AGRICULTURAL WASTE AS LOW COST ADSORBENT FOR THE REMOVAL OF FE (II) IONS FROM AQUEOUS SOLUTION

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ABSTRACT

This study investigates the efficiency of durian leaves as a low cost agriculture waste (bio adsorbent) that could remediate aqueous solution free of Fe (II) ions. The influence of four parameters, namely pH, initial metal concentration and contact time, mixing rate and particle size of adsorbent on the performance of durian leaves have been studied in batch method at room temperature. It was found that the maximum adsorption is reached at pH 6. Moreover, the process tends to be rapid the initial 5 minutes and equilibrated in 60 minutes with uptake of more than 45%. The Freundlich and Langmuir isotherm models are used to describe the biosorption of Fe(II) ions onto durian leaves. The Langmuir model tends to fit the equilibrium data better by giving a correlation coefficient of 0.7736 and maximum adsorption capacity is found to be at 3.914 mg/g. The results obtained prove that durian leaves have great potential to be used as low cost bio adsorbent in order to remove heavy metals in wastewater.

Keywords: *Agricultural Waste, Aqueous Solution, Adsorbent, Fe (II) Ions, Durian leaves, Low cost.*

INTRODUCTION

Wastewater is any water that has been critically damaged by human's anthropogenic domination. It is generated by the means of domestic, industrial, commercial, or agricultural activities as well as surface runoff or storm water. Since the emergence of the Industrial Revolution, industrial wastewater has become one of the crucial sources of water pollution. Heavy metals are among the significant pollutants that have been adversely affecting the purity of surface water. They enter the aquatic environment through the discharge of industrial wastes, storm water runoff, mining activities, smokestack discharge, and automobile emission. Many heavy metals are necessary elements for humans, animals, and plants in trace amounts. Howsoever, consumption of large amounts leads to acute and chronic toxicity which are linked to learning disabilities, cancers and even death. Chaturvedi and Dave (2012) stated that iron is a standout amongst the richest heavy metals found in the earth's crust. It happens normally in water, insoluble forms. This characteristic of the element leads to the excessive iron presence in groundwater. The origin of this particular heavy metal is not only by nature but also industrial.

Common industrial sources of iron pollution comprise mining, steel and iron production, and metal corrosion. Iron remediation is considered among the puzzling issues in producing consumable water due to its aesthetic problems, health concerns and economical controversy. Terrible metallic taste, reddish brown discoloration, blemishing nature and high turbidity are the major aesthetic problems caused by the iron existence in water. Iron compounds absorbed by the soil, rocks and minerals infiltrate towards groundwater that is further used for drinking and crop irrigation purposes. Corrosion is also a major dispute caused by iron occurrence. Greater water acidity and increased level of dissolved oxygen in water with the presence of iron leads to greater corrosion. Certain microscopic organisms flourish with raised levels of iron, and might stick to pipe surfaces as a suitable natural surroundings. These microscopic organisms might get to be sufficiently dense in population to cause clogging in pipes and deflate flow rates. This may head towards puncture or leakage in pipes if the pipes are constructed of iron. Propitiously, iron uptake has no clinical effects on our health if it's consumed in average amount as it is considered as a necessary nutrient in our body (Josoh et. al., 2005)

In current years, researches of the removal of heavy metals such as lead, copper, cadmium, zinc nickel and iron from solutions by adsorption using agricultural materials were given ample attention such as Sawdust (Yasemin and Zeki, 2007), Pomegranate (El-Ashtoukhy, et.al., 2008), Micro particles of dry plants (Benhima, et.al., 2008), waste tea leaves (Ahluwalia and Goya, 2005), saraca indica leaf (Goyal, et.al., 2008), tobacco stems (Li, et.al., 2008), neem leaf powder (Bhattacharyya and Sharma, 2004]. Removal of iron have been studied by (Anusha and RajaMurugadoss, 2014) using Almond shell as adsorbent, Tilapia Mossambica Fish scale-Adsorption has been used by (Zayadi and Othman, 2013), while (Kadir, et.al., 2013) used rice bran as adsorbent for the ferum ion removal from the solution.

There are existing technologies such as precipitation, ion exchange, solvent extraction and liquid membrane that are presently in use in order to remove heavy metals from wastewaters. But these natural materials have the aptitude to be utilized as low cost adsorbents because they serve as unused resources, are generally at hand and are also environmentally friendly (Abdel-Ghani, 2007) Natural adsorbents or more fondly known as biosorbents that were previously used for research of removal of heavy metal such as maize bran, sawdust, tea leaves, pomegranate peel, wood ash, neem leaf and more. In this study, durian leaf is being used as a low cost adsorbent.

Durian (Durio Zibethinus) is an exotic fruit which is well known within South East Asia regions. It is being consumed in massive amount all over many tropical countries and therefore huge areas are being reserved for durian plantations. According to the Agriculture Department Fruit Crop Statistics, 2013 the hectarage value for durian plantation has been 75,713.1 ha for the year 2013 whereas the annual production was 373,087 tonnes. It is found to be the largest fruit plantation within Malaysia.

Durian is one of the most available agricultural waste found in the South Asia region. Due to the high consumption of durian, massive amount of the peels and leaves are disposed, causing a severe problem in the community. The largest amount of durian leaf waste is also generated that subsequently is thrown into landfills thereby taking the landfill space. This study is conducted based on the utilizations of durian leaves as low cost adsorbent for the removal of ferum ions from aqueous solution and to determine the effect of pH, the effect of initial concentration of Fe (II) ions and contact time, effects of mixing rate and the effect of particle size on the adsorption of Fe(II) ions on the surfaces of durian leaves.

MATERIALS AND METHODS

Preparation of Adsorbent

The durian leaves were collected at a fruit yard situated in Mentakab, Pahang, Malaysia and Hulu Langat, Selangor, Malaysia. Mature leaves were collected to ensure the cell walls of the leaves are still rigid and functional. These leaves were then rinsed thoroughly to remove all impurities and dust on the leaves. Rinsed leaves were dried under the sunlight for 7 days and made sure the leaves turned golden brown. Further drying was done using heat of an oven at 105°C for 24 hours. The dried leaves were then ground into fine powder form using a blender. An airtight container was used to store and seal the ground powder to ensure no contact of atmospheric moisture.

Preparation of Adsorbate

Fe(II) stock solution was prepared at a concentration of 500 mg/l by the dilution of exactly 1.464 g of $PbSO_4$ with 500 ml of distilled water in a 500 ml volumetric flask. This particular stock solution was then further diluted to preferred concentrations that were required during the later stage of the experimental study.
Molecular weight of $FeSO_4$ = 278.02 g/mol
Formula weight of Fe = 55.845 g/mol

$$\frac{500 \text{ mg of Fe}}{\text{L}} \times \frac{1\ g\ of\ Fe}{1000\ mg\ of\ Fe} \times \frac{278.02\ g/molof\ \text{FeSO4}}{55.845\ g/mol\ of\ Fe} \times\ 1L. \qquad (1)$$
$$= 1.25\ g\ of\ \text{PbSO4}$$

Procedure

Batch experiments were conducted by mixing 1.5 g of durian leaf powder with 300 ml of Fe solution in a 500 ml beaker using the jar, tester at desired initial Fe concentration, pH of the solution, contact time and mixing time. The mixing rate was given at 100 rpm for 2 hours until equilibrium was reached. Then, the mixing was halted and the powder was removed from the solution using a filter paper. The filtrate was then sampled to measure the concentration of Fe(II) ion using a spectrophotometer. All samples were carried out under the same standard condition as stated and the average results are computed.

The effect of pH on this particular study was investigated over a PH range 2 – 8. The batch experiment was carried out by mixing 1.5 g of durian leaf powder in 300 ml of Fe (II) stock solution at concentration of 10mg/L in a 500 ml beaker. The sample was mixed at a mixing rate of 100 RPM with 2 hours of contact time. The mixing rate was constant until the experiment reaches equilibrium. The pH of the solution is altered by dropping appropriate addition of 1.0 M of Hydrochloric acid (HCl) and/or 1.0 M of Sodium hydroxide (NaOH) to the 10mg/L lead solution.

The effect of both these scopes upon the rate of adsorption of durian leaf powder and Fe ions was investigated simultaneously. The study was conducted by mixing 1.5 g of durian leaf powder with 300 ml of 5 mg/L Fe(II) solution using a 500 ml beaker. Jar test was then carried out to mix the sample at 100 rpm over various time periods such as 5, 10, 20, 30, 60, and 120 minutes. The step above was then repeated at different concentrations of Fe(II) solution (3.0 mg/L, 10 mg/L, 20 mg/L and 30 mg/L).

The effect of mixing rate upon the rate of adsorption of durian leaf powder and Fe ions was investigated by adding 1.5 g of durian leaf powder to 300 ml of 5 mg/L Fe(II) solution in a 500 ml beaker and mixed using jar test equipment over time periods of 5, 10, 20, 30, 60 and 120 minutes. The mixing rate was manipulated at 50, 100, and 150 rpm.

The effect of the particle size of adsorbent upon the rate of adsorption of durian leaf powder and Fe ions was investigated by adding 1.5 g of durian leaf powder to 300 ml of 5 mg/L Fe(II) solution in a 500 ml beaker and mixed using jar test equipment over a stirring speed of 100 rpm for 120 minutes. The above step was repeated for 5, 10, 20, 30, and 60 minutes and also by manipulating the particle size of the durian leaf powder by < 0.600 mm and > 0.600 mm. The size of the adsorbent particle was analysed using sieve analysis.

The influence of durian leaf powder on the adsorption of Fe (II) ions was studied in this study. Langmuir and Freundlich were the two isotherm models being used here in order to interpolate the graphical analysis of the adsorption equilibrium. The survey was directed from the result of the effect of contact time (5, 10, 20, 30, 60 and 120 minutes) and initial concentration of metal ion (3.0 mg/L, 5mg/L, 10 mg/L, 20 mg/L and 30 mg/L). The equation below was used to calculate the quantity of Fe ion adsorbed by the durian leaf powder.

$$q = (C_o - C_e) V/m. \quad (2)$$

where, q_e = Amount of Fe(II) ions adsorbed at equilibrium (mg/g), C_o = Initial concentration of Fe(II) solution (mg/L), C_e = Concentration of Fe(II) at the equilibrium state (mg/L), V = Volume of metal solution (L), m = mass of adsorbent (g)

An adsorption isotherm model is a curve relating the equilibrium concentration of a solute to the surface of an adsorbent, qe, to the concentration of the solute in the liquid, Ce, with which it is in contact. It is also an equation relating the amount of solute adsorbed onto the solid and the equilibrium concentration of the solute in solution at a given temperature.

RESULT AND DISCUSSION

Effect of PH

The consequence of pH of the Fe (II) solution upon the adsorption efficiency was studied by altering the pH of the solution within a range of 2 – 8 (Figure 1). The result showed that the absorption rate increased at the beginning from pH 2 to 5. At pH 2 which has the highest acidity value, the concentration of Fe (II) ion removed was at least. This is because at low pH the concentration of H^+ ions is greater. Hydrogen ions tend to compete with metal ions for the adsorption site of the adsorbent. This ascribes that at higher concentration of H^+, the adsorbent becomes more positively charged. This hinders the electrostatic attraction between the metal and the adsorbent. The maximum metal uptake is around pH 6.0 by 81.0%. At this point, the concentration of hydrogen ions would be at least. Thus, more negatively charged adsorption site of adsorbent will be available for metal ion attraction.

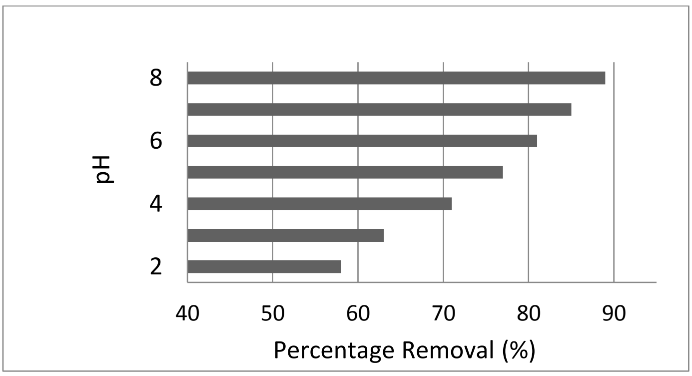


Figure 1: Effect of pH of Fe (II) solution on the uptake of Fe(II) ions by durian.

Effect Of Initial Concentration of Fe(II) ions and Contact Time

Equilibrium time is a crucial operational aspect to ensure an economical wastewater treatment process. During the initial few minutes, faster rate of absorption was observed at all different concentrations (53.0%, 71%, 60.5%, 49.5%, 42.3%)(Figure 1). Almost half of the concentration has been adsorbed within initial few minutes in regard of different concentrations. This is due to the availability of the larger surface area of the adsorbent for the adsorption of metals. With time, the removal efficiency rate becomes almost negligible. This is because of the swift depletion of the adsorption sites.

As the agitation time prolongs, the adsorption coherence increases until adsorption equilibrium is established. It is found that all concentrations attained equilibrium at the 60th minute of mixing (Figure 3). The rapid metal uptake was by 58.5%, 83%, 73.5%, 54.5%, and 46.3% of initial concentration of 3 mg/L, 5 mg/L, 10 mg/L, 20 mg/L and 30 mg/L respectively.

As per the initial concentration of Fe(II) ion factor, the removal mechanism is described as below. Initial removal is rapid with an inflating concentration of metal ion and slowed down with higher concentrations. The metal uptake was the highest when the initial concentration was 5 mg/L by 83.0%, whereas the metal uptake was only by 46.3% at an initial concentration of 30 mg/L. This is because of lower concentration the ratio of the metal ion number of the adsorption sites that are available is small.

At higher concentration, the adsorption specific sites become saturated and the exchange sites are filled. When the amount of adsorbent is fixed, the concentration of metal absorbed increases with increasing concentration of metal. However, the percentage of removal of metal ions decreases. Rapid metal uptake is found to be when the concentration of the metal solution is 5 mg/L.

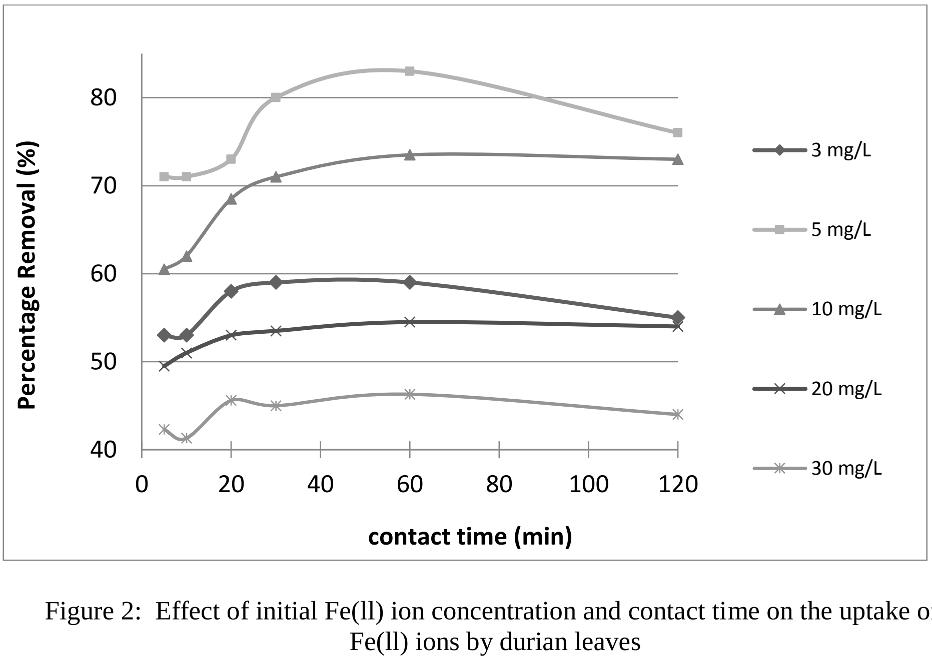
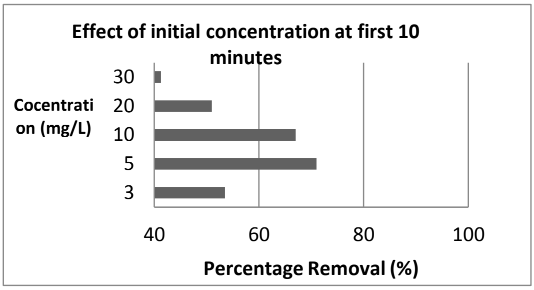


Figure 2: Effect of initial Fe(ll) ion concentration and contact time on the uptake of Fe(ll) ions by durian leaves



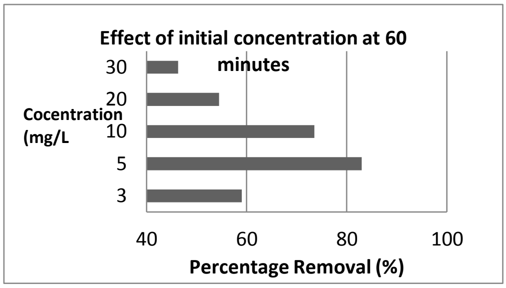


Figure 3: Effect of initial Fe(ll) ion concentration and contact time on the uptake of Fe(ll) ions by durian leaves in the first 10 minutes and 60th minutes

Effect of Mixing Time

It is the combination of both stirring speed and time taken to stir the sample. In this particular study, the adsorption capacity that is affected by the speed of mixing and time taken to mix resulted in the following:-
As the speed of the stirring increases, the adsorption capacity is increased in terms of boundary layer thickness. During the initial 5 minutes the metal uptake was by 49.0%, 61.0%, 66.0% for the mixing rate 50rpm, 100rpm and 150rpm respectively (Figure 4). By raising the speed of mixing, the thickness of the adsorbent particles' boundary layer is reduced. Hence, this made it available for more concentration of Fe ion to encounter with the adsorbent surface as shown in Figure 5. However, at a vigorous speed, the ferum ions desorbed from the adsorbent surfaces by breaking their newly formed unstable bond. Therefore, stirring speed should be maintained at an average rate.

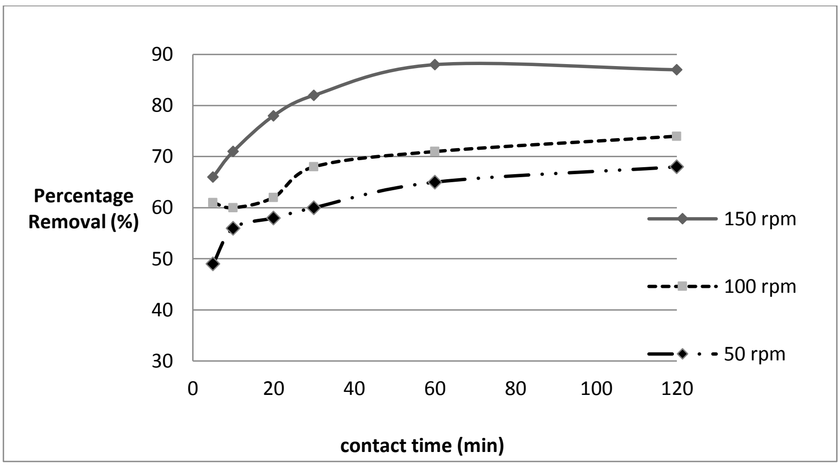


Figure 4: Effect of mixing time on the uptake of Fe(ll) ions by durian leaves

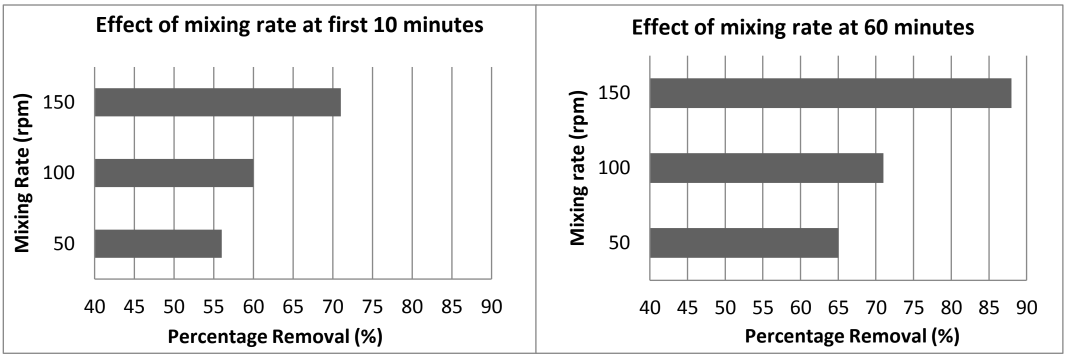


Figure 5: Effect of mixing time on the uptake of Fe (ll) ions by durian leaves at the first 10th minute and 60th minute

Effect of Particle Size of Adsorbent

Particle size of adsorbent has a significant influence on the adsorption capacity. The increase in the area per unit weight of the adsorbent has a limited effect on the metal adsorption rate. This experiment is conducted by using two different particle size, which were < 0.600 mm and > 0.600 mm and they were able to remove Fe (II) ions by 59.0% and 48.0 respectively during the initial 5 minutes. As per this study, the percentage of metal removal has increased with the decrease of particle size. This is due to the fact that smaller particles have larger surface areas. They tend to yield shorter time to reach equilibrium (Amuda, O. et.al., 2007).

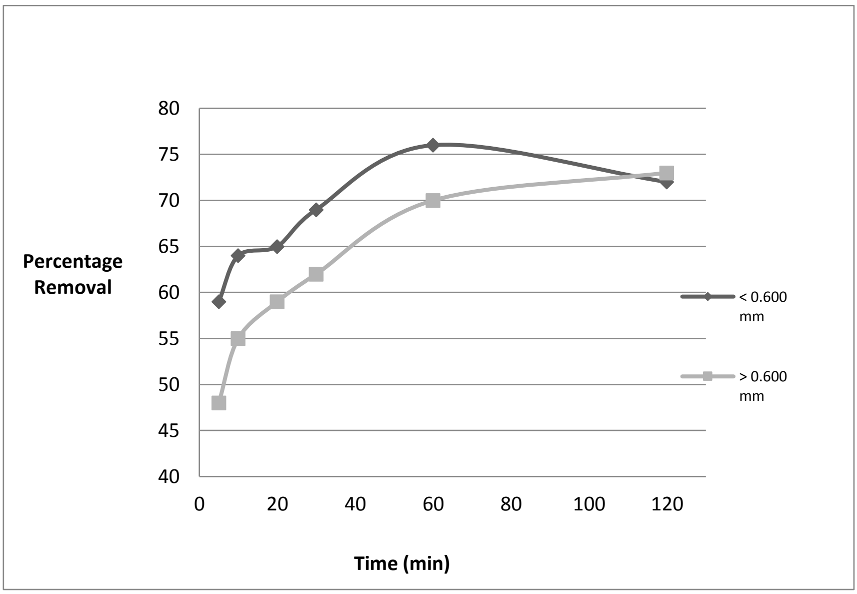


Figure 6: Effect of particle size of adsorbent on the uptake of Fe (ll) ions by durian leaves

BIOSORPTION EQUILIBRIUM ISOTHERMS

Freundlich Isotherm Model

The plot of log q_e vs log C_e is illustrated in Figure 7. This plot shows the Freundlich isotherm model that describes the adsorption relationship between Fe(II) ions and the durian leaves. The graph gives out a correlation coefficient of 0.7397 which is close to unity. This testifies that the data obtained can adjust well with Freundlich isotherm model. The plot gives out the values of K_F and n as 1.6203 and 1.788 respectively. The adsorption process carried out is considered affirmative as the value of n lies between the ranges of 1 to 10.

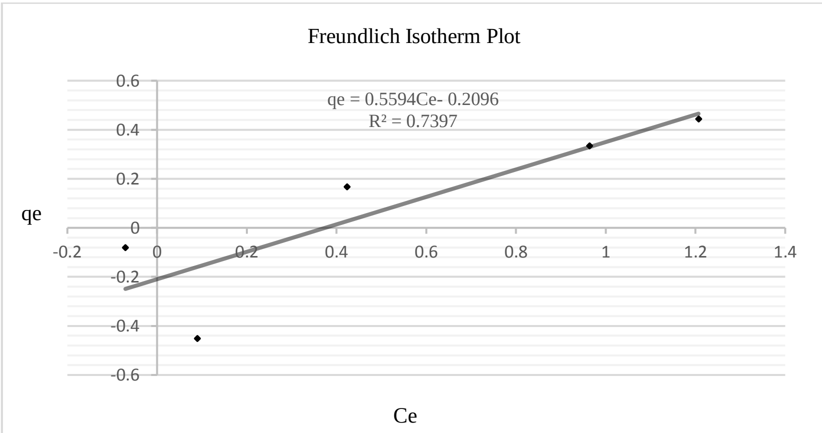


Figure7: Freundlich isotherm plot for the adsorption of Fe(II) ions onto durian leaves

Langmuir Isotherm Model

The plot of C_e/ q_e vs C_e is illustrated in Figure 8. This plot shows the Langmuir isotherm model that also describes the adsorption relationship between Fe(II) ions and the durian leaves. The graph gives out a correlation coefficient of 0.7736 which is close to unity. This testifies that the data obtained can also adjust well with the Langmuir isotherm model. According the Langmuir Equation, the maximum adsorption capacity for Fe(II) ions is 3.914 mg/g.

All the R_L values of each initial concentration of Fe solution studied were in the range of 0 and 1. This justifies that the adsorption of Fe(II) ions onto durian leaves is modelled in a favourable isotherm shape.

Table 1: Initial Fe (II) ion concentration and their R_L values

C_o (mg/L)	R_L
3.0	0.6937
5.0	0.5760
10.0	0.4045

20.0	0.2535
30.0	0.1846

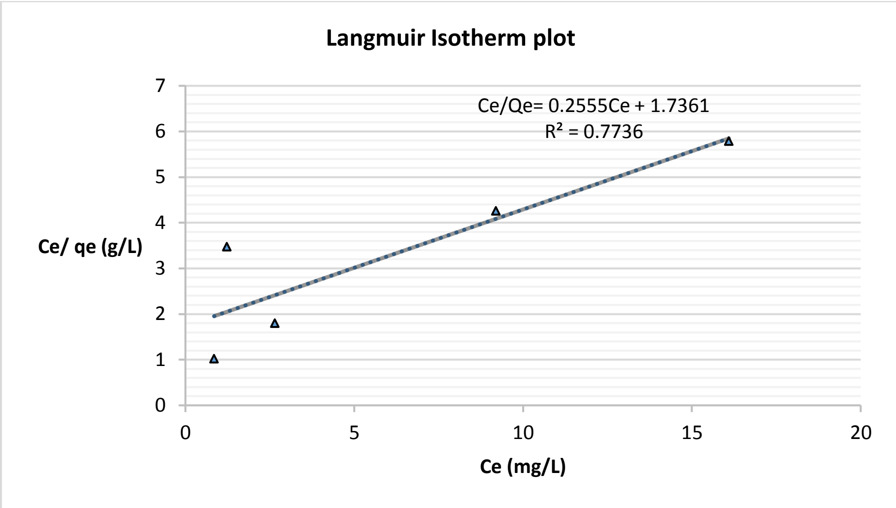


Figure 8: Langmuir isotherm plot for the adsorption of Fe (II) ions onto durian leaves

It is proved that the adsorption data obtained can confirm well to both Freundlich and Langmuir isotherm models. However, the data tend to fit better towards a Langmuir Isotherm model as the correlation coefficient plotted using this model (0.7736) is much closer towards unity.

Table 2: Isotherm parameters for Freundlich and Langmuir Isotherms

Freundlich isotherm			Langmuir isotherm		
q_m (mg/g)	K_L	R^2	K_F (mg/g)	n	R^2
3.914	0.1472	0.7736	1.6203	1.788	0.7397

Table 3 Comparison of Fe(II) ions removal by different adsorbents

Adsorbent	**q_m**	**Reference**
Durian leaves	3.9140 mg/g	Current study
Granular activated carbon	3.6010 mg/g	Josoh et.al., 2005
Cucumis Melo Rind	4.9800 mg/g	Othman, N. and Asharuddin, S.M. 2013

Josoh, et al. (2005) who studied the adsorption of iron onto granular activated carbon also obtained a similar type data. Cucumis melo rind is used by (Othman and Asharuddin 2013) to remove Fe(II) ion at a maximum capacity of 4.98 mg/g. All those above researches had come up with the suggestion of using the Langmuir model for graphical modulation of form removal process through adsorption.

CONCLUSION

The result obtained from this study showed that the removal of Fe (II) ions from solution is highly influenced and affected by pH of the solution, contact time and initial metal ion concentration, mixing rate and the particle size of adsorbent. Equilibrium is reached at the 60^{th} minute of batch mixing process and the optimum pH for adsorption is found to be pH 6. The increase in contact time and a decrease in Fe (II) ion concentration tends to increase the rate of removal of Fe (II) ion. The optimum concentration is thus considered to be 5 mg/L.

The equilibrium data adjusted well with the Langmuir isotherm model by giving out a correlation coefficient of 0.7736. This indicates that a monolayer pattern is followed by the adsorption mechanism of Fe (II) ion onto durian leaves. The maximum adsorption capacity determined using the Langmuir isotherm model is 3.914 mg/g. The characterization of this process proves that durian leave has high potential to be used as an alternative bio adsorbent for Fe (II) ion removal in aqueous solution through the adsorption mechanism since it is effective, cost saving, abundant in amount, and can be obtained easily.

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