Remediation of Heavy Metals Using Selected Agricultural Waste: Sunflower Husk and Durian Leaves

Manal M Abood, F Istiaque and N N Azhari
Civil Engineering Department, Faculty of Engineering, Infrastructure University Kuala Lumpur (IUKL), 4300, Kajang, Selangor, Malaysia

Abstract. This study revealed the behaviour of sunflower husk (SFH) and durian leaves (DL) as an adsorbent that could treat the aqueous solution to be free of heavy metal ions. The batch method was utilized. The influence of pH, contact time and initial metal concentration were described. The impact of pH on the uptake levels of the metal particles by both selected adsorbents were delineated between pH 4 to pH11. It was observed that the best value of pH for copper and zinc removal was 8 in case of SFH and it was 9 for DL. The process tends to be rapid the initial 10 minutes for SFH and 5 minutes for DL and an equilibrium time of two hours was needed for the copper and zinc particles adsorption onto SFH and an equilibrium time of one hour was needed for the copper and zinc adsorption onto DL. The Freundlich and Langmuir isotherm models are used to decide the adsorption parameters. The Freundlich isotherm model tends to fit the equilibrium data better than Langmuir isotherm model. The outcomes demonstrated that SFH and DL hold great potential to be utilized as low cost dry biomass adsorbent in the order SFH < DL.

1. Introduction
Wastewater Wastewater refers to the release from assembling plants, rural exercises, household, business and commercial. Or it might be a surface water and storm water. Most recent couple of decades, industrial wastewater has moved toward becoming one of the primary sources of water contamination. The purification of surface water has been influenced by the appearance of heavy metal as the significant contaminations for the aquatic conditions through the release of industrial wastes, storm water runoff, and human exercises. Although numerous heavy metals are essential for people, plants and animals in follow sums, however, the utilization of bigger sums prompts intense and perpetual harmfulness which connected to learning incapacities, cancers, and sometimes death. [1].

Over the most recent couple of years numerous inquiries about have been led to opined the removal of heavy metals by utilizing agricultural materials such as Sawdust [2], Pomegranate [3], Micro particles of dry plants [4], waste tea leaves [5], saraca indica leaf [6], tobacco stems [7], neem leaf powder [8], [9] Studied the removal of iron utilizing the shell of almond as adsorbent, and [10] utilized the Tilapia Mossambica as an Adsorbed, while [11] describe the utilization of rice husk as adsorbent for the removal of iron particle from the solution.

The existing technology, in generally, dissolvable extraction, precipitation, liquid film and ion exchange are presently being utilized to remove heavy metals from wastewaters. However, these regular materials have a proficiency to be applied as adsorbents with minimal cost as they serve as unused resources, are for the most part naturally well-disposed and are likewise within reach [12]. Normal adsorbents or all the more delicately known as bio sorbents that were previously used for research of utilization of heavy metal such as pomegranate peel, tea leaves, sawdust, , maize bran,
wood ash. In this research, Sunflower Husk (SFH) and Durian Leaf (DL) are being used as a low cost adsorbent. In the South East Asia areas, Durian (Durio Zibethinus) is an outlandish organic product which is notable. Numerous tropical nations devour it in an enormous sum, along these lines durian estates covers a colossal regions in this locale. The estimation of hectare in repeating crops was 75,713.1 hectares in 2013, while the yearly creation added up to 373,087 million tons. It was observed to be the biggest organic product cultivate inside Malaysia as indicated by the Agriculture Department Fruit Crop Statistics.

As an organic product creation, durian estates can be viewed as one of the biggest waste producing natural product area. The durian leaves has been chosen to be studied as an adsorbent for the utilization of heavy metals from industrial waste released since it is of no utilization for any commercial purposes.

The yearly making of sunflower was 9,273,000 tons as shown by the oil world section, it is seen to be the greatest bloom home in Malaysia. It is being devoured enormously all over tropical region, and thusly, huge zones are being put something aside for sunflower estate.

This study is a part of full research has been conducted to predict the utilization of SFH and DL as adsorbent with a minimal cost for the remediation of zinc and copper particles from aqueous solution and to determine the impact of pH, initial concentration of Zn (II) and Cu (II) particles and contact time, on the uptake of Zn (II) and Cu (II) particles on the surfaces of SFH and DL.

2. Methodology

2.1 Preparation of adsorbent materials

SFH was collected from the local market. It was washed softly using the distilled water to remove dust, then it was ground using laboratory mill, sieved to 0.5-0.8 mm before use. From local house yard in Kajang, Selangor Malaysia, DL were collected. To remove dust and different pollutions, each leaf was washed thoroughly by utilizing tap water. The DL were dried under daylight for 7 days until the point when the leaves transformed into darker shading. The leaves were additionally dried in a broiler at 105°C for 1 day, at that point grounded into powder shape by utilizing blender. To ensure no contact of atmospheric moisture, the DL was put away in impermeable compartment and seal the ground powder.

2.2 Reagents and chemicals

Solutions of various concentrations were gotten by diluting the stock solution with distilled water. Stock solutions of Zinc sulfate, Copper sulfate 1000 mg/l were utilized as adsorbate, zinc and copper concentrations were controlled by spectrophotometer. All experiments were completed in 500 ml glass bottles at the research centre temperature of 25 ± 2°C, and every one of the synthetic concoctions utilized were of diagnostic review reagent.

2.3 Experimental work

Exploratory work utilizing batch adsorption strategy were performed by mixing a series of jugs containing different measures of SFH and DL and heavy metal particles independently at ideal pH. 1.5 g of the two adsorbents with 300 ml of copper in form of copper sulphate mixed in a 500 ml beaker, similarly, zinc in form of zinc sulphate had been mixed in a 500 ml beaker. The pH was adjusted to a desire value using 0.1M of H₂SO₄ and 0.1M of NaOH and the pH was balanced, a jar test machine was used at 150 rpm mixing rate and keep running for 2 hours of contact time until equilibrium is come to. At that point, toward the finish of mixing the adsorbent particles were isolated from the suspensions by filtration through 0.40 µm filter paper. The filtrate is then sampled to measure the concentration of copper and zinc ions using a spectrophotometer. All samples are done under standard condition and the normal outcomes are figured.
3. Results and Discussion

3.1 Viability of pH
By modifying the pH of the solution within a range of 3 – 11, the result of pH of the selected heavy metal solutions upon the adsorption of SFH and DL effectiveness was displayed. The outcomes got as shown in Fig. 1(a) and (b) demonstrated that zinc and copper ions were adequately adsorbed in pH range (4-9), and the adsorption rate expanded toward the start from pH 5 to 8. At pH 4 which has the highest acidity value, the concentration of zinc and copper particles removed was at a minimum. This is due to fact that the H⁺ ions will be greater at low pH the concentration. Hydrogen particles have a tendency to contend with metal particles for adsorption site of the adsorbent. This credits at higher grouping of H+, the adsorbent turns out to be all the more emphatically charged. This obstructs the electrostatic fascination between the metal and the adsorbent. Most extreme adsorption happened for zinc and copper particles by utilizing DL take place at pH 7 while the greatest adsorption of zinc and copper utilizing SFH take place at pH6. Presently, the gathering of hydrogen particles would be in any event. This is in concurrence with the outcomes acquired by [5] for adsorption of heavy metals onto tea leaves.

3.2 Initial concentration impact
The impact of initial concentration on Copper and Zinc remediation was investigated and completed at 25 ± 2 °C utilizing various initial metal ion concentrations (10, 20, 40, 60, 80 and 100 mg/l) at rpm 150 and optimum ph. The outcomes are shown in Figure 2 (a) and (b), which demonstrated that the percentage uptake decreases with the increments in primary stage of metal ion concentration. This is on account of there were no more adsorption locales on the adsorption surface of the adsorbent material. The outcomes showed that the copper uptake for the initial 20 minutes was 85% by utilizing DL and 70 % by utilizing SFH, while the zinc uptake following 20 minutes was 90% utilizing DL and 77% utilizing SFH.
It was discovered that the level of remediation of metal ions decreases with the increments of primary concentration. Rapid metal uptake is observed to be when the concentration of the metal solution is 10 mg/L.

3.3 Contact time impact
The impact of contact time on the remediation efficiency of SFH and DL for copper and zinc particles was considered: the outcomes are shown in Figure 3(a) and (b). The uptake of metal particles in the initial 20 minutes, utilizing SFH was 63% for zinc and 48% for copper at equilibrium 81% of Cu particles and 70% of Zn particles are remediate. While by utilizing DL, the percentage uptake reach to 70% of Cu and 78% of Zn following 20 minutes and reach to 83% for Cu and 93% for Zn at equilibrium following 2 hours.

Figure 1. Impact of pH on copper and zinc uptake using SFH and DL
Figure 2. Impact of initial concentration on copper and zinc uptake using SFH and DL

Figure 3. Impact of contact time on copper and zinc uptake using SFH and DL

3.4 Freundlich isotherm model

The Freundlich Model, an adsorption isotherm, is an observational connection between the concentration of the solute in the fluid and the concentration of a solute on the surface of an adsorbent. This relation is to give an expression incorporating the surface heterogeneity and the exponential distribution of active sites and their energies. The Freundlich isotherm is defined as:

\[ Q_e = K C_e^{1/n} \]  

Ce is the equilibrium concentration in mg/l, qe = amount of adsorbate adsorbed per unit weight of adsorbent (mg/g). “k” is a parameter identified to the temperature and “n” is a constant for the adsorption framework under investigation. The plots of log Qe versus log Ce are shown in Figure 4(a) and (b); the adsorption of Zinc and copper particles onto the SFH and DL gave a straight line with R² equivalent to 0.93 for copper and equivalent to 0.98 for zinc in DL and gave R² equivalent to 0.96 for copper and equivalent to 0.85 for zinc in SFH; estimation of “n” somewhere in the range of 0.9 and 1.2 demonstrate a good adsorption. The constants and R² for Freundlich isotherm model are listed in table 1.
Figure 4. Plot of Freundlich for both adsorbents, SFH and DL for copper and zinc removal

Table 1. Constant for uptake of copper and zinc onto SFH and DL (Freundlich Model)

| Heavy Metal | Adsorbent | Freundlich constant | R²  |
|-------------|-----------|---------------------|-----|
|             |           | k       | n       |     |
| Cu          | SFH       | 0.12    | 1.2     | 0.96|
|             | DL        | 0.12    | 1.19    | 0.93|
| Zn          | SFH       | 0.13    | 0.96    | 0.85|
|             | DL        | 0.19    | 1.2     | 0.98|

3.5 Langmuir isotherm model

The Langmuir equation depends on the assumptions that greatest adsorption relates to an immersed mono-layer of adsorbate particles on the adsorbent surface, that the vitality of adsorption is steady, and that there is no transmigration of adsorbate in the plane of the surface.

The Langmuir isotherm is defined as:

$$Q_e = (K_LQ_mC_e)(1+ K_LC_e)$$

Where $Q_m$ and $K_L$ are Langmuir constants identified with the sorption limit, and sorption vitality, respectively. $C_e$ is the equilibrium concentration in mg/l, and $q_e$ is the amount of adsorbate adsorbed per unit weight of adsorbent (mg/g). The plots of $C_e/q_e$ versus $C_e$ are shown in Figure 5(a) and (b): the adsorption of copper and Zinc particles on SFH and DL gave a straight line with correlation coefficient, $R^2$ equivalent to 0.97 for copper and 0.88 zinc with DL, and $R^2$ equivalent to 0.94 for copper and 0.87 for zinc with SFH. It can be concluded that exploratory information were better fitted to the Freundlich equation than to the Langmuir equation, and hence it is more reasonable for the examination of kinetics particularly for DL. The constants and correlation coefficients for Langmuir isotherm model are recorded in table 2.
Figure 5. Plot of Langmuir for both adsorbents, SFH and DL for copper and zinc removal

Table 2. Constant for sorption of copper and zinc onto SFH and DL (Langmuir Model)

| Heavy Metal | Adsorbent | Langmuir constant | R²   |
|-------------|-----------|-------------------|------|
| Cu          | SFH       | 0.20              | 0.94 |
|             | DL        | 0.18              | 0.97 |
| Zn          | SFH       | 0.12              | 0.87 |
|             | DL        | 0.09              | 0.88 |

4. Conclusion
The exploratory technique was utilized; parameters for example, pH, contact time and metal concentration were studied at an surrounding temperature 25± 2º C, the optimum pH comparing to the most extreme adsorption of copper and zinc remediation was 7–9. Copper and Zinc particles were adsorbed onto the adsorbents very quickly within the initial 20 min, while balance was accomplished within 2h for copper and zinc particles. It very well may be said that the minimal-cost adsorbent like sunflower husk (SFH) and Durian leaves (DL) is successful for the remediation of copper and zinc particles from aqueous solutions. The Freundlich isotherm better fitted the experimental data since the correlation coefficient for the Freundlich isotherm was higher than that of the Langmuir isotherm for the two metals.

5. Acknowledgments
Financial support from Department of Civil Engineering, Faculty of Engineering and Technology Infrastructure, Infrastructure University Kuala Lumpur (IUKL) and collaboration with research management centre (RMC) is highly appreciated to complete this research.

6. References
[1] Chaturvedi S and Dave P N 2012 Desalination. 303 1
[2] Yasemin B and Zeki T 2007. Journal of Environmental Sciences. 19 160
[3] El- Ashtoukhyy E S, Amin N and Abdelwahab O Desalination 223 162
[4] Benhima H Chiban M Sinan F Seta P and Persin M 2008. Colloids and Surfaces B: Biointerfaces 61 10
[5] Ahluwalia S and Goya D 2005. Engineering in Life Sciences 5 2
[6] Goyal P Sharma P, Srivastava S, and Srivastava M 2008. Environmental Science Technology 5 1, 27.
[7] Li W, Zhang L, Peng J, Li N, Zhang S and Guo S 2008. Industrial Crops and Products 28 295
[8] Bhattacharyya K G., and Sharma A 2004. *Journal of Hazardous Materials* B**113**, 97
[9] Anusha D G and Raja Murugadoss, DJ 2014. *International Journal of Scientific Research* 3 10.
[10] Zayadi N and Othman N 2013. *International Journal of Integrated Engineering*, 5 23.
[11] Kadir A , Abdullah A and Wai L 2013. *University Hussein Onn*.
[12] AbdelGhani N, Hefny M. and El-Chaghaby G. 2007 *Int. J. Environ. Sci. Tech*, 4 1 67.