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Biosorption of Pb and Cu from aqueous solution using banana peel powder

Rosliza Mohd Salim[a,*], Ahmed Jalal Khan Chowdhury[c], Ruzaina Rayathulhan[b], Kamaruzzaman Yunus[b], Md. Zaidul Islam Sarkar[d]

[a]*Department of Chemistry, Kulliyyah of Science, International Islamic University of Malaysia (IIUM), Kuantan, Pahang, Malaysia, Tel. +60 13 9023838; Fax: +60 9 5716781; email: ros_liza@iium.edu.my*
[b]*Department of Biotechnology, Kulliyyah of Science, International Islamic University of Malaysia (IIUM), Kuantan, Pahang, Malaysia*
[c]*Department of Marine Science, Kulliyyah of Science, International Islamic University of Malaysia (IIUM), Kuantan, Pahang, Malaysia*
[d]*Kulliyyah of Pharmacy, International Islamic University Malaysia (IIUM), Kuantan, Pahang, Malaysia*

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ABSTRACT

Banana peel is considered as a dominant agricultural waste which causes more disposal problem everywhere. This disposal problem could be handled by changing it into an advantage whereby utilizing banana peel to be used as an adsorbent to remove heavy metals from water. Based on the above perspectives, an adsorption capability of banana peel was evaluated in removing toxic heavy metals Pb and Cu from aqueous solution. The banana peel was chemically modified (BPPT) by treating it with 0.1 M sodium hydroxide to examine the improvement in the adsorption capacity compared to the untreated form (BPPU). The parameters such as adsorbent mass, initial pH, initial concentration and contact time were tested accordingly. The adsorbent mass with the highest adsorption capacity for both Pb and Cu were 0.9 g. As for the effect of pH, adsorption of Pb and Cu was favourable at pH 7 and pH 9, respectively. The effects of concentration and contact time on peel extract, the maximum adsorption for Pb has shown at 4 mg/L at 120 min for BPPU and was 6 mg/L at 150 min for BPPT. As for Cu, both untreated and treated adsorbent achieved the highest adsorption rate at concentration of 2 mg/L with contact time at 120 min. Atomic absorption spectrophotometer (AAS) was used to measure the concentration of toxic metals. Scanning electron microscope was used to observe the differences in morphology of the peel between BPPT and BPPU before and after adsorption. Fourier transform infrared spectroscopy was used to determine the functional groups present in it which was responsible for the adsorption process. Equilibrium data of both metals were well fitted with the Langmuir and Freundlich isotherm models with ($R^2 \approx 0.99$). R_L values for both Pb and Cu also ranged in between 0 and 1 indicating a favourable adsorption process based on the Langmuir isotherm. Overall BPPT proved to have higher adsorption capacity than BPPU. BPPT gives the highest maximum coverage capacity (Q_o) for Pb adsorption with 89.286 and 5.720 mg/g

*Corresponding author.

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for Cu in a favourable condition. Therefore, it could be concluded that banana peel could be recognized as potential and environmentally friendly agro-based waste material which could be utilized as low-cost adsorbents to remove toxic metal from industrial wastewater.

Keywords: Banana Peel; Heavy Metals; Adsorption; Kinetics; Isotherm

1. Introduction

Heavy metal toxicity is frequently the result of long-term low-level exposure to pollutants common in our environment. Generally, heavy metals are components of effluents in many different industries such as mining, plating and others. Nowadays, the presence of heavy metals, lead and copper, in the environment is a major concern due to its toxicity potential which might harm living organisms. They can accumulate in bones, brain, liver, kidney and muscles and may cause many serious disorders and diseases like anaemia, kidney, nervous disorders and even death [1–3]. They also create pollution problems to the environment [4]. When these contaminants are found in effluent, they may increase fertility of the sediment and water column and consequently lead to euthrophication, can progressively lead to oxygen deficiency, algal bloom and death of aquatic life in open waters [5]. Even if the concentration of heavy metal is low, it can accumulate in a biological system and cause long-term effect [6]. Conventional methods of removing heavy metals are chemical precipitation, lime coagulation, ion exchange, solvent extraction and reverse osmosis but they are expensive and non-environmentally friendly [7]. These disadvantages have led researchers to develop a new technology which involves using biological materials for biosorption of toxic metals from water [8]. Biosorption is a modern technology for heavy metal removal from industrial effluents; it is used as an alternative to conventional methods such as chemical precipitation, ion exchange and chelation by synthetic resins, membrane filtration and adsorption onto activated carbon. Cost-efficient technologies are needed to remove toxic heavy metals from industrial wastewater and to prevent their discharge into environment [9]. Adsorption is sometimes used to remove certain species that cannot be effectively removed from wastewater stream by other conventional technologies [10,11].

Agricultural by-products are mainly made up of lignin and cellulose, and are rich in different kinds of functional groups such as alcohols, aldehydes, ketones and carboxylic. Using agricultural by-product is metal selective, regenerative and does not produce sludge. Thus, the same agricultural waste can be reused as biosorbents for a number of cycles [12].

Instead of using activated carbon, they are turning to a more economical method for eliminating heavy metals such as agro-based inexpensive adsorbents. Modified materials displayed better adsorption capacity and capability of some was comparable to that of commercial activated carbons and synthetic resins [13]. Agricultural wastes were observed as low-cost adsorbents and can be viable alternatives to activated carbon for the treatment of metal-contaminated wastewater. The potential agricultural and agro-processing industry wastes which were treated as metal adsorbents from wastewater are sugarcane bagasse, orange peel, rice husk, coconut shell oil palm shell, sawdust, rambhutan seed, *Chrysophyllum albidum* seeds and *Phanerochaete chrysosporium* [14–17].

Banana is a common fruit, which is consumed in the world and is easily available in large quantities. The peel which represents about 40% of the total weight of fresh banana is discarded as waste in municipal landfills. Moreover, in Malaysia's industrial processing, the amount of green and ripe banana, especially the species used for *Pisang goreng* (fried banana), i.e. *Musa paradisiaca* variety *Nangka* and *M. paradisiaca* variety *Tanduk* are responsible for enormous waste which is not conducive for the environment if they are not managed or recycled appropriately [18].

Banana peel is produced everywhere. The disposal problem could be handled by changing it into an advantage whereby utilizing banana peel as an adsorbent to remove heavy metals from water. In a recent study, banana peel extracts (*M. paradisiaca* L.) have shown their potential as antimicrobial alternatives and they may be effective as a natural source of antimicrobial agent in pharmaceutical industries [19].

2. Materials and methods

2.1. Preparation of adsorbent

Banana peels (*M. paradisiaca* L.) were collected from local market which was cultivated at Raub, Pahang Agricultural firm. The banana peel was washed thoroughly with tap water to remove any impurities or dirt. The peel was then left to dry under the sunlight for a few days to remove free water. Then for both batches, the peels were weighed and divided equally into two portions to make the untreated and treated samples of banana peels, BPPU and BPPT.

The chemical retting process was conducted using distilled water and NaOH. One portion was soaked in distilled water for an hour to make BPPU. The other was soaked in sodium hydroxide (NaOH solution) for 1 h. Then the sample was dried further in the oven with 105˚C for 24 h. Finally, the dried banana peel samples were grinded into powder and sieved between 200 and 400 μm sieve sizes.

2.2. Batch experiments: adsorption studies

2.2.1. Effect of adsorbent mass

The effect of different mass of banana peel powder (BPPU and BPPT) on toxic metal adsorption was investigated using masses ranged (0.1, 0.3, 0.5, 0.7 and 0.9 g) of the adsorbent powder in 100 mL of each toxic metal (Pb and Cu) containing fixed concentration of 10 mg/L and under constant stirring speed of 500 rpm. The two different types of BPPU and BPPT were experimented separately. The experiment was run for an hour and the solution was filtered using filter paper and filter funnel. The filtrate was analysed via atomic absorption spectrometer (AAS). The residue was observed under scanning electron microscope (SEM).

2.2.2. Effect of initial pH

Effect of initial pH on toxic metal adsorption capacity was studied using five different pH values (pH 1, 3, 5, 7 and 9). Solution of hydrochloric acid HCl and NaOH was used to manipulate the initial acid and alkali level of the adsorption environment to desired pH level. A mass of 0.5 g of banana peel powder was placed in 100 mL of each toxic metal solution, Pb and Cu, with fixed concentration of 10 mg/L under constant stirring speed of 500 rpm using magnetic stirring plate. Each experiment was run for an hour and the solution was filtered using filter paper and filter funnel. The filtrate was then analysed via AAS. The residue was observed under SEM.

2.2.3. Effect initial concentration and contact time

Effect of different metal concentrations on toxic metal adsorption was determined by varying the concentration metal solution in the range (2, 4, 6, 8 and 10 mg/L) for Pb and Cu. A mass of 0.5 g of banana peel powder was added into 100 mL of each toxic metal, Pb and Cu. Both BPPU and BPPT were tested in a separate experiment. The different time intervals to test the effect of contact time were from 0 to 150 min at 15-min interval for the first hour and 30-min interval for the next 1½ h. A constant stirring speed of 500 rpm was applied. Every 15 min for the first hour, about 10 mL of the toxic metal solution was filtered directly from the beaker into a falcon tube using a dropper. The concentration of the filtered one was then analysed through AAS and the residue was examined using SEM. The adsorption density of each sample was calculated. Adsorption density is represented by q_t and the unit of mg/g (mg of toxic metal solution/g of BPP) would be calculated using this formula:

$$q_t = \frac{(C_o - C_t)V}{M} \tag{1}$$

where C_o is the initial concentration of toxic metal solution (mg/L), C_t is the concentration of toxic metal solution at a given time t (mg/L), V is the volume of solution (L) and M is the mass of adsorbent used (g).

2.3. Adsorbent characterization

2.3.1. Scanning electron microscope

SEM was used to observe morphology of the banana peel powder. BPP samples must first be prepared before they can be observed using SEM. A carbon tape was placed on the cylinder stubs before the samples were sprinkled on it. After the samples had mounted on the tape, it was blown to allow only a single layer on a sample on the tape to prevent overlaps. Then, the stubs with BPP were placed into the coater and left to run for 30 min to coat it with gold.

2.3.2. Attenuated total reflectance (ATR)–Fourier transform infrared spectroscopy (FTIR)

Generally to analyse solid sample using ATR–FTIR, the single-reflection attenuated total reflectance (ATR) accessories; diamond was preferred for most applications because of its robustness and durability. Once the crystal area was cleaned and the background collected, just an adequate amount of the sample was placed onto the small crystal area to cover the area. The height of the sample was not to be more than a few millimetres. After the sample had been placed on the crystal area, the pressure arm was positioned over the sample area. Using the Spectrum 100 Series

Universal ATR accessory, the pressure arm was locked into a precise position above the diamond crystal. Then, force was applied onto the sample, pushing it onto the diamond surface. The spectrum was first viewed in "Preview Mode" to fine tune the exerted force. Pressure was applied until the strongest bands with an intensity extending beyond 70% were formed, namely from a baseline at 100% down to 70%. Once the spectrum was obtained, data were collected in the normal manner. Finally, the crystal area was cleaned using a solvent (water, methanol, isopropanol)-soaked tissue. "Preview Mode" was used to check that the crystal area was cleaned before being used again [20].

3. Results and discussion

3.1. Adsorbent preparation

NaOH chemically modifies the structure of the peel and increases the proportion of active surface present on the adsorbent [21]. Therefore, some of the banana peel was treated with 0.1 M NaOH to investigate any improvement in the ability of the banana peel in adsorbing toxic metal ions. Then, it was transferred into the oven and let to dry completely for 24 h at 105˚C. After that, when the peel became crisp, it was crushed and ground into powder form. It was observed that throughout the process of preparing BPP, the banana peel have lost its moisture content. The total water loss was 13.2% for BPPU and 19.21% for BPPT. This was during the peel was dried thoroughly in the oven before grinding. The total water loss was not high as banana peel originally does not have high water content.

3.1.1. Effect of adsorbent mass

The effect of different adsorbent masses on toxic metal adsorption, the mass of banana peel powder was varied (0.1, 0.3, 0.5, 0.7 and 0.9 g) while the volume, concentration and temperature of toxic metal solution were kept constant at 100 ml, 10 mg/L and 30 ± 2˚C, respectively. The experiment was carried out for 1 h with the agitation speed of 500 rpm and at the end the solution was filtered with type-1 filter paper. pH of the toxic metal solution was kept at its natural level. This was done to ensure consistency between each of the toxic metal solutions. Generally, all toxic metal has around the same pH level which is acidic. Pb has shown an initial pH of 2.16, while Cu showed an initial pH of 2.27. Generally, a decrease in adsorption density was observed with the increase of adsorbent mass for both Pb and Cu adsorption. The adsorption density for Pb reduced from 3.883 to 0.903 mg/g when the mass of BPPU used increased from 0.1 to 0.9 g. As for Cu, the adsorption density had dropped from 2.341 mg/g at 0.1 g to 0.739 mg/g at 0.9 g of BPPU. BPPU has higher selectivity towards Pb ions compared to Cu. Fig. 1 shows the result for percentage of toxic metal ions removal with the increase of adsorbent mass for Pb and Cu using BPPU. The graph shows a positive trend whereby the higher the mass of BPPU present in the solution, the higher the toxic metal uptake by the BPPU particles. The highest percentage of removal was at 0.9 g of BPPU with 80% for Pb and 66% for Cu. The equilibrium was achieved when all the toxic metal ions have bounded to the sorbent which was the banana peel powder. Equilibrium was established between the molecules bounded to the sorbent and the unabsorbed molecules in the solution. The decrease in adsorption density with increased adsorbent of mass was due to the saturation of adsorbent by adsorbate. Generally, the available amount of adsorption sites is limited to the mass of adsorbent as with higher amount of adsorbent mass, the higher quantity of adsorption sites. The value of adsorption density was higher using BPPT compared to BPPU of the same mass. For both Pb and Cu, the adsorption density decreases with the increase in adsorbent mass from 0.1 to 0.9 g with 7.060 to 0.991 mg/g for Pb and 3.702 to 0.950 mg/g for Cu. This shows the improved ability of BPPT to adsorb higher amount of toxic metal ions per gram of adsorbent mass. From Fig. 2, it can be observed that with the increased amount of the adsorbent mass, the percentage of toxic metal ions removal also increases. Lead showed better removal capacity compared to Cu with the highest removal percentage for Pb to be 88%

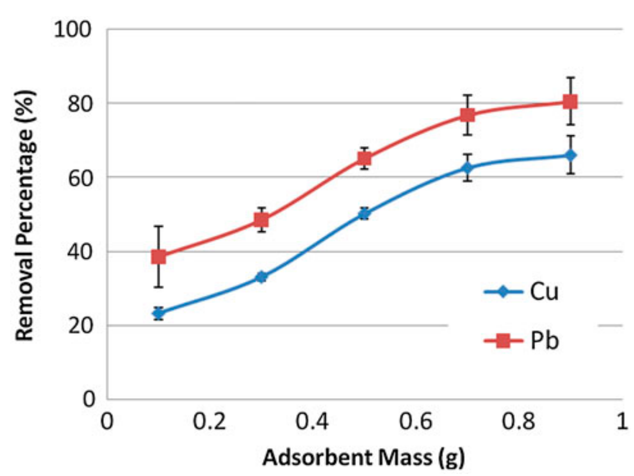

Fig. 1. Effect of adsorbent mass on percentage of toxic metal ions removal using BPPU.

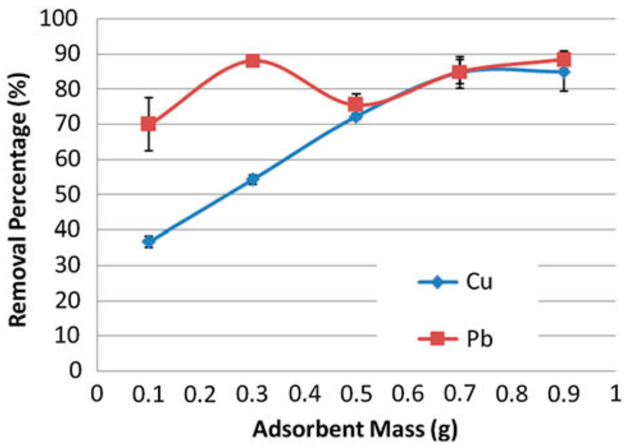

Fig. 2. Effect of adsorbent mass on percentage of toxic metal ions removal using BPPT.

and Cu 85% at 0.9 g. However, for Pb, there was no steady increase in the removal percentage with the increase of the adsorbent mass as at 0.3 g of adsorbent, the removal percentage shoot up to 88%, higher than the removal rate at 0.5 and 0.7 g. It can be seen that the trend for Cu removal shows that it is approaching equilibrium, while for Pb, it is still increasing (Fig. 2). In fact, the adsorption efficiency is dependent on the amount of adsorbent added [22]. With the increasing amount of adsorbent, there is an increase in available binding sites in the adsorbent for toxic metals to bind on. The sudden increase of removal percentage at 0.3 g of the adsorbent mass could be due to the size of particles. Other studies showed that a smaller particle size has greater metal removal percentage due to the greater accessibility to pores and greater surface area for adsorption [23]. Since the adsorbent used for this experiment ranges from 200 to 400 μm in size, it could be that most of the adsorbent weight at 0.3 g contained the BPP of a smaller particle size. From the result of BPPT, it could be concluded that treating the adsorbent with NaOH seems to increase the toxic metal adsorption capacity of the banana peel powder compared to BPPU.

3.1.2. Effect of initial pH

The initial pH of 100 mL of toxic metal solution at 10 mg/L was adjusted using 0.1 M NaOH and 10% HCl. The experiment was run for 1 h using 0.5 g of BPPU or BPPT. At the end, the solutions were filtered and the filtrate was analysed using AAS to find out the concentration of the toxic metal after adsorption. It could also be observed that the colour of the toxic metal solution, the filtrate changes after adsorption depends on the pH value. From pH 1 to 9, the colour shade was from light yellow to dark brown. From Table 1, the highest adsorption density achieved using BPPU differs for both metals, Pb and Cu. Generally, for both metals at pH 1, the adsorption was very low but it was shot up to 1.648 mg/g for Pb and 1.348 mg/g for Cu at pH 3. As for Pb, the highest adsorption density was at pH 7 with 1.752 mg/g and for Cu at pH 9 with 1.692 mg/g. However, it could be observed that the results from pH 5 to 9 are approximately the same. It seems that the pH at these values do not have much effect on the adsorption rate. From Fig. 3, it can be seen that pH of the toxic metal solutions, Pb and Cu, increases as toxic metal removal percentage increases. The highest Pb removal percentage using BPPU was 92% at pH 7 and for Cu, 85% at pH 9. However, from pH 5 to 9, there was not much difference in the toxic metal removal percentage as they are almost consistent. The result obtained differs from the previous study which revealed that the adsorption density of Cu is very much dependent on

Table 1
Effect of initial pH on adsorption density using BPPU

Toxic metal	Initial pH	Adsorption density, q_e (mg/g) ± SD (%)
Pb	1.01	0.185 ± 2.6
	3.02	1.648 ± 6.2
	5.07	1.720 ± 2.2
	7.02	1.752 ± 0.3
	9.05	1.742 ± 0.05
Cu	1.04	0.139 ± 0.6
	3.04	1.348 ± 4.9
	5.06	1.500 ± 2.5
	7.04	1.633 ± 0.3
	9.06	1.692 ± 1.9

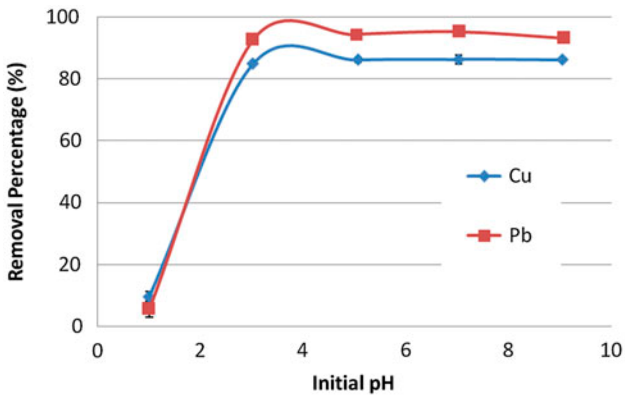

Fig. 3. Effect of initial pH on percentage of toxic metal ions removal using BPPT.

the pH condition [24]. It increased with pH but achieved maximum value at pH 6 and higher than that the adsorption declined. For the study, the condition which differed was that the experiment was run for 24 h at 120 rpm. Meanwhile for this experiment, it was run for only 1 h with 500 rpm. Such result obtained could possibly be because the contact time was not long enough to give a similar result as was observed in the previous studies. A study on adsorption of cadmium on orange peel reported that low pH only produced minimal adsorption due to the higher concentration and mobility of the H^+, which are preferentially adsorbed instead of the toxic metal ions [25]. At higher pH, H^+ is present in a lower number and thus the greater number of ligand with negative charged results in greater adsorption.

Fig. 3 shows the result on the effect of initial pH on the adsorption density for BPPT in removing Pb and Cu from aqueous solution. The optimum density for both metals using BPPT was at pH 7, with 1.811 mg/g for Pb and 1.712 mg/g for Cu, which was higher than the result using BPPU. It could be observed that the toxic metal removal percentage was the highest at pH 7 for both Pb and Cu with 95% for Pb and 86% for Cu. Although pH 7 has shown the highest value, but pH 5–9 has shown the removal percentage almost consistent despite having different pH conditions. Very low adsorption capability was observed at pH 1 which was acidic condition with the removal percentage being 6% for Pb and 10% for Cu. Similarly, a study was conducted on adsorption using orange peel, sawdust and bagasse to remove Cu from aqueous solution. There is an optimum pH for adsorption. Beyond optimum condition, the adsorption rate decreases [26]. Theoretically, at lower pH, H^+ competes with metal cations to obtain available adsorption sites. Simultaneously, at a very high pH value (basic condition), metal cations will react with hydroxide ions thus precipitate as metal hydroxide. The result showed that the retention of Cu by orange peel increases with the increasing pH between 2–6.2 and decreases slightly at higher pH. The increase in the adsorption efficiency is due to the interaction of ion exchange mechanism of Cu^{2+}, $Cu(OH)^+$ and $Cu(OH)_2$ with the functional groups present in the peel [27]. Carboxylic group present in the peel also helps in the interaction with copper ions. Decreasing of adsorption conversely is due to the formation of soluble hydroxyl complexes. BPPT has a higher adsorption density compared to BPPU due to the treatment of the banana peel with NaOH. The treatment chemically modifies the structure thus improves the toxic metal adsorption capacity. Overall, pH of metal solution does have an effect on toxic metal adsorption as it affects the surface properties of adsorbents, the ionic state of functional groups and species of metals.

3.1.3. Effect of initial concentration and contact time

The toxic metal removal percentage for toxic metals, Pb and Cu ions, using BPPU increases with the increase of contact time up to a certain minute and then decreases (Figs. 4 and 5). As for the removal of Pb ions using BPPU at concentration 4 mg/L, the adsorption density increases from 0.681 to 0.769 mg/g at 0 to 120 min and then decreases to 0.752 mg/g at 150 min. Referring to Fig. 4, the suitable condition for the removal of Pb is at 120 min with concentration 4 mg/L with the percentage of 86%. When using BPPU in removing Pb ions, concentration of both 2 and 4 mg/L has an overall high removal percentage with the average being above 80% throughout the whole 2.5 h of contact time. For the removal of Cu ions by BPPU as

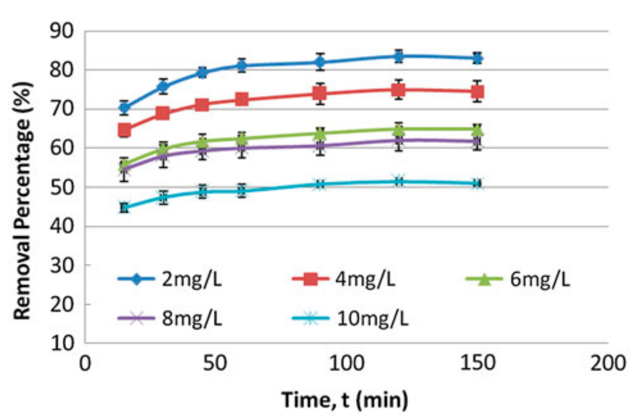

Fig. 4. Effect of initial concentration and contact time on percentage of Cu ions removal using BPPU.

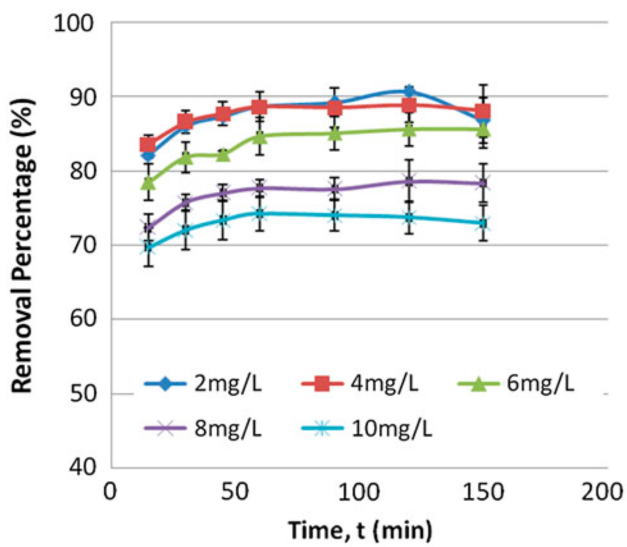

Fig. 5. Effect of initial concentration and contact time on percentage of Cu ions removal using BPPT.

seen in Fig. 5, the highest removal percentage was observed to be 84% at 120 min with concentration of 2 mg/L. However, the value decreases a little to 83% at 150 min. The adsorption density also increases with the increase in contact time from 15 to 120 min with 0.264 to 0.314 mg/g and reduced to 0.312 mg/g at 150 min.

From Figs. 4 and 5, it can also be observed that the activity of removing toxic metal for all concentrations was exponential for the first hour and then it progressed towards achieving equilibrium for the next 1.5 h. This could be explained as, with the increase of contact time, the vacant adsorption sites on the adsorbent surface decrease. The remaining vacant sites are also difficult to be occupied by toxic metal ions due to the formation of repulsive forces between the toxic metal on the solid surface and liquid phase. Apart from that, the higher the concentration of toxic metal solution, the more Pb and Cu ions are present in the solution; thus, the fiercer the competition for an empty adsorption site on the BPPU surface among the metal ions. During this study, the higher toxic metal concentration has shown lower removal percentage as the amount of Pb and Cu ions are much more than the available adsorption sites (Figs. 6 and 7). After all the adsorption sites had been occupied by the toxic metal ions, the adsorption rate decreased where no more adsorption would occur even if the contact time was prolonged.

The result obtained showed the same pattern as BPPU. The adsorption density increases as the initial concentration and contact time increase. Fig. 6 shows the percentage for removal of Pb ions using BPPT. This result also gives a similar trend for using BPPU but the maximum removal percentage was achieved at 150 min using concentration 6 mg/L with 86%. The highest adsorption density at that time was 1.068 mg/g. At this concentration, it shows an increase in the adsorption of Pb ions by BPPT for 2.5 h with no signs of achieving equilibrium. Fig. 7 shows the result for the removal of Cu ions from aqueous solution using BPPT. The maximum removal percentage was achieved at 120 min using concentration 2 mg/L with 90%. The adsorption density was recorded to be 0.382 mg/g. Generally, BPPT has better adsorption capacity compared to BPPU. For adsorption of both

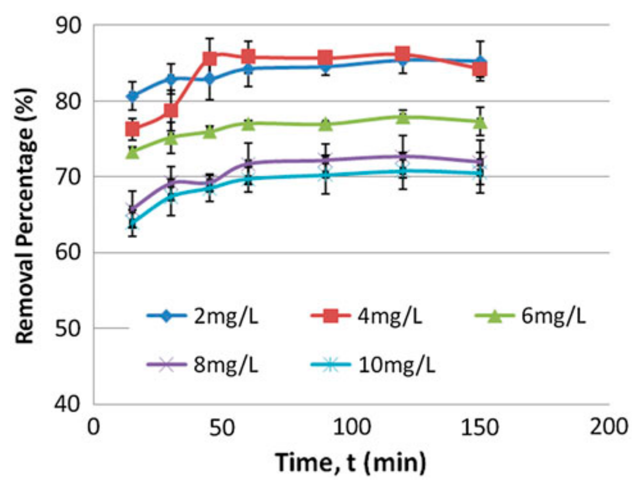

Fig. 6. Effect of initial concentration and contact time on percentage of Pb ions removal using BPPU.

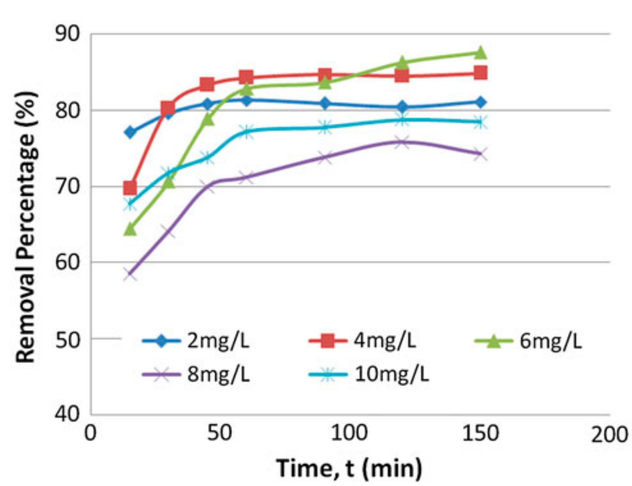

Fig. 7. Effect of initial concentration and contact time on percentage of Pb ions removal using BPPT.

Pb and Cu ions using BPPT, the adsorption rate initially increased rapidly and then started to slow down becoming almost constant after about 1 h of contact time except for Pb ions of 6 mg/L. This is similar to the result of BPPU. As the contact time increases, it leads to lack of active sites available on the adsorbent thus increase in the number of ions competing for the binding sites [28]. In fact, for the adsorption of Cu after 120 min, the adsorption density decreases which might be due to the saturation of adsorbents by copper. The result from this experiment also agrees with the findings on kinetics and thermodynamics of Cu(II) adsorption on oil shale waste [29]. The study stated that the increase in the initial toxic metal concentration could increase the amount of metal uptake per unit weight of the adsorbent (mg/g). The result of this study shows that the smooth and continuous uptake of metal by adsorbent leading to saturation suggested the possible monolayer coverage of Cu ions on the surface of the adsorbent. The only difference between using BPPU and BPPT is the value of the adsorption density and the percentage removal capacity. The removal percentage using BPPT was higher than that of the experiment using BPPU of the same concentration.

4. Adsorption isotherm

The two models differ in terms of principle. The Langmuir isotherm assumes that maximum adsorption corresponds to a saturated monolayer of adsorbate molecules on the adsorbent surface with the energy of adsorption being constant and no transmigration of adsorbate in the plane of the surface [23]. The linear form of the Langmuir equation is as follows:

$$\frac{1}{q_e} = \frac{1}{Q_o} + \frac{1}{bQ_oC_e} \qquad (2)$$

where q_e is the amount of adsorbent adsorbed (mg/g), C_e is the equilibrium concentration of adsorbate (mg/L), Q_o is the Langmuir constant related to maximum adsorption capacity (mg/g) and b is the Langmuir constant related to energy of adsorption (mg/L) (Table 2).

Freundlich isotherm is usually used for mathematical description of adsorption in an aqueous solution and helps to describe heterogeneous surface energies. The equation is expressed as follows:

$$\ln q_e = \ln K_F + (1/n) \ln C_e \qquad (3)$$

where K_F (mg/g) and n are the Freundlich constants which indicates the adsorption capacity and adsorption intensity, respectively. The constant values in Langmuir, b and Q_o, and the Freundlich, n and K_F, can be calculated from the slope and the y-intercept of the plot, respectively. Another magnitude that can be calculated from the Langmuir isotherm is the separation factor represented by R_L which is calculated using the following equation:

$$R_L = 1/1(1 + Q_oC_o) \qquad (4)$$

where C_o is the initial toxic metal ion concentration (mg/L) and Q_o is the Langmuir constant attained from the plotted graph. The values of R_L indicate the nature of isotherms [30].

For Langmuir isotherm, a plot of $1/q_e$ vs. $1/C_e$ for Pb and Cu adsorption onto BPPU and BPPT is presented, the Langmuir constant was calculated from the equation of the graph and is shown in Table 3. R^2 values for BPPU and BPPT for both Pb and Cu were determined to be approaching 1 with all values being around 0.99. This indicated that the adsorption data of Pb and Cu onto BPP were best fitted to the Langmuir isotherm model. The separation factor, R_L, from Table 4 indicates that Langmuir isotherm is favourable. From Table 3, it is observed that the maximum monolayer coverage capacity, Q_o, was found to be 89.286 mg/g for adsorption of Pb using BPPT. As for Pb BPPU, Cu BPPU and Cu BPPT, the adsorption capacites were 4.643, 2.433 and 5.720 mg/g, respectively. Overall, BPPT has higher adsorption capacity than BPPU.

Table 2
Equation of trend line configured from isotherm graph

Equation of slope	Langmuir isotherm	Freundlich isotherm
Pb BPPU	$y = 4.5996x + 0.2154$	$y = 0.8148x - 1.4635$
Pb BPPT	$y = 5.9683x + 0.0112$	$y = 0.9582x - 1.7345$
Cu BPPU	$y = 5.5025x + 0.411$	$y = 0.7222x - 1.6082$
Cu BPPT	$y = 4.8605x + 0.1748$	$y = 0.8411x - 1.5131$

Table 3
Values of isotherm constants calculated from equation of graph

	Langmuir isotherm			Freundlich isotherm		
	R^2	b (L/mg)	Q_o (mg/g)	R^2	K_F (mg/g) (mg/L)$^{1/n}$	n
Pb BPPU	0.9990	0.0468	4.643	0.9963	0.231	1.227
Pb BPPT	0.9964	0.00188	89.286	0.9905	0.176	1.044
Cu BPPU	0.9950	0.0747	2.433	0.9757	0.200	1.385
Cu BPPT	0.9994	0.0360	5.720	0.9956	0.220	1.189

Table 4
Values of R_L calculated using Langmuir isotherm

Pb			Cu		
C_o (mg/g)	R_L Pb BPPU	R_L Pb BPPT	C_o (mg/g)	R_L Cu BPPU	R_L Cu BPPT
2	0.914	0.996	2	0.870	0.933
4	0.842	0.993	4	0.770	0.874
6	0.781	0.989	6	0.691	0.822
8	0.727	0.985	8	0.626	0.776
10	0.681	0.982	10	0.572	0.735

As for the Freundlich isotherm, the slope ranging between 0 and 1 is a measurement of the adsorption intensity or surface heterogeneity. As the value gets closer to zero, it becomes more heterogeneous [31]. It was observed that the smaller is the value of $1/n$, the greater is the expected heterogeneity [32]. The higher $1/n$ value as in the result of Pb BPPT indicates that Pb is more favourable than Cu. When $1/n = 1$, it resides to a linear adsorption. It is considered a favourable sorption process if the n value lies between 1 and 10. The graph shows a straight line with the n value from the slope having values 1.044 to 1.385 which indicate a favourable adsorption. The data for Freundlich constants were calculated and are listed in Table 3.

From Table 3, the correlation coefficient, R^2, obtained for the Langmuir overall has a higher value than the Freundlich isotherm. Generally, both models fit the experimental data; there is a possibility of monolayer and heterolayer toxic metal ions formation on the BPP surface. The presence of active functional groups with non-uniform distribution and different intensity may lead to the differences in the energy level of the active sites on the banana peel thus affecting the adsorption capacity [33]. Active sites with higher energy level are said to form heterolayer coverage with chemical bonding, while those with lower energy level form a monolayer coverage due to electrostatic forces. Comparing both metals, BPP has shown a higher removal efficiency for Pb compared to Cu.

5. Adsorbent characterization

Fig. 8 shows the SEM images of BPPU and BPPT under different conditions which show that the morphology of blank samples for both BPPU and BPPT have not undergone any experimental runs. The morphology of the sample with the highest adsorption for the adsorbent mass was 0.9 g for both Pb and Cu. Meanwhile, the morphology of BPPU and BPPT tested at different pH with Pb at pH 7 and Cu at pH 9, did not show many changes between the natural BPP and each of the BPP that have been experimented with respective toxic metals. Generally, BPP before adsorption has a rough, irregular and uneven external surface. In BPPU with magnification of 5,000×, there could be a presence of spring-like structure known to be cellulose. For BPPT, it could be seen that there was a solid structure, almost crystal-like structures on the surface might indicate the presence of sodium compound from the treatment with NaOH. Perhaps the morphology of banana peel could be heterogeneous rough surface with crater-like pores. The particles having irregular shape and the surface exhibiting micro-rough texture are said to promote the adherence of toxic metal ions.

5.1. *Attenuated total reflectance–Fourier transform infrared spectroscopy (ATR–FTIR)*

Based on Fig. 9, the FTIR spectrum of BPPU and BPPT displays five adsorption peaks through infrared

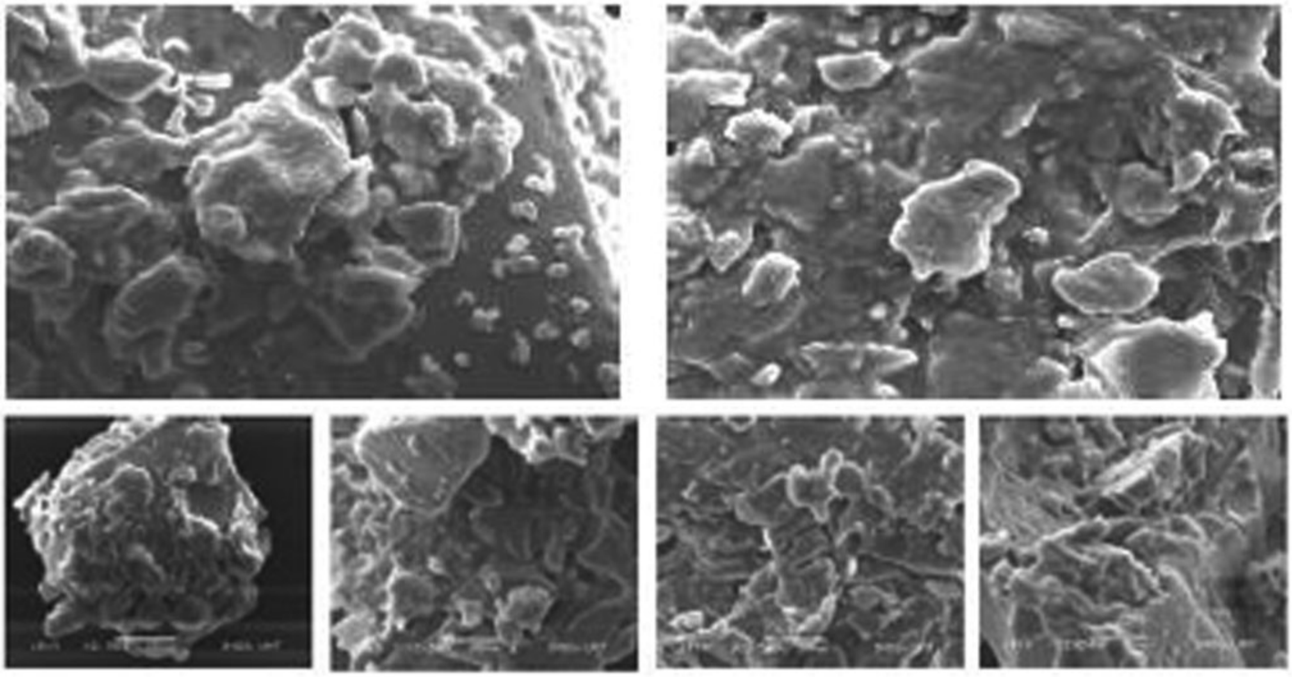

Fig. 8. SEM Images of banana peel.

spectroscopy [34]. FTIR analysis for both untreated and treated samples indicated the bands that have slightly different values but are around the same range. The bands for BPPU are at 3,321.09, 2,919.19, 1,594.89, 1,375.23 and 1,032.10 cm^{-1}, while for BPPT they are at 3,328.28, 2,948.17, 1,602.55, 1,375.62 and 1,032.10 cm^{-1}. Overall, BPPT seems to have slightly lower peak intensity compared to BPPU. The wide band at 3,321.09 and 3,328.28 cm^{-1} is attributed to the H-bonded, O–H and N–H stretching vibrations; the peak at 2,919.19, 2,948.17, 1,375.23 and 1,375.64 cm^{-1} are ascribed to the C–H stretching/bending vibrations. C=C stretching vibrations of aromatic compound can be seen at the region of 1,594.89 and 1,602.5 cm^{-1}. Finally, the peak at 1,032.10 and 1,037.36 cm^{-1} are attributed to the amine group with C–N stretching vibrations. Thus, it could be concluded that alcohols/phenols, carboxyl, amide, alkane, aromatic and amine groups were present in the banana peel. The carboxylic groups could play a major role in the adsorption of toxic metal for banana peel [35]. The carboxylic groups have pK_a value ranging from 3.8 to 4.8. At pH > 4, the carboxylic groups will be deprotonated and become negatively charged thus increasing the availability of binding sites for positively charged metal ions. Alternatively, for pH < 3, the carboxylic groups will be protonated and unavailable for binding with metal ions present in the solution. This is supported by the results obtained in this experiment for the test of pH whereby the adsorption rate is above pH 4.

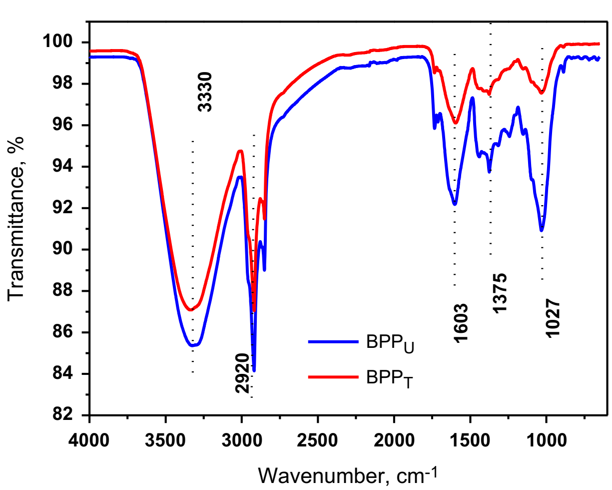

Fig. 9. FTIR spectrum of BPP.

6. Conclusion

Based on the findings of this study, it was observed that banana peel powder (BPP), both untreated (BPPU) and treated (BPPT), could be used for the removal of toxic metals, lead (Pb) and copper (Cu), from aqueous solutions. The amount of toxic metals adsorbed by BPPU and BPPT was found to increase with the increase in the adsorbent mass, pH, initial concentration and contact time. The result of this study shows that BPPT, banana peel that has been treated with NaOH, has a higher capacity to remove toxic metal ions compared to BPPU. Adsorption isotherms, Langmuir and Freundlich isotherms were used to analyse the experimental data. Banana peel also has a higher tendency to adsorb lead compared to copper. Maximum adsorption capacity of the banana peel known as the Langmuir's maximum monolayer coverage capacity (Q_o) states that 1 g of BPPT can adsorb 89.286 mg of lead under a favourable condition. This shows that chemical modification with NaOH established the adsorption condition more energetically favourable. FTIR analysis of banana peel showed the presence of functional groups indicating the nature of the banana peel, while SEM observation shows the micro-rough structure of the surface. Banana peel can be used as a natural source of adsorbent that will benefit the society as a whole rather than being discarded as waste. This will not only conserve the environment, but it could also be a low-cost natural adsorbent.

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References

[1] G.J. Brewer, Iron and copper toxicity in diseases of aging, particularly atherosclerosis and Alzheimer's disease, Exp. Biol. Med. 232(2) (2007) 323–335.
[2] P. Faller, Copper and zinc binding to amyloid: coordination, dynamics, aggregation, reactivity and metal-ion transfer, Chem. BioChem 10(18) (2009) 2837–2845.
[3] S. Larous, A.H. Meniai, M.B. Lehocine, Experimental study of the removal of copper from aqueous solutions by adsorption using sawdust, Desalination 185 (2005) 483–490.
[4] C. Karthika, N. Vennilamani, S. Pattabhi, M. Sekar, Utilization of sago waste as an adsorbent for the removal of Pb(II) from aqueous solution: Kinetic and isotherm studies, Int. J. Eng. Sci. Technol. 2(6) (2010) 1867–1879.
[5] O.S. Amuda, O.I. Ojo, T.I. Edewor, Biosorption of lead from industrial wastewater using *Chrysophyllum albidum* seed shell, Bioremed. J. 11(4) (2007) 183–194.
[6] I.O. Oboh, E.O. Aluyor, T.O.K. Audu, Biosorption of heavy metal ions from aqueous solutions using a biomaterial, Leonardo J. Sci. 14 (2009) 58–65.
[7] J. Anwar, S. Umer, W. Zaman, S. Muhammad, D. Amara, A. Shafiqu, Removal of Pb(II) and Cd(II) from water by adsorption on peels of banana. Bioresour. Technol. 101 (2009) 1752–1755.
[8] C. Liu, H.N. Ngo, W. Guo, K.-L. Tung, Optimal conditions for preparation of banana peels, sugarcane bagasse and watermelon rind in removing copper from water, Bioresour. Technol. 119 (2012) 349–354.
[9] M.A. Ashraf, M.A. Rahman, Y. Alias, I. Yusoff, Removal of Cd(II) onto *Raphanus sativus* peels biomass: Equilibrium, kinetics, and thermodynamics. Desalin. Water Treat. 51 (2013) 4402–4412.
[10] S. Liu, Food and Agricultural Wastewater Utilization and Treatment, Blackwell Publishing, UK, 2007, p. 73.
[11] M.A. Ashraf, I. Yusoff, I. Yusof, Y. Alias, Removal of acid yellow 17 dye from aueous solution using eco-friendly biosorbent. Desalin. Water Treat. 51 (2014) 4530–4545.
[12] M.A. Ashraf, I. Yusoff, Y. Alias, Study of contaminant transport at an open-tipping waste disposal site, Environ. Sci. Pollut. Res. 20(7) (2013) 4689–4710.
[13] K. Vijayaraghavan, Y.-S. Yun, Bacterial biosorbents and biosorption, Biotechnol. Adv. 26 (2008) 266–291.
[14] K. Nasim Ahmad, I. Shaliza, P. Subramaniam, Elimination of heavy metals from wastewater using agricultural waste as adsorbents, Malaysian J. Sci. 23 (2004) 43–51.
[15] K.C.A. Jalal, M. Sufian, A.B.M. Helaluddin, Y. Kamaruzzaman, Bioadsorption of heavy metals from synthetic waste water by tropical Rambutan seed, in: Z. Zainuddin (Ed.), Biotechnologies towards Sustainable Development in Malaysia, 2011, pp. 208–222.
[16] T.A. Johnson, N. Jain, H.C. Joshi, S. Prasad, Agricultural and agro-processing waste as low cost adsorbents for metal removal from wastewater: A review, J. Sci. Ind. Res. 67 (2008) 647–658.
[17] N.U. Asamudo, A.S. Daba, O.U. Ezeronye, Bioremediation of textile effluent using *Phanerochaete chrysosporium*. Afr. J. Biotechnol. 4(13) (2005) 1548-1553.
[18] S. Ramli, A.F.M. Alkarkhi, Y.S. Yong, A.M. Easa, Utilization of banana peel as a functional ingredient in yellow noodle. Asian J. Food Agro-Ind. 2(3) (2009) 321-329.
[19] S. Zuvairea Nazren Mohd, A. Qamar Uddin, K.C.A. Jalal, K. El Zawane, K. Abdul Viqar, A.B.M. Helal Uddin, N. Musa, Antimicrobial activity of banana (*Musa paradisiaca* L.) peels against food borne pathogenic microbes, J. Pure Appl. Microbiol. 8(5) (2014) 3627–3639.
[20] P. Elmer, FT-IR Spectroscopy Attenuated Total Reflectance (ATR). Available from: <http://www.utsc.utoronto.ca/~traceslab/ATR_FTIR.pdf> (Retrieved 17 April 2014).
[21] M.E. Argun, S. Dursun, Activation of pine bark surface with NaOH for lead removal, J. Int. Environ. Appl. Sci. 2 (2007) 5–10.

[22] A.K. Bhattacharya, T.K. Naiya, S.N. Mandal, S.K. Das, Adsorption, kinetics and equilibrium studies on removal of Cr(VI) from aqueous solutions using different low-cost adsorbents, Chem. Eng. J. 137(3) (2008) 529–541.

[23] R.H. Krishna, A.V.V.S. Swamy, Physico-chemical key parameters, Langmuir and Freundlich isotherm and Lagergren rate constant studies on the removal of divalent nickel from the aqueous solutions onto powder of calcined brick, Int. J. Eng. Res. Dev. 4(1) (2012) 29–38.

[24] M.A. Hossain, H.H. Ngo, W.S. Guo, T.V. Nguyen, Biosorption of Cu(II) from water by banana peel based biosorbent: Experiments and models of adsorption and desorption. J. Water Sustain. 2(1) (2012) 87–104.

[25] A.B.P. Marin, V.M. Zapata, J.F. Ortuno, M. Aquilar, J. Saez, M. Llorens, Removal of cadmium from aqueous solutions by adsorption onto orange waste, J. Hazard. Mater. 139 (2006) 122–131.

[26] A. Jamil, S. Umer, W. Zaman, S. Muhammad, D. Amara, A. Shafique, Removal of Pb(II) and Cd(II) from water by adsorption on peels of banana, Bioresour. Technol. 101 (2009) 1752–1755.

[27] A. Habib, I. Nazrul, I. Anarul, A.M. Shafiqul Alam, Removal of copper from aqueous solution using orange peel, sawdust and baggase. Pak. J. Anal. Environ. Chem. 8(1 & 2) (2007) 21–25.

[28] K.M.S. Surchi, Agricultural waste as low cost adsorbents for Pb removal: Kinetics, equilibrium and thermodynamics, Int. J. Chem. 3(3) (2011) 103–112.

[29] P.M. Pimentel, M.A.F. Melo, D.M.A., A.L.C. Assunção, D.M. Henrique, C.N., Jr. Silva, G. Gonzaler, Kinetics and thermodynamics of Cu(II) adsorption on oil shale waste, Fuel Process Technol. 89 (2007) 62–67.

[30] R.H. Krishna, A.V.V.S. Swamy, Phisico-chemical key parameters, Langmuir and Freundlich isotherm and Lagergren rate constant studies on the removal of divalent nickel from the aqueous solutions onto powder of calcined brick, Int. J. Eng. Res. Dev. 4(1) (2012) 29–38.

[31] K.Y. Foo, B.H. Hameed, Insights into the modeling of adsorption isotherm systems, Chem. Eng. J. 156 (2010) 2–10.

[32] A.O. Dada, A.P. Olalekan, A.M. Olantunya, O. Dada, Langmuir, Freundlich, Temkin and Dublin–Radushevich isotherms studies of equilibrium sorption of Zn^{2+} unto phosphoric acid modifies rice husk, J. Appl. Chem. 3(1) 2012 38–45

[33] M. Achak, A. Hafidi, N. Quazzani, S. Sayadi, L. Mandi, Low cost biosorbent "banana peel" for the removal of phenolic compounds from olive mill wastewater: Kinetic and equilibrium studies, J. Hazard. Mater. 166 (2008) 117–125.

[34] W. Reusch, Infrared Spectroscopy, [Online]. Available from: <http://www2.chemistry.msu.edu/faculty/reusch/virttxtjml/spectrpy/infrared/infrared.htm> (5 March 2013).

[35] J.R. Memon, S.Q. Memon, M.I. Bhanger, M.Y. Khuhawar, Banana peel: A green and economical sorbent for Cr(III) removal, Pak. J. Anal. Environ. Chem. 9(1) (2008) 20–25.