

EQUILIBRIUM AND THERMODYNAMIC MODELING FOR THE BIOSORPTION OF CU (II) IONS ON LIME (*CITRUS AURANTIFOLIA*) PEEL BIOSORBENTS

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Abstract:-

A novel biosorbent, derived from dried peels of lime (*Citrus aurantifolia*) was used for the removal of Cu (II) ions from aqueous solutions. The effects of pH, biosorbent dosage and temperature on the biosorption of Cu (II) ions were investigated in batch mode. At optimal conditions, with pH 5, 0.4 g/L of biosorbent dosage, 100 mg/L of initial Cu (II) concentration and temperature 80 °C, the maximum biosorption capacity obtained was 100 mg/g. Equilibrium data was best described by both the Langmuir and Freundlich model, indicating the involvement of more than one mechanism for the sorption process. Thermodynamic studies revealed that the biosorption process is favorable, spontaneous and endothermic in nature. The outcome of this study revealed that dried lime peel powder has good potential to be used as a low cost and **environmentally** friendly biosorbent for the removal of Cu (II) ions from aqueous solutions.

Keywords:- Biosorption; lime peels; heavy metals; Cu (II) ions; wastewater treatment

1. INTRODUCTION

Water pollution has raised concern these days as water is a basic resource that is essential to all life forms. Rapid development and urbanisation in many countries have increased the levels of water pollution. Most of these pollutants come from poorly treated industrial or agricultural effluents that are indiscriminately released into water bodies (Bhatnagar, et al., 2015). One type of pollutant that has caused great concern is heavy metals. Heavy metals are elements that have a specific gravity of more than five, and most of them are toxic to health and the environment. Some examples of toxic heavy metals found in industrial wastewaters include lead, mercury, cadmium, chromium, arsenic, zinc, copper and nickel. These metals are typically found in emissions of mining, refinery, sludge disposal and metal plating operations. Vast research has been carried out for the removal of the “big four” heavy metals, which are lead, chromium, cadmium and mercury (Volesky, 1990). After removal from wastewaters, these metals have very little reuse or recycle value due to their toxic nature. Therefore, in recent years, most researchers have been looking into the recovery of heavy metals which have more reuse or recycle significance, as they are becoming a limited and valuable resource due to their scarcity in nature. Even in low concentration effluents, the recovery of heavy metals has become important these days. One such metal is copper, which will be the focus of the present study. Copper is often found in the form of bivalent Cu (II) ions in wastewaters of metal plating, mine drainage, landfills, and sewage and paper mills. Besides released by human activities, Cu (II) ions are also discharged by natural sources, for example wind-blown dust, decaying vegetation, forest fires and sea spray. These toxic ions can cause various acute and chronic disorders such as hemolysis, liver and kidney damage, irritation of upper respiratory tract and gastrointestinal disturbances (Rao and Ikram, 2011). Other than human health, Cu (II) ions can also interrupt soil balance by influencing the activity of microorganisms and earthworms. Therefore, it is very important to remove Cu (II) ions from wastewater streams. Conventional methods used to remove heavy metals from wastewater include ion exchange, reverse osmosis, solvent extraction and chemical precipitation (Njikam and Schiewer, 2012). Though efficient, these methods are too costly and not suitable for the large volumes of wastewater with low metal ion concentrations that industries release today. Hence, other methods with lower cost and higher efficiency need to be considered (Ang, et al., 2013). One such technology is adsorption, which is relatively simple and effective. Activated carbon used to be the most popular adsorbent material, but it has now become less attractive due to its technical limitations and high regeneration costs. In recent years, low cost biomass materials have emerged as a cost-effective and efficient alternative for the removal of heavy metal ions from wastewaters. This new technology is known as biosorption or biological adsorption.

Biosorption is defined as ‘the passive and non-metabolically mediated process of metal ion binding by dead and inactive biomass’ (Kumar, et al., 2006). It is not to be confused with bioaccumulation, which involves live biomass cells that take up metals through their metabolic processes. The biosorption process is metabolism-independent, and the metal binding mechanisms could include one or more of the following: ion exchange, adsorption, microprecipitation, complexation, chelation or coordination. The biomass materials used for biosorption are called biosorbents. Biosorbents are usually by-products or waste materials from agriculture or industries, making them a low cost, abundant and easily available material (Volesky, 1990). Biosorption technology has several advantages, which besides the above, include high versatility, high metal selectivity, not concentration dependent, no nutrient requirements, no generation of toxic sludge, high tolerance for organics, holds the possibility of metal recovery and enables biosorbent regeneration and reuse (Volesky, 1990).

One type of biosorbent material that is cheap and abundant is citrus peels. Throughout the world, large amounts of citrus wastes are generated by the consumption of these fruits, which may be as high as 50% of the fruit’s weight (Bhatnagar, et al., 2010). Most of these peels are currently simply disposed as solid wastes or incinerated. Therefore, it is highly desirable to develop green and economic solutions to deal with these wastes, and a prudent method would be to use them as value-added biosorbent materials. Over the past few years, several studies have been carried out to test the efficacy of citrus peels as metal ion biosorbents (Schiewer and Patil, 2008). They include orange peels (Ajmal et al., 2000; Khormaei, et al., 2007; Li, et al., 2007; Njikam and Schiewer, 2012), grapefruit peels (Torab-Mostaedi, et al., 2013), pomelo peels (Liu et al., 2012; Tasaso, 2012) and lemon peels (Bhatnagar, et al., 2010). These studies have revealed that citrus peels indeed have the ability to bind heavy metal cations, because they are rich in pectic-cellulostic substances that contain the desirable active groups for metal ion biosorption. Moreover, citrus peels typically have a lower degree of alkylation in their pectin structure (Dronnet, et al., 1996). Alkylation refers to the substitution of an alkyl group for an active hydrogen atom in a compound. Hydrogen atoms in biomass materials are usually in the form of hydroxyls or carboxyls, which are active metal binding groups. If these groups are reduced or not available, it then decreases the biosorption capacity of the material. Thus, the low alkylation characteristic is important when it comes to choosing a fruit peel biosorbent for heavy metal ion biosorption.

Of the different citrus fruits, peels of lime (*Citrus aurantifolia*) are ones that are underresearched and warrants further study. To date, there has been no published work on lime peel’s potential as a metal ion sorbent. For the present study, lime peels were used for the removal and subsequent recovery of Cu (II) ions from aqueous solutions. Lime or also known as key lime, is the smallest and most useful amongst the family of citrus fruits. It originates from South Asia, and is grown today in many tropical countries such as Malaysia. This fruit is consumed as a beverage and used in culinary for most Asian dishes. Oil extracted from its peel is generally used in cosmetics, disinfectants and numerous other medicinal products. After applications from the agricultural, food and pharmaceutical industries, these lime peels are often discarded as waste. Being a low or zero cost and abundant waste resource in most countries, especially in South East Asia, lime peels become an attractive choice as a biosorbent. The present work tested the efficiency of lime peels for Cu (II) ion

biosorption under varied experimental conditions. The effects of pH, contact time, biosorbent dosage and temperature were studied. Following that, thermodynamic and equilibrium modeling were performed to assess the feasibility of using lime peels for Cu (II) ions biosorption from aqueous solutions.

2. Materials and Methods

2.1 Preparation of the biosorbent

Waste lime peels were obtained from a local restaurant serving lime juice. The endocarp and mesocarp (the inner layer - flesh or pulp, including seeds) was removed and the epicarp (outer layer - peels or skin) was washed with distilled water and chopped into smaller pieces (1-2 cm). The peels were then dried under the sun for 6-7 hours. After sun-drying (which helps to disinfect the material), the peels were left in the oven (Memmert, DO6838, Germany) at 60°C for 24 hours for complete physical moisture removal. Next, the dry peels were ground using a mechanical grinder (Retsch-ZM 200), and sieved to obtain particles between 80-100 µm in size. The lime peel powder (LIPP) was then stored at room temperature (28°C) in a desiccator and used for biosorption experiments.

2.2 Preparation of chemical solutions

All chemicals used in the study were of analytical grade, purchased from HmbG Chemicals. Copper chloride (CuCl₂) solution of 100 mg/L was prepared by dissolving the measured amount of CuCl₂ anhydrate salts in deionised water. The concentration of Cu (II) was fixed at this value to test the efficiency of LIPP biosorption at relatively low metal ion concentrations, which is typical for local metal-bearing wastewaters. Besides that, standard Cu (II) ion solutions of 5, 10, 15, 25 and 30 mg/L were prepared for Atomic Absorption Spectrometer (AAS, AAnalyst 400, and Perkin Elmer) calibration purpose. For pH adjustments and desorption experiments, 0.1 M of hydrochloric acid (HCl) and 0.1 M of sodium hydroxide (NaOH) solutions were prepared.

2.3 Experimental procedure

First pH experiments were carried out, by varying pH between 1.5 to 9.5 (pH adjusting chemicals were used for this purpose). A volume of 100 mL aqueous CuCl₂ solution with concentration of 100 mg/L and an LIPP dosage of 1.0 g/L were used. The solutions were placed in conical flasks in a water bath shaker and shaken for 3 hours at temperature 28°C, with an agitation speed of 100 rpm. The solution was centrifuged and the supernatant was tested its final Cu (II) ion concentration with the AAS.

Next, the contact time and biosorbent dosage experiments were carried out. LIPP of different dosages (0.4, 0.6, 0.8, 1.0 and 1.2 g/L) were mixed with 100 mL aqueous CuCl₂ of 100 mg/L concentration in five different conical flasks. Then, the flasks were placed in a water bath shaker at temperature 28°C. PH used was about 5 (determined from previous pH experiments) and agitation speed was 100 rpm. Experiments were carried out for a total time of 3 hours. 1 mL from the solution was pipetted out every 10 minutes for the first hour and then every 30 minutes for the next two hours. The 1 mL sample was diluted 10 times with deionised water (Type II (Pure) Elix) in a glass vial and sent for metal analysis with the AAS. Dilution was necessary for AAS testing because it was found that most accurate readings obtained for the equipment were 50 mg/L and below. From this set of experiments, the optimal LIPP dosage was determined. For the next set of experiments, the effect temperature on biosorption was studied. Experiments were carried out at the optimal conditions obtained from the biosorbent dosage experiments, and the temperature values used were 40, 50, 60, 70, 80 and 90°C. With all the data obtained, a detailed analysis and modeling of the biosorption process was carried out.

2.4 Analysis of data

Biosorption efficiency refers to how much metal ion in total the biosorbent can remove in a particular time period. The biosorption efficiency was determined using Eq. (1):

$$\% \text{biosorption} = \frac{C_0 - C_t}{C_0} \times 100\% \quad (1)$$

Where C_0 is the initial concentration of the adsorbate (mg/L) and C_t is the concentration of adsorbate at time, t (mg/L). The equation used to determine biosorption capacity, which refers to the amount of material adsorbed per unit mass of adsorbent, q_t (mg/g) is expressed in Eq. (2):

$$q_t = \frac{C_0 - C_t}{m} \quad (2)$$

Where C_0 is the initial concentration of the adsorbate (mg/L); C_t is the concentration of adsorbate at time t (mg/L); m is the biosorbent dosage or concentration (g/L).

2.5 Equilibrium modeling

For equilibrium studies, adsorption isotherms and models were analysed. An adsorption isotherm is a curve that represents the concentration of a solute on the surface of an adsorbent, to the concentration of the solute with the contacted liquid. Two well established types of adsorption isotherms, Langmuir and Freundlich, were used to evaluate the data obtained in this experiment. There are many adsorption isotherm models, but most of them work best in a gason-solid adsorption

system. Only the Langmuir and Freundlich isotherms seemed to give good interpretation of the more complex aqueous phase system (Febrianto, et al., 2009). Thus, for the present study, these two isotherm models were evaluated. The Langmuir model (Langmuir, 1918), which is used to describe the relationship between equilibrium metal uptake, q_e , (mg/g), and adsorbate final concentrations, C_e , (mg/L), is described in Eq. (3). This isotherm is based on the assumptions that (i) maximum adsorption corresponds to a saturated monolayer of adsorbate molecules on the adsorbent surface; (ii) the energy of adsorption is constant; and (iii) there is no transmigration of adsorbates in the plane of the surface.

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{K_L \cdot q_m} \quad (3)$$

Where q_e is the amount of adsorbed material per unit mass of biosorbent (mg/g) at equilibrium; q_m and K_L are the Langmuir constants related to adsorption capacity (mg/g) and energy of adsorption (L/mg) respectively. The Langmuir constant parameters can be determined by a plotting C_e/q_e against C_e graph.

The Freundlich isotherm, is one of the earliest equations that have been used in describing the adsorption process. It can be used for non-ideal sorption that involves heterogeneous adsorption because it is an empirical equation. The Freundlich model in its linearised form is given in Eq. (4).

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \quad (4)$$

Where q_e is the amount of adsorbed material per unit mass of biosorbent (mg/g) at equilibrium, C_e is the concentration of adsorbate at equilibrium (mg/L), K_f is the constant related to adsorption capacity of sorbent (mg/g), and n is the empirical constant related to the efficiency of the sorption, (L/mg).

2.6 Thermodynamic modeling

Thermodynamic parameters were calculated to study the adsorption nature of the LIPP biosorbent. The thermodynamic constants, which are the Gibbs free energy change (ΔG°), enthalpy change (ΔH°) and entropy change (ΔS°) were calculated to estimate the thermodynamic feasibility of the process and to confirm the nature of the biosorption process. The equations for calculation of thermodynamic parameters are given in Eqs. (5-7).

$$K_c = \frac{C_{ad}}{C_e} \quad (5)$$

Where K_c (L/g) is the equilibrium constant defined by q_e/C_e , C_{ad} is the equilibrium concentration of metal ions on adsorbent (mg/L), and C_e is the equilibrium concentration of metal ions in the solution (mg/L). For Gibbs free energy of the system, the relationship is given in Eq. (6):

$$\Delta G = -RT \ln K_c \quad (6)$$

Where T is the temperature in Kelvin and R is the gas constant with the value of 8.314 J/mol K. From Eq. (7), a graph of $\ln K_c$ against $1/T$, which is known as the Van't Hoff plot, can be plotted to determine the enthalpy and entropy values.

$$\ln K_c = \frac{\Delta S^\circ}{2.303 R} - \frac{\Delta H^\circ}{2.303 RT} \quad (7)$$

3. Results and Discussion

3.1 Effect of pH

pH is a very important parameter when it comes to biosorption studies. The pH determines the surface charge of the biosorbent material, as well as the degree of ionisation and speciation of the adsorbate (El-Ashtoukhy, et al., 2008). To determine the optimal pH for the biosorption of Cu (II) ions on LIPP, experiments using 1.0 g/L biosorbent dosage, 100 mg/L Cu (II) concentration at a water bath temperature of 28°C were carried out at different pH ranges, from about 1.5 to 9.5. From the results obtained (Fig. 1), it was found that pH about 5 was the most suitable, and gave highest biosorption efficiency (78 %). In general, at very low pH values (pH < 3), there are more hydrogen ions (H^+) present in the solution. This creates electrostatic repulsion between Cu (II) ions and the positively charged surfaces, creating competition for cation binding sites. At higher pH values (pH 3 – 5), there are lesser H^+ ions and more negatively charged ligands (hydroxyls and carboxyls) that result in greater metal ion biosorption (TorabMostaedi, et al., 2013). At very high pH values (pH > 7), there are more hydroxide ions (OH^-) present, which can cause the precipitation of Cu (II) ions as insoluble metal hydroxides (Pasavant, et al., 2006). Besides that, high pH values are known to cause degradation of the natural biosorbent material, thus undesirable (Pavan, et al., 2006). Hence, a pH of 5 was selected as the optimal for further experiments.

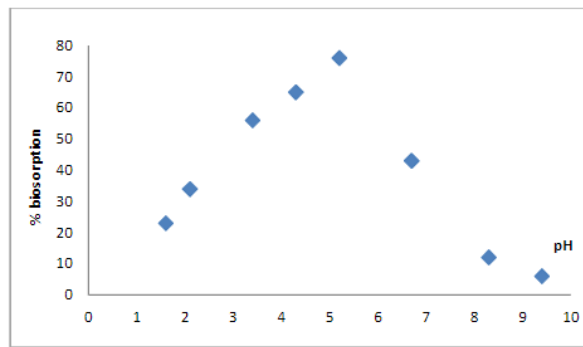


Fig. 1: Effect of solution pH (LIPP dosage = 1.0 g/L, $C_0 = 100$ mg/L, $T = 28^\circ\text{C}$)

3.2 Effect of contact time

Fig. 2 shows the relationship between amounts of Cu (II) ions adsorbed against time for the different LIPP biosorbent dosages used. The experimental conditions used were 100 mg/L Cu (II) ion concentration, pH 5 and total contact time of 180 min. From the plot, it can be seen that LIPP of all dosages reached equilibrium within 60 min. The time profiles depicted seemed to show a smooth curve, where in the first 20 minutes, there was rapid sorption taking place as a result of free binding sites available on the surface of LIPP, and thereafter it slowed down when the sites started getting saturated, until equilibrium was reached. It can be said that the whole sorption process was complete in 60 min. Thus equilibrium time for the biosorption of Cu (II) ions on LIPP was taken to be 60 min. Equilibrium time was found to be not dependent on the biosorbent dosage used. So this means the rate of Cu (II) ion uptake on all the active sites of the biosorbent is the same. Similar trends were observed by Bhatnagar, et al., (2010) for the biosorption of Co (II) ions on lemon peel sorbents. However time taken to reach equilibrium in their study was about 7 hours. Studies carried out by Torab-Mostaedi, et al., (2013) using grapefruit peels for Cd (II) and Ni (II) biosorption gave an equilibrium time of 60 min for both metal ions. When mosambi (sweet lime) peel sorbents were tested for the removal of Ni (II) ions, the equilibrium removal time obtained was about 90 min for the various experimental conditions used (Hema Krishna and Swamy, 2011). Studies show that equilibrium biosorption time depends on the type of citrus peel used and its affinity towards a particular metal ion type. Thus, each citrus peel is believed to have its unique metal ion adsorption properties.

3.3 Effect of biosorbent dosage

Fig. 2 also shows the relationship between biosorption capacity and biosorbent dosage. It can be observed that the highest amount of Cu (II) ions adsorbed was about 60 mg/g at a dosage of 0.4 g/L LIPP. Very low (0.2 g/L) or very high dosages (>1.0 g/L) seemed to give lower sorption values. Moderate dosages between 0.4 to 0.8 g/L were more stable, with higher sorption values, and reached equilibrium fairly quickly and smoothly. At very low biosorbent dosages, there could be insufficient active sites for metal ions to adsorb. At relatively high biosorbent dosages, the available metal ions are insufficient to cover all the exchangeable or active sites on the biosorbent, thus shows low metal uptake (Gong, et al., 2005; Saifuddin and Raziah, 2007). Besides that, this may be also due to the aggregation or overlapping of the fine biosorbent particles, which causes the decrease of available surface area and hence adsorption sites. This trend can also be explained because of the concentration gradient between solute in the solution, and the solute in the surface of the biosorbent. As a result, it is possible that the highest metal uptake would occur at lower biosorbent dosages. Similar observations were made for the biosorption of heavy metal ions on other citrus peels used in its raw form (Bhatnagar, et al., 2010; Torab-Mostaedi, et al., 2013). Thus, an LIPP dosage of 0.4 g/L was taken as optimal and used for all subsequent experiments.

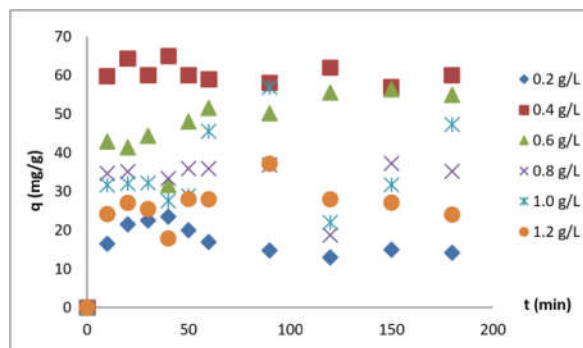


Fig. 2: Effect of contact time and biosorbent dosage ($C_0 = 100$ mg/L, pH 5, $T = 28^\circ\text{C}$)

3.4 Effect of temperature and thermodynamic studies

The temperatures selected for the study were 40, 50, 60, 70, 80 and 90°C . Temperature effect experiments were carried out at optimal conditions obtained from the previous tests. From Fig. 3, there seemed to be an overall increase in the biosorption capacity with temperature. The optimum temperature that gave highest biosorption capacity (100 mg/g) was 80°C .

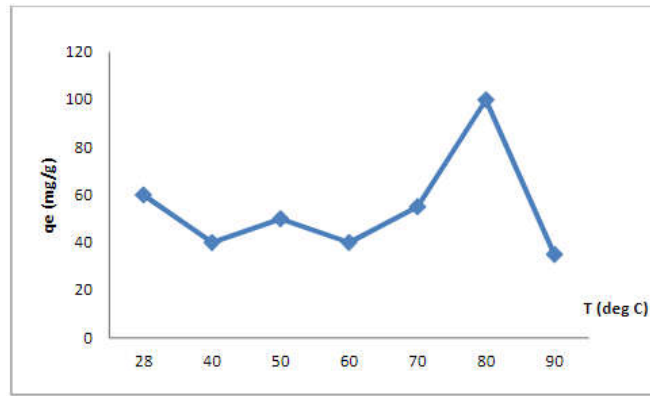


Fig. 3: Effect of temperature on biosorption capacity (LIPP dosage = 0.4 g/L, $C_0 = 100$ mg/L, pH 5, $T = 28^\circ\text{C}$, $t = 60$ min)

The enhancement of biosorption capacity with temperature could be attributed to the enlargement of pore size and activation of the biosorbent's surface. However, beyond 80°C , a drastic drop was observed in the adsorption capacity, thus very high temperatures were deemed unsuitable for Cu (II) biosorption on LIPP, as it is suspected that most surface active groups could be destroyed at this temperature range. The biosorption efficiency (Fig. 4) also showed the same trend, where it increased till temperature 80°C and then dropped thereafter with the increase in temperature.

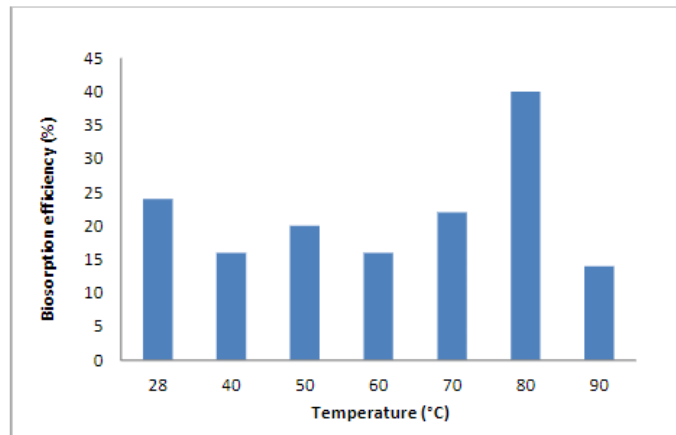


Fig. 4: Effect of temperature on biosorption efficiency (LIPP dosage = 0.4 g/L, $C_0 = 100$ mg/L, pH 5, $t = 60$ min)

For thermodynamic studies, the temperature range used to carry out analysis was between 40°C to 80°C , as there was more consistency in the results for this range of temperature. Fig. 5 shows the Van't Hoff plot of $\ln K_c$ against $1/T$. The plot showed good linearity ($R^2 > 0.99$), thus reliable data may be acquired from the correlations. The values of ΔG° , ΔH° , and ΔS° were obtained from the slope and intercept of the graph and tabulated in Table 1.

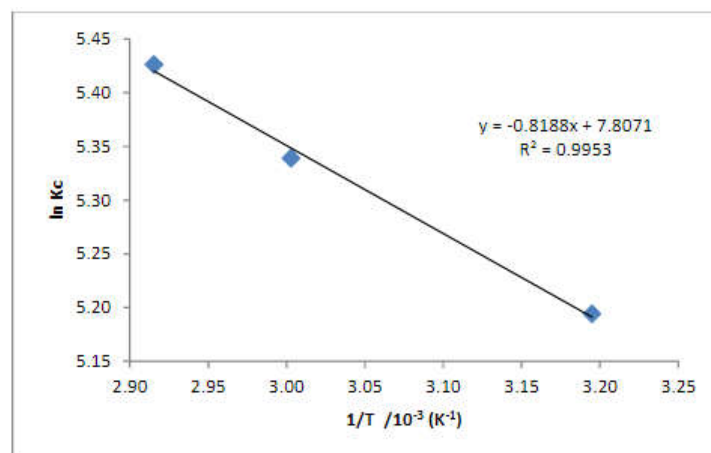


Fig. 5: Van't Hoff plot for Cu (II) biosorption on LiPP at optimal conditions (LIPP dosage = 0.4 g/L, $C_0 = 100$ mg/L, pH 5, $t = 60$ min)

From Table 1, the positive value of enthalpy (ΔH°) confirms the endothermic nature of adsorption process. This means, energy is absorbed for the formation of bonds between the metal ions and biosorbent. The reason is because the bonding

is short-ranged, and as a result, energy is needed to overcome the repulsive forces of attractions as Cu (II) ions bind in a short distance from the biosorbent (Ang, et al., 2013). This is why the optimal temperature that gave highest biosorption capacity was relatively high (80°C), as external source of heat energy is required for the endothermic reaction to occur. Moreover, for relatively larger ions such as Cu (II), higher temperature is needed for swelling of the internal cellulose structures to expose metal binding active groups for the purpose of adsorption (Nurchi and Villaescusa, 2008). From literature, ΔH° values below 4.184 kJ/mol (1 kcal/mol) indicate strong physisorption, and values above 20.92 kJ/mol (5 kcal/mol) indicate strong chemisorption (Ozer and Ozer, 2003). In this study, the value of ΔH° is 6.81 kJ/mol, which means the mechanism of Cu (II) sorption on LIPP could be a combination of physisorption and chemisorption, depending on the type of metal binding sites involved. It is however, suspected that the biosorption mechanism could be predominantly of the chemisorption type because of its endothermic nature. Thus, there is believed to be strong physical and chemical bonding between Cu (II) ions and the LIPP biosorbent.

The positive value of ΔS° (64.91 kJ/mol) shows increased disorder and randomness on the surface of LIPP. It also indicates the strong affinity of LIPP towards Cu (II) ions. This phenomenon is expected as a consequence of mass transfer of Cu (II) ions from the bulk liquid phase to the solid phase, which in turn introduces relative disorderness at the solid-liquid interface. The system occurs spontaneously due to a rise of entropy as the system shifts to a state which is more uniform and stable. Positive entropy values also indicate that there may be some structural changes in both the adsorbate and biosorbent during the adsorption process (Ang, et al., 2013). On the other hand, the values of ΔG° which are negative indicate that the biosorption of Cu (II) ions by LIPP is favourable and spontaneous, thus making the process a thermodynamically feasible one.

Table 1: Values of ΔG° , ΔH° , and ΔS° for LIPP at optimal conditions (LIPP dosage = 0.4 g/L, C_o = 100 mg/L, pH 5, t = 60 min)

| T (K) | Kc | ΔG° (kJ/mol) | ΔS° (kJ/mol) | ΔH° (kJ/mol) |
|-------|--------|------------------------------|------------------------------|------------------------------|
| 313 | 180.18 | -13.52 | 64.91 | 6.81 |
| 323 | 250.00 | -14.83 | | |
| 333 | 208.33 | -14.78 | | |
| 343 | 227.27 | -15.47 | | |
| 353 | 404.86 | -17.62 | | |

3.5 Equilibrium modelling

The theoretical Langmuir isotherm is suitable for an adsorption of a solute from a liquid solution as monolayer adsorption on a surface containing a finite number of identical sites. Fig. 6 shows the linear plots of C_e/q_e versus C_e for the Langmuir model, and the values of q_m and K_L were determined from the slope and intercept of the graph respectively. All the data obtained for the Langmuir isotherm are tabulated in Table 2. LIPP is found to give a positive value for the monolayer sorption capacity, q_m which was found to be 120.5 mg/g. This value is close to the actual sorption capacity obtained through experiments at optimal conditions, which is 100 mg/g. The variation is just about 17%. The correlation coefficient value was also reasonable and acceptable ($R^2 = 0.8645 \approx 0.9$). Further evaluation of the essential characteristics of the Langmuir isotherm was carried out by determining the dimensionless constant separation factor or equilibrium parameter, R_L , as given in Eq. (8):

$$R_L = \frac{1}{1 + K_L C_0} \quad (8)$$

Where K_L is Langmuir's equilibrium constant and C_0 is the initial concentration of metal ion (Naveen Prasad, et al., 2008). From literature, it is known that an R_L value between 0 and 1 indicates favourable adsorption (El-Ashtouky, et al., 2008). In this experiment, R_L for LIPP was found to be 0.36, thus indicating favourable adsorption. Therefore, LIPP can be said to fit well the Langmuir isotherm, and it can assumed that one of the mechanisms is the uptake of Cu (II) ions on a homogeneous surface via monolayer sorption without any interaction between adsorbed ions (Hema and Arivoli, 2007). In other words, this means that the sorption of Cu (II) ions may have taken place at the specific functional groups or active sites on the surface LIPP, with chemisorption as the predominant mechanism.

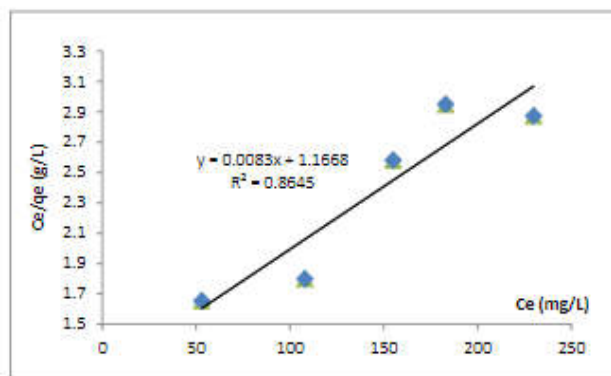


Fig. 6: Langmuir isotherm for Cu (II) sorption on LIPP

The applicability of the Freundlich adsorption isotherm was evaluated by plotting $\log q_e$ against $\log C_e$. The graph obtained Fig. 7 gives a straight line where slopes and intercepts correspond to values of adsorption affinity, n and constant related to adsorption capacity, K_f respectively.

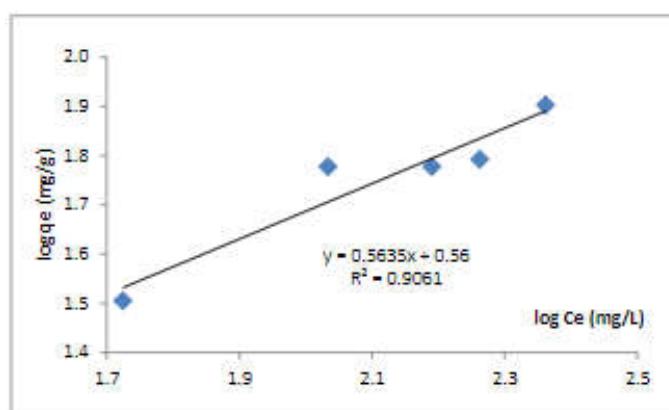


Fig. 7: Freundlich isotherm for Cu (II) sorption on LIPP

All the data obtained from the graph in Fig. 7 are illustrated in Table 2. The correlation coefficient, R^2 , seemed to be relatively high ($R^2 = 0.9061 \approx 0.9$) for the Freundlich isotherm, thus giving an almost similar fit like the Langmuir isotherm model. Moreover, the value of n is between 1 to 10 ($n = 1.77$), signifying beneficial and favourable adsorption on LIPP (Kadirvelu and Namasivayam, 2000). Thus, for LIPP, it can be said that the uptake of metal ions also occurs on a heterogeneous surface by multilayer adsorption process (Hema, et al., 2006), which means there could be a combination of physisorption (mainly Van de Waal's forces) as well as chemisorption (ion exchange, complexation, coordination, chelation or a combination of these interactions) mechanism taking place in the metal ion binding process. From the results obtained in the equilibrium modeling, it is suspected that LIPP may have several different types of active and exchange sites on its surface for metal ion biosorption. With the high temperatures used at optimal sorption conditions, most probably a large amount of these sites have been exposed for metal ion uptake. The main mechanism is suspected to be of the chemisorption type, followed by some physisorption. Thus, there is believed to be strong affinity and binding between Cu (II) ions and LIPP.

Table 2: Constant parameters obtained for Langmuir and Freundlich isotherms

| <u>Langmuir Isotherm</u> | |
|----------------------------|----------------------|
| K_L | 0.0071 |
| q_m | 120.5 |
| R^2 | $0.8645 \approx 0.9$ |
| <u>Freundlich isotherm</u> | |
| K_F | 3.63 |
| n | 1.77 |
| R^2 | $0.9061 \approx 0.9$ |

Compared to several other types of natural agricultural waste biosorbents studied for the past 15 years, LIPP was found to have relatively higher sorption capacity for the effective removal of Cu (II) ions from aqueous solutions (Table 3). This could probably due to the number of active groups available for metal ion biosorption and the different sorption mechanisms involved. Moreover, substances which contain cellulose and pectin are known to have superior metal sorption capacities due to the presence of polygalacturonic acid that is concentrated with hydroxyl and carboxyl groups (Khormaei, et al., 2007). This makes natural or unmodified LIPP a good choice for the biosorption of Cu (II) ions from aqueous solutions.

Table 3: Cu (II) biosorption with various natural agricultural waste biomass

| Biosorbent | q _{max} (mg/g) | Reference |
|------------------------|-------------------------|----------------------------|
| Apple residues | 10.80 | Ho Lee, et al., 1998 |
| Sugar beet pulp | 21.00 | Reddad, et al., 2002 |
| Olive mill residue | 13.50 | Pagnanellia, et al., 2002 |
| Peanut hull pellet | 12.00 | Johnson, et al., 2002 |
| Grape waste stalks | 9.60 | Villescusa, et al., 2004 |
| Wheat bran | 14.72 | Farajzadeh and Monji, 2004 |
| Wheat shells | 8.26 | Basci, et al., 2004 |
| Red capsicum seeds | 28.40 | Ozcan, et al., 2005 |
| Carrot residue | 32.74 | Nasernejad, et al., 2005 |
| Papaya wood | 19.88 | Saeed, et al., 2005 |
| Ponkan orange peel | 83.84 | Pavan, et al., 2006 |
| Banana peels | 4.75 | Kurniawan, et al., 2006 |
| Sour orange residue | 21.70 | Khormaei, et al., 2007 |
| Potato peels | 0.3877 | Aman, et al., 2008 |
| Pomegranate peel | 1.3185 | El-Ashtoukhy, et al., 2008 |
| Hazelnut shells | 0.0635 | Demirbas, et al., 2008 |
| Mango peel waste | 46.09 | Iqbal, et al., 2009 |
| Gooseberry fruit waste | 9.50 | Rao and Ikram, 2011 |
| Cashew nut shells | 20.00 | SenthilKumar, et al., 2011 |

4. Conclusions

As a conclusion, it can be said that natural LIPP is a good choice of biosorbent for the cost effective and efficient removal of Cu (II) ions from aqueous solutions. Maximum biosorption capacity obtained at optimal experimental conditions (pH 5, 0.4 g/L of LIPP dosage, 100 mg/L of initial Cu (II) concentration, equilibrium time 60 min and temperature 80°C) was 100 mg/g. With equilibrium modeling, it was found that the sorption process fit both the Langmuir and Freundlich model, indicating more than one type of sorption mechanism present, with chemisorption being the predominant type. The theoretical maximum biosorption capacity obtained from equilibrium modeling was 120.5 mg/g, which is in very close agreement with the experimental value. From thermodynamic modeling, the biosorption process was found to be favorable, spontaneous and endothermic in nature. This study illustrated an alternative solution for the management of unwanted citrus peel wastes, where lime peels with minimal processing could be used as a natural biosorbent for the removal of heavy metal ions such as Cu (II) from low strength wastewater.

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