The Elimination of Heavy Metals-Containing Wastewater by Adsorption using Adsorbent Made from Paphia Undulata ("Siput Retak Seribu")

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***Abstract*— Water is widely used in household area and in industries. In order to keep the clean water supply in line, wastewaters needed to be treated before they can be reuse again. The objectives of this study were to prepare adsorbent made from Paphia Undulata ("Siput Retak Seribu') and investigate its effectiveness in removing heavy metals of zinc and iron. The effects of initial adsorbent dosage and contact time were studied. The maximum uptake of zinc ions was obtained at 99% with the dose of 0.75 g of calcined adsorbent and 97% with the dose of 0.50 g for iron. The optimum contact time for zinc and iron to be 99% removed by the calcined adsorbent from the synthetic wastewater was in 30 minutes. The Paphia Undulata could be considered as an effective, low-cost adsorbent to be used for heavy metals removal from wastewater.**

Keywords*— adsorption, heavy metals, Paphia Undulata, wastewater

I. INTRODUCTION

In general, water is one of the essentials that needed by all living things such as plants and animals. Water is obtained from two natural sources; surface water such as fresh water, lakes and rivers; and ground water such as well and borehole. Water does not exist in pure composition as it may contain contaminants that arise from surrounding, mostly by the human activities. The human activities used in this context are from industrial, where they converted raw materials into useful desirable products. However, they also generate waste products in the form of solid, liquid or gas that leads to the creation of hazards, pollution and loses of energy. Most of solid wastes and wastewaters are discharged into the soil and water bodies. Hence, they pose a serious threat to human and routine functioning of ecosystem.

Tariq et al. (2006) investigated that high levels of pollutants in river water causes an increase in biological oxygen demand (BOD), chemical oxygen demand (COD), total dissolved solids (TDS), total suspended solids (TSS), toxic metals such as cadmium, chromium, nickel and lead. Wastewaters containing toxic metals are mainly from textile industries, metal plating, mining operations, tanneries, alloy industries and storage batteries industries [1]. Thus, making such water no longer appropriate for drinking, irrigation and aquatic life [2].

There are several treatments available that can be used to treat wastewater. The treatments are reduction and precipitation [3], coagulation-flocculation [4], electroflocculation [5], adsorption [6], ion-exchange [7], reverse osmosis [8], electrodialysis [9] and membrane and ultramembrane filtration [10]. However, these methods consume high capital and regeneration costs of the materials. Recent studies have shown that heavy metals can be removed by adsorption using shells such as cockle shells [11] and eggshells [12] as an adsorbent.

In this study, the adsorbents were made from the shells of Paphia Undulata ("Siput Retak Seribu"). They are easily obtained near the coastal area, mostly in Perlis, Malaysia due to their abundance. The chemical composition found in this shell was mainly from carbonate group which were calcium carbonate, $CaCO_3$ and calcium oxide, CaO. The carbonate ions were responsible in attracting the heavy metals ions through adsorption and subsequently, removing them from wastewater.

The present study was aimed to:

- prepare and characterize adsorbent made from the shells of Paphia Undulata ("Siput Retak Seibu");
- study the effectiveness of the prepared adsorbent in removing heavy metals such as zinc and iron from the synthetic textile wastewater.

The effect of the initial amount dosage of adsorbent and contact time on the adsorption performance of Paphia Undulata was studied.

II. METHODOLOGY

A. Preparation of the Adsorbent

Five kilogram of Paphia Undulata shells was bought from the local market. Paphia Undulata shells underwent physical wash where the shells were cleaned by using deionized water several times to ensure the dust particles were removed completely. The shells were dried in an oven with temperature of 100°C for 24 hours to remove any moisture within the shells. Once the shells dried completely, the shells were crush by using cutting mill until they turned to powder form. For calcinations, the sample was placed in a crucible and heated up to 500, 600 and 700°C with a constant heating rate of 20°C/min in a furnace. The shells powders were sieved to 355 micron and were stored in sealed plastic bags.

B. Preparation of the Synthetic Wastewater

Synthetic wastewater samples were prepared by using analytical grade of zinc (II) sulphate from R&M, Malaysia and iron (III) chloride from Merck, Malaysia. Two 1 L of stock solutions contained 20 ppm of each heavy metal. For the pH adjustment throughout the experiment, 0.1 M HCl and 0.1 M NaOH solutions were used as necessary.

C. Preparation of Samples for Various Initial Adsorbent Dosage

Synthetic wastewater containing 20 ppm of each heavy metal was prepared by combining them with 1 L of distilled water to obtain 20 ppm of stock solutions. 50 mL of the synthetic

wastewaters from each heavy metal were taken and were inserted into 5 different 200 mL conical flasks. For each adsorbent, 5 sets of experiment were conducted at multiple initial dosage of adsorbent of 0, 0.25, 0.50, 0.75 and 1 g. The samples were placed in the incubator shaker for 2 hours. Afterwards, the solutions were filtered to separate the adsorbent and the solution.

D. Preparation of Samples for Various Contact Time

Synthetic wastewater containing 20 ppm of each heavy metal was prepared by combining them with 1 L of distilled water to obtain 20 ppm of stock solutions. 50 mL of the synthetic wastewaters from each heavy metal were taken and were inserted into 3 different 200 mL conical flasks. For each adsorbent, 3 sets of experiment were conducted with interval of 30 minutes. 1 g of adsorbent was to be added to each of these flasks and were placed in the incubator shaker for 30, 60 and 90 minutes. Afterwards, the solutions were filtered to separate the adsorbent and the solution.

E. Characterization of Adsorbent

The functional group present in the adsorbent was determined by Fourier Transform Spectroscopy (FT-IR). Meanwhile, the surface area and total pore volume of adsorbent was measured by using the Brunauer-Emmett-Teller method. The porosity of the adsorbent samples was measured by collecting the nitrogen gas adsorption and desorption isotherms at $P/P_o = 0.99$ at 77 K from which the BET surface area was calculated. Both equipment situated at Instrumentation Laboratory II, Faculty of Chemical Engineering, Universiti Teknologi MARA, UiTM Shah Alam, Selangor.

F. Heavy Metal Analysis

Metal concentrations were measured by Atomic Adsorption Spectroscopy (AAS). The samples were analysed by Instrumentation Laboratory II at the Faculty of Chemical Engineering, Universiti Teknologi MARA, UiTM Shah Alam, Selangor. The metal analyses were compared for the final concentration of wastewater after adsorption had occurred and the deviation was found to be minor.

III. RESULTS AND DISCUSSION

A. Characterization of the Adsorbent using FT-IR and BET analysis

The characterization of the adsorbents was conducted by using FT-IR to determine the functional groups present. Fig. 1 displayed the peak of frequency level of uncalcined adsorbent and calcine adsorbent at a temperature of 500, 600 and 700°C. The chosen temperature was the optimum temperature of Paphia Undulata before its chemical composition started to degenerate. The chemical composition found in the uncalcined adsorbent was calcium carbonate, $CaCO_3$. This can be seen by the adsorption peak produced at 1456.89 cm^{-1} and was assigned to carbonate ions. The peak at 1082.53 cm^{-1} was referred to C-O strong site stretching.

Calcination is a process where the adsorbent was burned in a high temperature furnace in order to increase a certain amount of a chemical composition. Calcinations was conducted to convert $CaCO_3$ into CaO and hence, increasing the amount of CaO in the adsorbent. The temperature implied was 500, 600 and 700°C for 2 h in a furnace with a heating rate of 20°C/min. In order to confirm the existence of CaO, calcination adsorbents underwent FT-IR analysis.

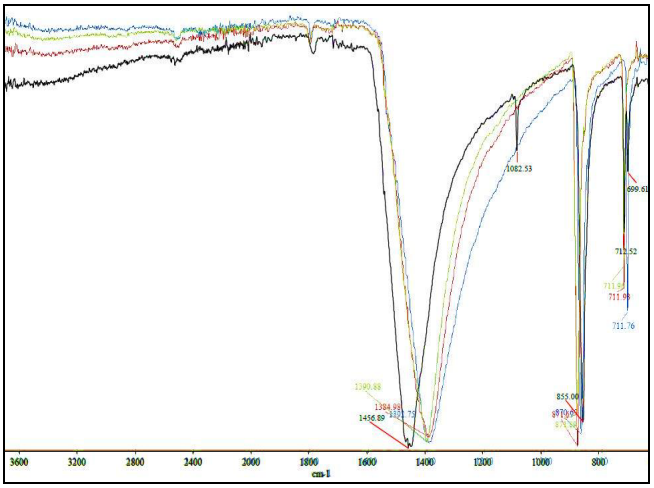

Fig.1: Peak of frequency level of uncalcined adsorbent (black line) and calcine adsorbent at 500°C (green line), 600°C (red line) and 700°C (blue line).

Table 1: Band shift before and after calcination process.

Types of adsorbent	Wavelength (cm^{-1})		Percentage band shift (%)
	Before	After	
Uncalcined	1456.89	1456.89	-
	1082.53	1082.53	-
Calcine at 500°C	1456.89	1390.88	4.53
	1082.53	871.89	19.46
Calcine at 600°C	1456.89	1384.98	4.95
	1082.53	871.67	19.48
Calcine at 700°C	1456.89	1392.75	4.40
	1082.53	870.69	19.57

As for calcine adsorbents, the FT-IR spectra formed ranging from 1500 to 1400 cm^{-1}. The only difference was they have shifted to the left side towards 1400 to 700 cm^{-1}. This indicated that the $CaCO_3$ had changed structure and its amount was decreasing to form CaO. The statement can be supported by the characteristic bands of the CaO structure at 711.76, 711.93, 711.96, 870.69, 871.67, 871.89, 1384.98, 1390.88 and 1392.75 cm^{-1}. The percentage band shift can be seen in Table 1.

BET method is essential in understanding the potential of an adsorbent in the adsorption process. Hence, the adsorbent was extensively tested by using the BET method for measuring the surface area and pore volume. The results of the adsorbent after BET analysis can be seen in Table 2.

Table 2: The physical properties of adsorbent made from Paphia Undulata tested using BET method.

Types of adsorbent	BET surface area (m^2/g)	Total pore volume (cm^3/g)
Uncalcined	2.3871	0.010858
Calcined at 500°C	0.8609	0.002579
Calcined at 600°C	0.6710	0.002072
Calcined at 700°C	0.6121	0.001482

In order to determine the highest BET surface area, the ratio analysis was conducted by determining in 1 m^2/g, how much the pore volume will be. The calculations can be seen in Table 3.

Table 3: Comparison by using ratio to determine highest BET surface area.

Types of adsorbent	BET surface area (m^2/g)	Total pore volume (m^3/g)
Uncalcined	1.0000	1.1×10^{-8}
Calcined at 500°C	1.0000	2.9×10^{-9}
Calcined at 600°C	1.0000	3.1×10^{-9}
Calcined at 700°C	1.0000	2.4×10^{-9}

From the results shown in Table 3, it can be depicted that the calcine adsorbent at 600°C has the highest BET surface area,

0.6710 m^2/g compared to others. For every 1 g of 1 m^2 of adsorbent surface area, the pore volume will be 3.1 x 10^{-9} m^3. The amount of pores was high and this affected the rate of adsorption as there were high amount of vacant sites for the metal ions to bind.

Meanwhile, the uncalcined adsorbent has the smallest pore volume, 0.010858 cm^3/g even though it had the largest surface area. Smaller pore volume resulted in less attachment of metal ions and adsorbent as less area was applicable for the adsorption to occur. The reduction in surface area may be due to the formation of calcium deficient apatites [13]. Roughly, the results concluded that Paphia Undulata had an extensive allocation for surface area and excellent pore volume, regardless uncalcined or calcine.

B. Factors Affecting the Adsorption of Heavy Metals Ions - Initial Adsorbent Dosage

The initial adsorbent dosage was varied from 0, 0.25, 0.50, 0.75 and 1 gram. The wastewater samples containing each adsorbent (uncalcined, calcined 500, 600 and 700°C) were placed in the incubator shaker for 2 h with rotary speed of 250 rpm at a room temperature. The initial concentration of wastewater containing zinc and iron of 20 ppm were expected to be reduced. In order to obtain more accurate data, the experiment was conducted in triplicates and the average of concentration was taken as the final concentration of wastewater.

The final concentration for zinc and iron obtained presented in Table 4 and 5, respectively. The percentage removal efficiency was calculated by using Equation 1;

$$\%R.E = \frac{C_o - C_f}{C_o} \times 100\% \qquad \text{Equation 1}$$

where C_o and C_f were the initial and final concentration of the wastewater after adsorption experiment, respectively. Adsorption was mainly a surface phenomenon as the amounts of the sites available were vacant for adsorption hence; the mass of adsorbent can extensively affect adsorption efficiency.

The zinc removal increased as the amount of the adsorbent increased and reached a maximum value at 0.75 g except for 'Calcine 700' when it was suddenly decreased. The calcination of adsorbent at 700°C caused a physical change as it turned to black compared to uncalcined adsorbent, which was white. The darker physical appearance of adsorbent may depicted that some of the adsorbent may have turned to ash. It was assumed that calcine adsorbent at 700°C has the composition of 50% of calcined adsorbent and 50% of ash and there were no vacant sites for metal ions to bind. Consequently, it affected the rate of zinc removal as ash cannot remove the zinc ions and thus explaining the decreased curve of "Calcine 700" in Fig. 2.

Table 4: Final concentration of zinc based on various initial adsorbent dosage using uncalcined, calcine adsorbent at 500, 600 and 700°C.

Types of asdorbent	Dosage (g)	Final conc. (ppm)	% R. E
Uncalcined	0.25	0.0204	99.89
	0.50	0.0268	99.86
	0.75	0.0273	99.80
	1.00	0.0251	99.87
Calcine at 500°C	0.25	0.1085	99.45
	0.50	0.0652	99.67
	0.75	0.0156	99.92
	1.00	0.0124	99.93
Calcine at 600°C	0.25	0.3819	98.09
	0.50	0.0090	99.95
	0.75	0.0222	99.88
	1.00	0.0349	99.82
Calcine at 700°C	0.25	0.0643	99.67
	0.50	0.0038	99.98
	0.75	0.0393	99.80
	1.00	0.1841	99.07

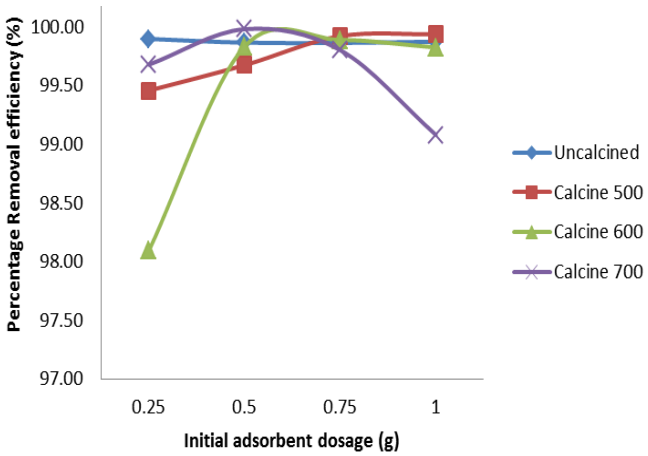

Fig. 2: Percentage removal of zinc using uncalcined and calcine adsorbent at 500, 600 and 700°C on initial adsorbent dosage.

Table 5: Final concentration of iron based on various initial adsorbent dosage using uncalcined and calcine adsorbent at 500, 600 and 700°C.

Types of asdorbent	Dosage (g)	Final conc. (ppm)	% R. E
Uncalcined	0.25	0.5852	97.07
	0.50	0.5577	97.21
	0.75	0.6065	96.96
	1.00	0.5940	97.03
Calcine at 500°C	0.25	0.5840	97.07
	0.50	0.5777	97.11
	0.75	0.5965	97.01
	1.00	0.5840	97.08
Calcine at 600°C	0.25	0.5690	97.15
	0.50	0.5840	97.08
	0.75	0.5752	97.12
	1.00	0.5352	97.32
Calcine at 700°C	0.25	0.5364	97.31
	0.50	0.5151	97.42
	0.75	0.5652	97.17
	1.00	0.5665	97.16

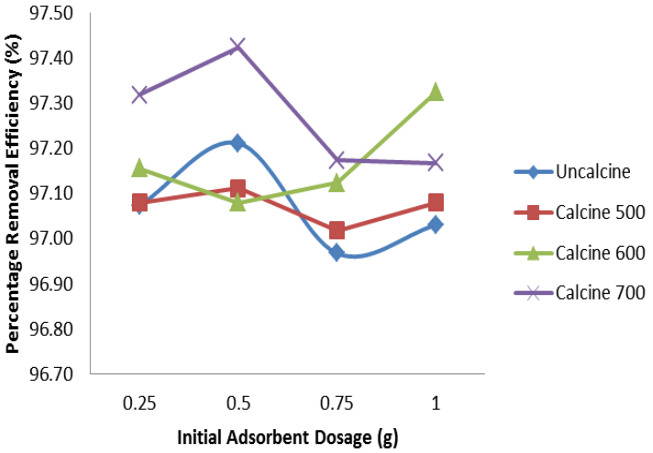

Fig. 3: Percentage removal of iron using uncalcined and calcine adsorbent at 500, 600 and 700°C on initial adsorbent dosage.

As for iron, the results of the adsorption were unexpected as there were fluctuations for all types of adsorbent. These findings suggested that the heavy metal removal may be affected by the pH and temperature of the synthetic wastewater, error in weighing the adsorbent or error in measuring the volume of the synthetic wastewater causing the metal ions to behave inappropriately. In order to avoid this from occurring, a thorough check-up of the synthetic wastewater containing adsorbent must first be conducted.

Regardless, the highest percentage of iron removal was by using 0.5 g based on the majority results.

C. Factors Affecting the Adsorption of Heavy Metals Ions - Contact Time

The percentage removal efficiency and the time required to reach the equilibrium were indicators of the adsorbate transfer kinetics from the liquid phase to the adsorbent surface. The change of zinc and iron adsorption onto shells of Paphia Undulata versus contact time was presented in Fig. 4 and 5, respectively.

Table 6 showed the final concentration of zinc and Fig. 4 showed the trends for zinc removal in contact time. Based on Fig. 4, the suitable adsorbent used to remove zinc in wastewater was uncalcined adsorbent and calcine adsorbent at 500 and 600°C. They successfully removed 99% of zinc in 30 minutes compared to calcined adsorbent at 700°C. The percentage removal increased slowly using calcined adsorbent at 700°C indicated that there was only limited surface area for the zinc ions to interact. The high temperature of calcinations had caused defection on the adsorbent surface area.

Table 6: Final concentration of zinc based on various contact time using uncalcined adsorbent.

Types of asdorbent	Contact time (min)	Final conc. (ppm)	% R. E
Uncalcined	30	0.0740	99.62
	60	0.0391	99.80
	90	0.0371	99.81
Calcine at 500°C	30	0.0491	99.75
	60	0.0447	99.77
	90	0.0636	99.68
Calcine at 600°C	30	0.1135	99.43
	60	0.0088	99.95
	90	0.0043	99.97
Calcine at 700°C	30	2.8109	85.94
	60	2.4351	87.82
	90	1.6898	91.55

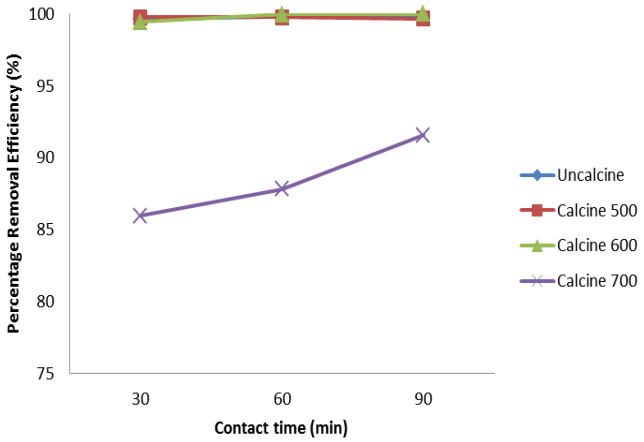

Fig. 4: Percentage removal of zinc using uncalcined and calcine adsorbent at 500, 600 and 700°C on contact time.

Table 7 displayed the final concentration of iron on various contact time and Fig. 5 was the data plotted for percentage removal efficiency versus contact time. For the removal of iron, the optimum contact time for uncalcined adsorbent and calcined adsorbent at 500 and 700°C was found to be in 30 minutes. Whereas, for calcined adsorbent at 600°C, 60 minutes was needed for it to become equilibrium. The slow rate can be due to the surface pores of adsorbent has been covered and troubled the metal ions to enter the interior of the pores in the first place. Hence, it can be concluded that the optimum contact time to remove iron almost completely was in 30 minutes. The shorter optimum time is preferable as it represent an economic advantage for waste water treatment.

Table 7: Final concentration of iron based on various contact time using uncalcined adsorbent and calcined adsorbent at 500, 600 and 700°C.

Types of asdorbent	Contact time (min)	Final conc. (ppm)	% R. E
Uncalcined	30	0.0132	99.93
	60	0.0127	99.93
	90	0.0115	99.94
Calcine at 500°C	30	0.0051	99.97
	60	0.0076	99.96
	90	0.0090	99.95
Calcine at 600°C	30	0.0247	99.87
	60	0.0041	99.97
	90	0.0558	99.72
Calcine at 700°C	30	0.0262	99.86
	60	0.0529	99.73
	90	0.0737	99.63

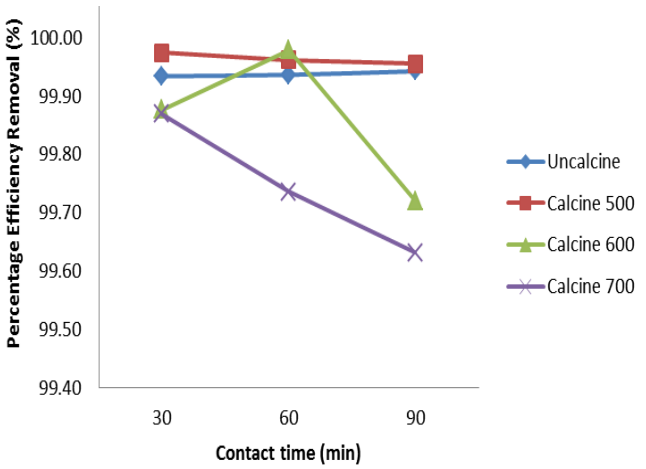

Fig. 5: Percentage removal of iron using uncalcined and calcine adsorbent at 500, 600 and 700°C on contact time.

IV. Conclusion

As a conclusion, the objectives of this study were met as it was found that the adsorbent made from the shells of Paphia Undulata has successfully removed the zinc and iron contained in the synthetic wastewater. The suitable dosage in discarding the highest zinc and iron concentration was 0.75 g and 0.50 g, respectively by using calcined adsorbent. As for optimum contact time, calcined adsorbent successfully removed zinc and iron in 30 minutes. This showed natural adsorbent especially that undergone calcination is a very efficient adsorbent for treating the wastewater. For future research, other parameters can be explored and implemented in this study to give a better understanding in the adsorption process using natural adsorbent.

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