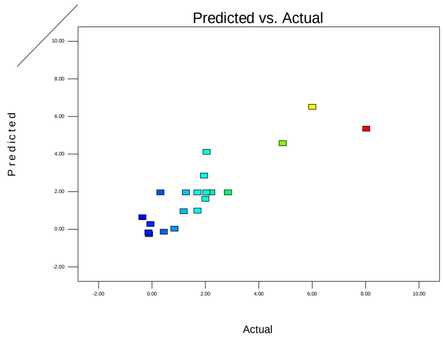
qe = 1.95 +2.77A2 -2.11B2 + 1.78AC [Equation 5]

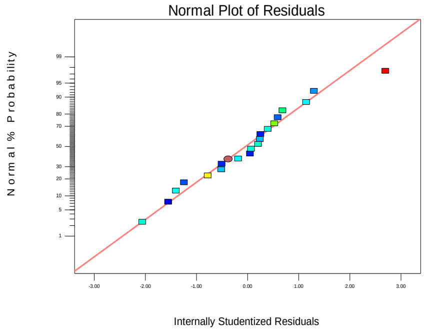
Table 2: ANOVA for metal uptake

Source	Sum of Squares	DF	Mean Square	F Value	Prob > F	
Model	68.67	9	7.63	3.91	0.0223	significant
A	3.82	1	3.82	1.96	0.1918	
B	0.00	1	0.00	0.00	0.9679	
C	1.10	1	1.10	0.56	0.4705	
A2	21.14	1	21.14	10.84	0.0081	
B2	12.22	1	12.22	6.27	0.0313	
C2	1.24	1	1.24	0.63	0.4442	
AB	7.79	1	7.79	3.99	0.0735	
AC	25.35	1	25.35	13.00	0.0048	
BC	5.44	1	5.44	2.79	0.1260	
Residual	19.50	10	1.95			
Lack of Fit	15.72	5	3.14	4.16	0.0719	not significant
Pure Error	3.78	5	0.76			

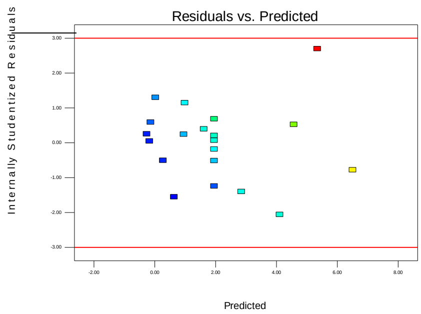
Cor Total	88.17	19			
R^2	0.7788			Predicted R^2	-0.5008
Adjusted R^2	0.5797			Adeq Precision	6.856

Residual, which is the difference between observed and predicted response, could be analyzed through various types of plot to assess the usefulness of the model. This was carried out by recognizing outliers and investigating diagnostic plots as depicted in Figure 1. Fig.1(a) shows how close the actual (experimental) values were to the predicted (calculated from the suggested model) values. 1(b) demonstrates the normal probability of residuals for metal uptake. Since most of the points lie on the straight line, it can be said that a good plot had been produced with normally dispersed residuals [Alidokht et al., 2011]. The sole error in the plot was the red point on the far right. 1(c) reflects the residual versus predicted response plots in order to check the assumption of variance. The plot is supposed to be a random scatter within an unvarying magnitude across the graph [Hassani et al., 2013]. In this case, the residuals had been changing arbitrarily from a range of +3 and -3.





(a) (b)



(c)

Figure 1: (a) Predicted vs Actual Response; (b) Normal Probability plot of Residuals; (c) Residual vs Predicted plot

C. Effect and interaction of model parameters

The perturbation plots were used to get a picture of how the three different variables (pH, temperature and adsorbent dosage) separately effects the response (metal uptake). Even though the perturbation plots cannot be used to illustrate the interaction between the three variables, it still showed an intersection point where all the factors have the same effect on the metal uptake. Sensitivity of the factor could be implied from the steepness of the curve. The steeper the lines were, more sensitive the metal uptake was to that particular variable. [Anderson & Whitecomb, 2005] From figure 2, A showed the steepest curve, followed by B and C. Therefore, from the slope of the curves, it could be deduced that, pH had positive effects on biosorption while temperature and adsorbent dosage had negative effects.

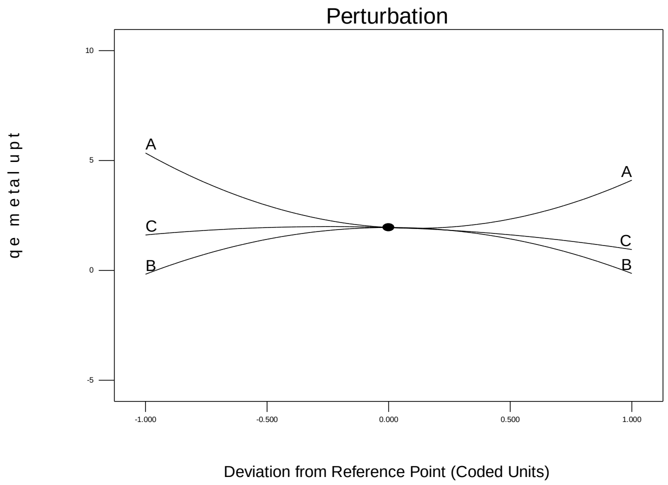
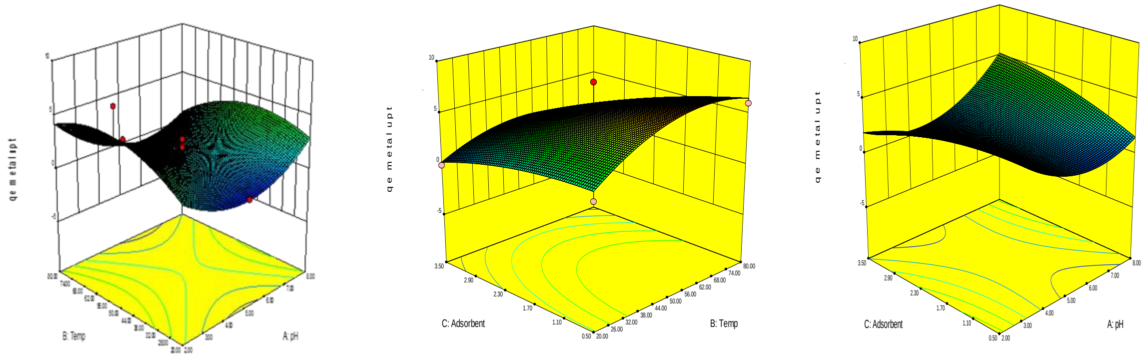


Figure 2 Perturbation plot

3D response surface graphs were also produced using the Design Expert software. These graphics represented the quadratic model equation to find out the optimum conditions for the experiment. The 3D surface plots are depicted in Figure 3. These plots were produced by altering two factors and keeping the other one constant. For example, in figure 3(a), the adsorbent dosage(C) was kept constant while the pH(A) and temperature(B) were changed. According to 3(a), the metal uptakes were highest when the pH was below 2.5 and the temperature was in the range of 44°C to 68°C. For 3(b), optimum metal uptake occurred at pH below 2.5 and adsorbent dosage less than 1.7g/l. Likewise, for 3(c), optimum temperature was above 60°C and adsorbent dosage less than 1.7g/l.



(a) (b) (c)

Figure 3: 3D Surface plots with interactions between (a) AB, (b) AC and (c) BC

D. Biosorption of dry sludge at optimum conditions

The optimal condition determined by the Design Expert is pH 2, 63°C and adsorbent dosage of 0.5 g/l. The optimum conditions were first verified in Cu(II) synthetic solution and then used for Cu(II) removal from industrial sludge solution. Table 3 reflects the optimum conditions and the metal uptake by PNP.

Table 3: Experimental results at optimum conditions

PARAMETER			Q_E (METAL UPTAKE, MG/G)			ADSORPTION (%)	
PH [A]	TEMPERATURE (°C) [B]	ADSORBENT DOSAGE (G/L) [C]	PREDICTIVE	SYNTHETIC	SLUDGE	SYNTHETIC	SLUDGE
2	63	0.5	7.18	6.46	2.67	68.34	38.87
% DIFFERENCE FROM PREDICTIVE VALUE				**10.0%**	**62.8%**		

As it could be seen from the table above, the predicted and experimental results had a huge difference, which signifies that there must be other factors that need to be considered when dealing with real wastewater. Since, the sludge contained other heavy metals, there ought to be competition among themselves to be adsorbed by the adsorbent. Therefore, further analysis should be done on the biosorbent to determine the type of metals absorbed.

A metal analysis was also carried out using ICP-AES to determine the metals content of the sludge. Table 4 shows that the sludge also contained noteworthy amount of Zn(II), Ni(II), Sn(II) and Cr(VI). Therefore, it is highly likely that these metals were also adsorbed onto the biosorbent.

Table 4: Sludge Metal Analysis

Metal	Concentration (mg/kg)
Cr(VI)	65
Cu(II)	362
Mg	1.67
Ni(II)	96
Sn(II)	92
Zn(II)	1230
Fe(II)	3.37
Cd(II)	1.4
As(II)	8

E. Effect of Contact Time

Figure 4 illustrated the presence of Cu(II) before and after the experiments using industrial sludge solution. At 30 mins the concentration did not decrease significantly from the 15 mins plot. The adsorption was 31.42% and 31.74% at 15 and 30 mins, respectively. There was a very small increment in the Cu(II) absorption. This could be due to the precipitation of the Cu(II) ions from the sample solution (Gupta et al., 2006).

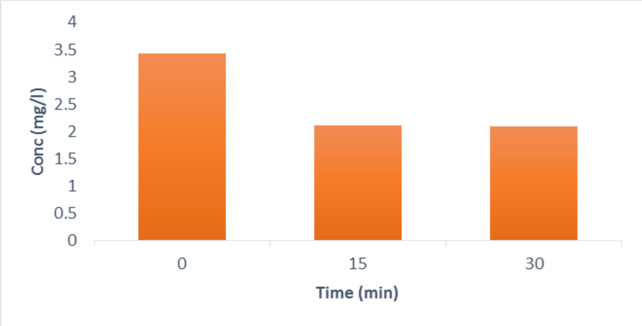
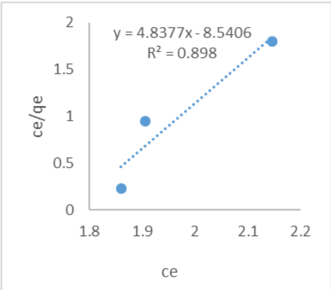


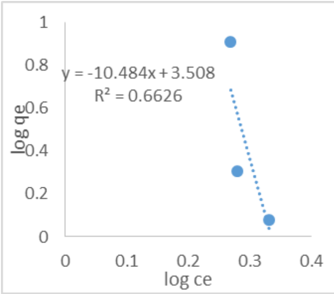
Figure 4: Presence of Cu (II) before and after experiment using industrial sludge solution

F. Adsorption Isotherms

From Figure 5 (a) and (b), it can be observed that the experimental results fit the Langmuir isotherm more than Freundlich. Hence, it could be deduced that, during the biosorption of Cu(II) using PNP, single layer adsorption takes place and that the surface of PNP is energetically homogeneous. [Mitrogiannis et al 2015]



(a)



(b)

Figure 5: Cu(II) removal in synthetic solution data fitting (a) Langmuir Isotherm and (b) Freundlich Isotherm

IV. CONCLUSION

The aim of the study was to determine the optimum conditions for removal of Cu(II) from industrial sludge using Phyllanthus Niruri powder (PNP). This optimization process was carried out by producing a model using the Response Surface Methodology (RSM) for Central Composite Diagram (CCD). The optimized conditions were determined by the software is pH 2, temperature 63^{o}C and adsorbent dosage 0.5g/l to attain metal uptake of 7.18 mg/g in the industrial sludge solution. When the experiments were carried at suggested conditions, the metal uptake only went up to 2.67mg/g. The optimum contact time were found to be 15 minutes for the process. The results fitted Langmuir isotherm model, hence single layer adsorption took place. The deviation in result could be due to competition amongst the other metals present in the industrial sludge solution that decreased Cu(II) biosorption. Further analysis should be done on the biosorbent to determine the metals adsorbed. Phyllanthus Niruri powder can be used as biosorbents to remove Cu(II) especially when present in trace amounts.

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