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ADSORPTION OF ZINC, COPPER, AND IRON FROM SYNTHETIC WASTEWATER USING WATERMELON (*Citrullus Lanatus*), MANGO (*Mangifera Indica L.*), AND RAMBUTAN PEELS (*Nephelium Lappaceum L.*) AS BIO-SORBENTS

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Abstract

Fruit waste is one of the contributors to solid municipal waste. This study investigates the adsorption capacity of pretreated fruit peels like rambutan peels, watermelon peels, and mango peels in removing iron, copper, and zinc metal ions, initiated at a concentration of 100 mg/L. Experimental findings identified that pretreated rambutan peels is particularly good for iron (17.4mg/g, 87%) and zinc (14mg/g, 70%) metal ions adsorption compared to pretreated watermelon peels and mango peels. As for the adsorption of copper metal ions, the three fruit peels investigated share identical outcomes. The adsorption isotherm and kinetics models were later used to analyse the adsorption mechanism of the fruit peels. The result showed that the adsorption of iron (for three fruit peels), copper (for pretreated mango and watermelon peels), and zinc (for pretreated rambutan and mango peels) metal ions were favourable to Langmuir isotherm, which indicated a monolayer adsorption process. Whilst, the adsorption of copper (for pretreated rambutan peels) and zinc (for pretreated watermelon peels) metal ions were favourable to Freundlich isotherm, indicating a multilayer adsorption process. Pseudo Second Order model also highlighted chemisorption as the dominant adsorption process in this study as it fits well with a high correlation coefficient of regression is 0.97. Thus, it can be concluded fruit waste peels can be repurposed to serve as an economical alternative adsorbent in metal ions adsorption.

Keywords: Adsorption isotherms, Adsorption kinetics, Heavy metal ions, Mango peels, Rambutan peels, Watermelon peel,.

1. Introduction

Agricultural waste and food waste are one of the biggest contributors to the solid municipal waste volume in developing countries [1]. As reported by the deputy chief executive officer in the Department of Statistics Malaysia, Malaysia produced 16, 688 tons of leftovers daily in the year 2019, and this number of leftovers is sufficient to feed 12 million people three times per day [2, 3]. Moreover, it became severe when the announcement of the Movement Control Order (MCO) happened suddenly in Malaysia after Covid-19 had been declared a pandemic on March 2020 by World Health Organization (WHO) [4]. This shocking up phenomenon causes the food such as fruits and vegetables stocked up and it indirectly causes the food waste in Malaysia to increase drastically by 100% [3, 4].

Malaysia is a tropical country that produces a wide variety of tropical fruits. Due to the increase in the land area and productivity, it was found that the production of tropical fruits in Malaysia is increasing every year and more than 1.45 million tons of tropical fruits were produced in the year 2017 [5]. Fruits as one of the raw materials used for different products, the unavoidable waste of the production are the peel and the seed of the fruits [6]. Based on the research done by Harsh Kumar et al. in the year 2020, the amount of waste generated during the process of fruits and vegetables is around 25% to 30% of the total product [7]. These unavoidable fruit wastes have become one of the main components of municipal waste that impacts the current environment as it led not only to the landfill space problem but also generates air pollution [8, 9]. Therefore, Malaysia has taken a few approaches to enhance solid waste management, by following the standard hierarchy of waste management [10]. These involve five steps: reuse, reduce, recycling, treatment, and disposal. The government promotes and encourages the reuse and reduce method which can ultimately reduce landfill waste [10]. Due to this, many of the related scientific activities funded emphasize innovation and sustainability projects [11]. Through the studies, it was found those solid wastes such as fruit peels have a high potential to be reused for different applications [11]. It can be used as natural fertilizers, biosorbents, antioxidant agents, and biorefinery feedstock [12-15].

As a developing country, Malaysia is a country that is abundant in water resources; nevertheless, they are still facing a water crisis due to increasing water demand with unmatched water supply, lack of good water management, and effective basin planning [16]. It is undeniable that the rising pollution level also rings alarm bells to the water supply if it is not tackled now. Currently, Malaysia has 2986 river basins whereby 98% of the water supply comes from rivers, streams, and lakes [17]. Hence, the illegal discharge and dumping into the river have caused frequent water disruption issues in Malaysia. Examples of the serious incidents found are such as chemical toxic pollution in Kim Kim River, frequent odour and heavy metal pollution in Semenyih River, heavy metal pollution in the sea off Teluk Bahang, and Sungai Tengah river mouth in Penang, organic and heavy metal pollution in Malacca River [18-21]. The irresponsible anthropogenic activities have therefore led to an increase in water treatment operation and maintenance costs [22, 23]. Besides, the river water pollution even needs to be a concern, particularly for the Orang Asli community who live in the closet possible associated with nature. Orang Asli is also known as indigenous people and contributes 0.7% of the total population in Malaysia [24]. Their main water supply for their daily uses is from rivers located nearby to the village [24]. The use of untreated water supply increases the prevalence of the diseases such as T. Trichiura, hookworm, and A. Lumbricoides [24]. However, high technology and high cost of water treatment might not be suitable for the community. Therefore, it is a need to invest in and identify low-cost and alternative materials used for contaminated water treatment.

As referred to early, Malaysia produces a wide range of tropical fruits. Based on the Fruit Crops Statistic 2020 in Malaysia, showed that around 134,225.38 metric tons of watermelon, 49, 957.59 metric tons of rambutan, and 12, 834.40 metric tons of mango are produced annually [25]. This abundance of fruit peel wastes has a high potential to be reused and therefore this study is made to repurpose the agricultural waste that is usually just thrown away into something useful which is for contaminated water treatment. With respect to this, this study had been conducted to focus on: (1) the adsorbent capacity from sodium hydroxide (NaOH) pretreated rambutan, watermelon, and mango peels for adsorbing selected heavy metal ions in water; (2) the effectiveness of these pretreated rambutan (RP), watermelon (WP), and mango peels (MP) as adsorbents using adsorption isotherms and kinetics models.

2. Materials and methods

The materials preparation and the methods used to conduct the experiments were explained in the following section.

2.1. Materials preparation

The procedure of this experiment would start with procuring the waste peel samples, which are mango peels, watermelon peels, and rambutan peels. The waste peel samples were obtained from the local general store in Malaysia. The waste peels were washed in distilled water. Then, the peels were dried, cut, crushed, and sieved into small pieces of less than 2.36 mm pieces. After that, the peels were collected to a minimum of 51g per fruit peel. The smaller the size, the bigger the surface area of the adsorbent. Considering the limitation of grinding equipment and simplifying the material preparation, the size of the peels was taken as the sieve size where the peels can be crushed with a mortar in an adequate amount of time. The waste peels would then be submerged in 2000 ml of NaOH solution with a concentration of 0.1 mol/L for 1 hour at room temperature with stable stirring conditions. The waste peels were then filtered out and rinsed with tap water to neutralize the pH value. The peels then will be oven-dried for 24 hours in the oven at 60^{o} Celsius.

2.2. Heavy metal solution preparation

The heavy metal chemicals were procured from a chemical store. The heavy metals used in this study were iron, copper, and zinc. These heavy metals were selected because these were one of the main sources found in landfill systems that can have a potentially adverse effect on the surrounding environment [26]. The various types of waste such as metal waste components, household hazardous waste, scrap metal, and electronic waste contribute to the high concentration of heavy metal ions (such as iron, copper, and zinc) and pose a potential risk to the soils and natural water sources [27, 28]. To examine the adsorption ability of the selected fruit peels, the 1000 mg/L concentration of heavy metal stock solutions were prepared separately for each metal ions (iron, copper, and zinc) according to EPA Method 6010D [29].

The iron stock solution was prepared by using Iron (III) Oxide. The copper stock solution was prepared by using Copper II Oxide. While the zinc stock solution was prepared by using Zinc Oxide. All the heavy metal stock solutions were then diluted with distilled water to a concentration of 100 mg/L.

2.3. Batch adsorption setup

There are about 10 g of adsorbents (sodium hydroxide pretreated rambutan, watermelon, and mango peels respectively) were mixed with 2 litres of 100 mg/L heavy metal solution (iron, copper, and zinc respectively) using a magnetic stirrer. Each of the adsorbents (sodium hydroxide pretreated rambutan, watermelon, and mango peels respectively) were tested individually with different heavy metal solutions (iron, copper, and zinc respectively). The stirring process was conducted constantly and maintained for about 2 hours. Every 20 minutes, the aqueous sample was collected for lab testing. After finding the equilibrium time, the experiment was repeated for 5g and 2g of the fruit waste peels, with 2 litres of heavy metal solution at the equilibrium time.

2.4. Lab Testing

The measurement for these three tested parameters was conducted with Iris Visible Spectrophotometer in the Environmental laboratory. For iron, it is an adaptation of the EPA Phenanthroline method 315B with the wavelength set as 525 nm [30]. For copper, it is an adaptation of the EPA method with the wavelength length set as 560 nm [30]. For zinc, it is an adaptation of the Standard Methods for the Examination of Water and Wastewater, 18th Edition, Zincon Method [31]. In this method, the wavelength was set as 620 nm.

2.5. Analytical Methods

To evaluate further the adsorption process of the heavy metal ions onto the respective fruit peels, the data collected was studied by using adsorption isotherm models and adsorption kinetic models. The adsorption isotherm models such as Langmuir, Freundlich, and Temkin isotherm models were used to find the maximum adsorption capacity and the adsorption mechanism of the waste peels, as shown in Eqs. (1) to (4).

Langmuir: $$q_e = \frac{(Q_o K_L C_e)}{(1+K_L C_e)} \tag{1}$$

$$R_L = \frac{1}{1+K_L C_0} \tag{2}$$

Freundlich: $$q_e = K_f {C_e}^{1/n} \tag{3}$$

Temkin: $$q_e = B \ln A_T + B \ln C_e \tag{4}$$

Then, the adsorption kinetics of the heavy metal ions onto the fruits peels was calculated by using Pseudo first order, Pseudo second order, Elovich, and Intra-particle diffusion reaction, as shown in the Eqs. (5) to (8).

Pseudo first order model: $$\log(q_e - q_t) = \log q_e - \left(\frac{k_1}{2.303}\right) t \tag{5}$$

Pseudo second order model: $\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \left(\frac{1}{q_e}\right)(t)$ (6)

Elovich model: $q_t = \left(\frac{1}{\beta}\right) \ln \alpha\beta + \frac{1}{\beta} \ln t$ (7)

Intra-particle diffusion model: $q_t = k_{id} t^{1/2} + C$ (8)

The difference between the waste peel's properties of each fruit to the adsorption capacity was compared and discussed. The data and graphs for the isotherms, kinetics, and experiment results were shown.

3. Results and Discussion

The result obtained from the experiments were further discussed and analysed in the following section.

3.1. Effectiveness of heavy metal adsorption with biosorbents

To determine the adsorption effectiveness of various fruits waste peels to the heavy metal ions. Figures 1 to 3 shows the percentage removal of iron, copper, and zinc respectively by alkaline pretreated rambutan, watermelon, and mango peels. The adsorption condition is at room condition temperature (25ºC) with a pH of 7 for the soluble.

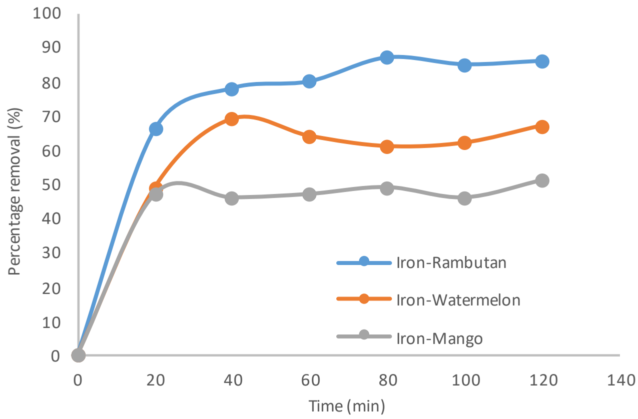


Fig. 1. Percentage removal of Iron by various alkaline pretreated fruit peels (RP, MP, and WP).

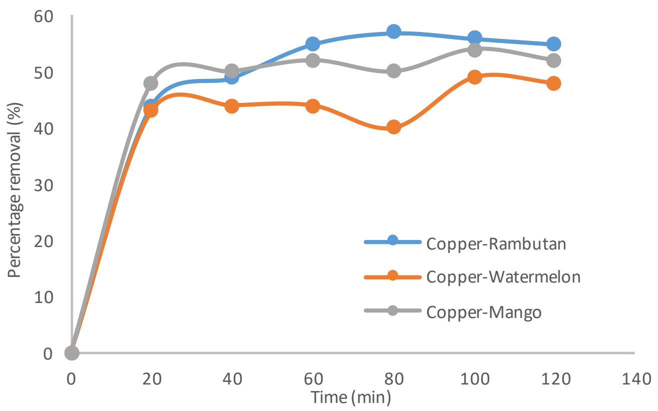


Fig. 2. Percentage removal of copper by various alkaline pretreated fruit peels (RP, MP, and WP).

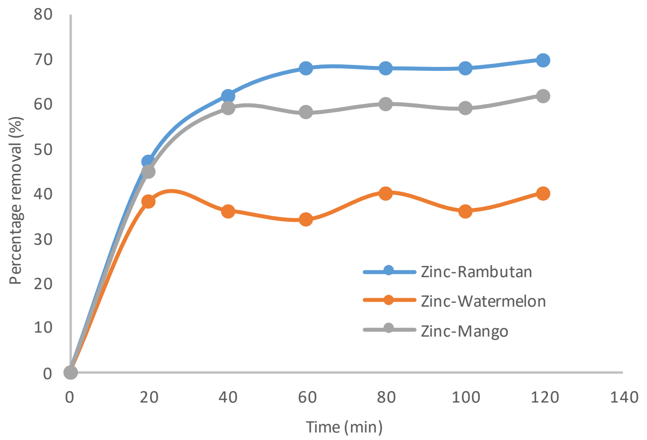


Fig. 3. Percentage removal of zinc by various alkaline pretreated fruit peels (RP, MP, and WP).

Overall, the result obtained from the adsorption batch experiments found that the adsorption system reaches the equilibrium time in less than 1 hour, with the first 20 minutes the removal of the heavy metals is considered rather fast as compared to the results after 20 minutes of the experiment. The adsorption process is slowing down until it reaches 60 minutes, where after the removal of the heavy metals starting to ne stagnant. After the saturation point, the concentration of the heavy metal would then fluctuate with a slight increase and decrease.

As reported by previous studies, peaks found in the FTIR spectrum of the fruit waste peel such as RP, WP, and MP showed that rich in carboxylate (-COO-), carboxylic (-COOH), and hydroxide (-OH) groups. These are the group that provides an additional active surface for the heavy metal ions adsorption into the adsorbents [32-36]. It was found that there is a sharp rise in the adsorption for the first 20 minutes. The high active surface area of the adsorbents made the rapid adsorption of heavy metal on the surrounding area. However, once the surface area is getting more saturated, the adsorption is getting slower as the surface area has no more places for the heavy metal to be attached to itself [37]. After the saturation, there is usually a fluctuation with a slight increase and decrease in the heavy metal concentration. This can be explained by the Fluctuation Adsorption Theory (FAT) where the equilibrium fluctuations are caused by all the characteristics of thermodynamics when there is a decrease in the volume of a system.

The main factor of this direct result of the discrete structure of substances at the level of atom-molecular [38] and at the same time the physisorption properties of the substances are reversible [39]. Part of the amount of the heavy metals adsorbed to the adsorbent is caused by physisorption which is attraction forces caused by Van der Waal forces. The other part of the amount of the heavy metals is adsorbed on top of the saturated surface of the adsorbent causing it to stack on top of the other heavy metal ions.

This multilayer physisorption is not binding as strongly as chemisorption which in this study is the adsorption caused by chemical bonding of the hydroxyl group ion exchanging with the heavy metal ions [39]. Because the binding is not strong when the adsorbent is mixed and stirred inside the solution, some of the heavy metal ion concentration might be desorbed into the water causing it to detach itself from the adsorbent and causing the heavy metal concentration to increase again slightly. As it is stirred slowly the adsorbent will adsorb back again a small amount of the detached heavy metal ion, therefore there was a small fluctuation after the saturation period (±5 mg/l of the final heavy metal concentration).

The monitored result in Figs. 1 to 3 show that the order of the iron concentration removal from highest to lowest are RP> WP> MP where the percentage removal is 87%, 67%, and 53% respectively. Then, the removal of copper from highest to lowest are RP> MP> WP where the percentage removal are 55%, 52%, and 48% respectively. The same order is applied to the zinc solution where the zinc removal by the RP was the highest (70%), followed by MP (59%), and WP (38%). From all these 3 figures (Figs. 1 to 3), it shows that the RP shows the most efficiency in adsorbing the iron, copper and zinc heavy metals compared to the other 2 fruit peels (WP and MP).

Several studies also reported that the lignocellulosic is an important aspect related to the removal of heavy metals. Therefore, Table 1 summarises the lignocellulosic content of the three different fruit peels.

Table 1. Lignocellussic content of the three different fruit peels.

Types of fruit peels	Cellulose content (% w/w)	Hemicellulose content (% w/w)	Lignin content (% w/w)	References
Rambutan peels	24.28±2.30	11.62 ± 2.31	35.34 ± 2.05	[40]
	17.5 ± 0.2	19.2 ± 0.0		[41]
	24	[redacted]	35	[42]
Mango Peels	38.35	13.9	27.9	[43]
	40	25	15	[44]
	31.3+-0.98	10.42+-2.12	5.95+-1.33	[45]
	35.07+-1.08	15.33+-3.29	27.06+-0.19	[46]
	[redacted]	14.51%	17.25	[47]
	34.23+-0.4	14.52+-0.8	17.25+-0.1	[48]
Watermelon peels	58+-0.92	14+-0.33	11+-0.11	[49]
	26.71+-0.7	11.45+-0.1	9.87+-0.3	[48]

	37.79±0.31	30.90±2.26	10.35±0.29	[50]

From the lignocellulosic properties of the peels, the cellulose and hemicellulose value of rambutan peels is the lowest among the three fruit peels [43, 51, 52]. Nevertheless, the rambutan showed the highest adsorption ability for the selected heavy metals compared to the other two fruit peels. Theoretically, lignin, cellulose, and hemicellulose are the important biopolymers that lead to high adsorption capacity for the heavy metal ions [53]. Among these three components in the fruit peels, high lignin content in the rambutan peels consists of hydroxyl and carboxyl groups, which have the metal chelating ability, and it causes the peels to react well in adsorbing metal ions [54]. In addition, the alkaline pretreatment of the fruit peels has further changed the properties of peels and made their adsorption capacity higher by increasing the cellulose content [55].

The alkaline pretreatment also causes the reduction of lignin and the formation of hydroxyl group which increases surface area and increases the bonding properties of the peels to cation ion [56]. The rambutan peels' surface area would be enlarged more and more hydroxyl groups would be formed, which make it able to adsorb more heavy metals than the other two waste peels.

From the result of the experiment, the most suited heavy metal the adsorbent can adsorb based on this experiment can be sorted from highest to lowest percentage of removal of the heavy metal. The most suited heavy metal that RP adsorb would be Iron > Zinc > Copper. The most suited heavy metal that MP could adsorb would be Zinc > Copper > Iron. The most suited heavy metal that WP adsorb would be Iron > Copper > Zinc.

3.2. Adsorption isotherm analysis

Adsorption isotherm is an empirical model used to estimate the pollutants in the solution adsorbed into the adsorbent. The adsorption isotherm can be defined as a graphical representation to show the adsorption relationship between the adsorbate to the adsorbent and its distribution [57]. To investigate the adsorption isotherms, the collected data were analysed by using the Langmuir isotherm, Freundlich isotherm, and Temkin isotherms. Figure 4 shows the Langmuir, Freundlich and Temkin isotherm of Iron, Copper, and Zinc metal ions adsorption by using RP (Blue line), MP (grey line), and WP (Orange line) respectively. For the Langmuir isotherm model, the linear plot of C_e/q_e against C_e is utilized to evaluate the qmax and the K_L. While the linear plot of log q_e against log C_e is utilized to evaluate the K_f and the n in Freundlich isotherm. The A_T and the B parameters in the Temkin isotherm are evaluated from the linear plot of q_e against ln C_e. Based on the gradient and intercept of the linear graph, Table 2 shows the parameters and correlation coefficients of Langmuir, Freundlich, and Temkin isotherm models for various heavy metal ions (iron, copper, and zinc) onto the various fruit peels (RP, MP and WP).

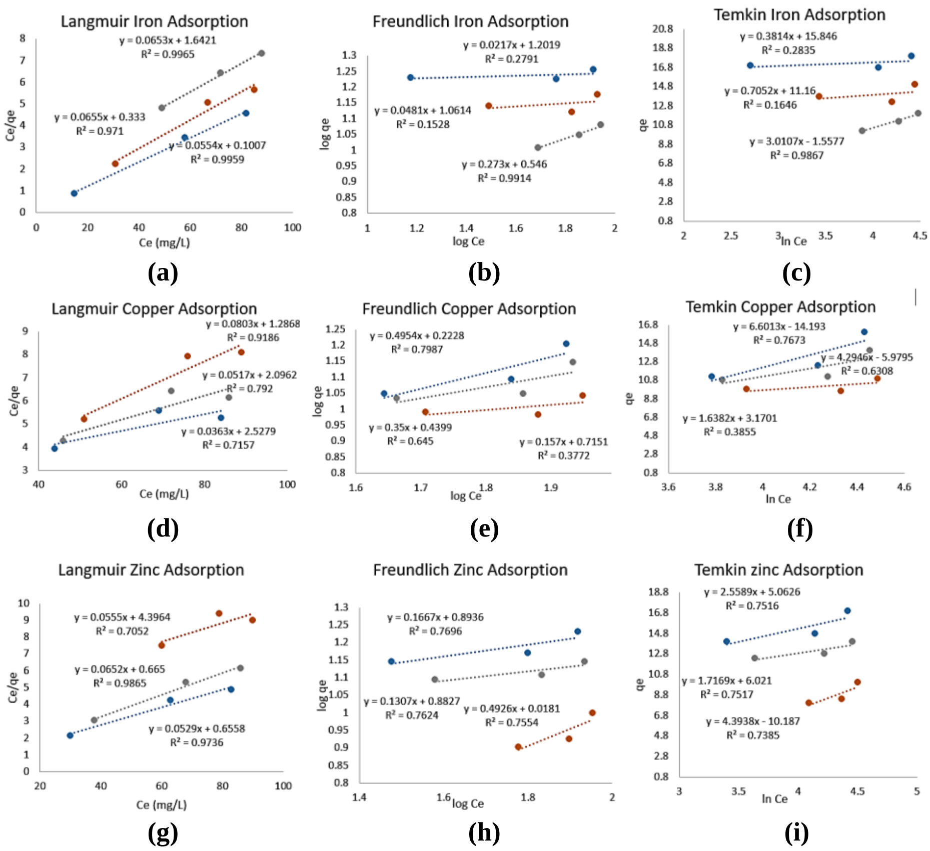


Fig. 4. The Langmuir, Freundlich and Temkin isotherm of Iron (a, b, c), Copper (d, e, f) and Zinc (g, h, i) metal ions adsorption by using RP (Blue line), MP (grey line), and WP (Orange line) respectively.

Table 2. Langmuir, Freundlich, and Temkin isotherm result.

Rambutan								
	Langmuir				**Freundlich**			
	K_L (L/mg)	**q_{max} (mg/g)**	**R_L**	**R^2**	**K_f (mg/g)(mg/L)**	**1/n**	**n**	**R^2**
Iron	0.55015	18.0505	0.01754	0.996	15.9184	0.022	46.083	0.279
Copper	0.01436	27.5482	0.29104	0.716	1.670321	0.495	2.01857	0.799
Zinc	0.080665	18.9036	0.09934	0.974	7.827084	0.166	5.9988	0.767
	Temkin							
	A_T (L/mg)	**B**	**R^2**					
Iron	1.106E+18	0.3814	0.2835					
Copper	0.116481	6.6013	0.7673					
Zinc	7.231368	2.5589	0.7516					
Mango								
	Langmuir				**Freundlich**			
	K_L (L/mg)	**q_{max} (mg/g)**	**R_L**	**R^2**	**K_f (mg/g)(mg/L)**	**1/n**	**n**	**R^2**
Iron	0.039766	15.31394	0.16731	0.997	3.515604	0.273	3.66300	0.991
Copper	0.024664	19.34236	0.2239	0.792	2.753595	0.35	2.85714	0.645

Zinc	0.098045	15.33742	0.08471	0.987	7.633083	0.131	7.65111	0.762
		Temkin						
	A_T(L/mg)	**B**	**R^2**					
Iron	0.596076	3.0107	0.9867					
Copper	0.248496	4.2946	0.6308					
Zinc	33.34480	1.7169	0.7517					
				Watermelon				
		Langmuir				**Freundlich**		
	K_L (L/mg)	**q_{max} (mg/g)**	**R_L**	**R^2**	**K_f (mg/g)(mg/L)**	**1/n**	**n**	**R^2**
Iron	0.196697	15.26718	0.04615	0.971	11.51861	0.0481	20.79002	0.1528
Copper	0.062403	12.4533	0.121355	0.919	5.189195	0.157	6.369427	0.3772
Zinc	0.012624	18.01802	0.30652	0.705	1.042557	0.4926	2.030045	0.755
		Temkin						
	AT(L/mg)	**B**	**R^2**					
Iron	7461730	0.7052	0.1646					
Copper	6.92481	1.6382	0.3855					
Zinc	0.098422	4.3938	0.7385					

The result from Fig. 4 and Table 2 indicated that most of the heavy metal ions adsorption on RP, MP, and WP were favourable to Langmuir isotherm except for the zinc adsorption on WP and copper adsorption on RP. The accuracy and compatibility of the adsorption system with using the Langmuir isotherm can be seen in the R^2 value. The closer it is to one, the more compatible it is to be used the Langmuir isotherm as the assumption of the model coincides with the adsorption system. Table 2 revealed that the regression coefficient value of Langmuir isotherm is 0.9959 (iron by RP), 0.9736 (zinc by RP), 0.9965 (iron by MP), 0.792 (copper by MP), 0.9865 (zinc by MP), 0.971 (iron by WP), and 0.9186 (copper by WP).

Based on the assumption of the Langmuir isotherm model, it can predict that the monolayer adsorptions of heavy metal ions take place on the surface of the adsorbents [58]. Moreover, the maximum monolayer coverage capacity (q_{max}), which was found by the calculation in the Eq. (1), was obtained to be in the range of 12.4533 mg/g to 19.34236 mg/g. The effectiveness of the pollutants adsorption by fruit peels in ascending order was copper by MP (19.34236 mg/g), zinc and iron by RP (18.90359 mg/g and 18.05054 mg/g respectively), zinc and iron by MP (15.33742 mg/g and 15.31394 mg/g respectively), and lastly iron and copper by WP (15.26718 mg/g and 12.4533 mg/g respectively). Then, the R_L in the Langmuir isotherm is a dimensionless separation factor, the value of the separation factor indicates the nature of the adsorption process. With $R_L > 1$ means the adsorption is unfavourable and $0<R_L<1$ means favourable adsorption [59]. From Table 2, the R_L is in the range of 0.018 to 0.72, which shows that the adsorption process for all the systems was favourable to the model.

Principally, many factors affect the adsorption affinity between heavy metal ions and fruit peels. The factors are such as molecular weight, ionic radii, the surface roughness of the peels, and the different adsorption capacities of the carbonyl groups that react with metal ions in the solution [60]. The greater the surface area of the adsorbent, the greater will be the adsorption. It was predicted that has possible the surface area that inherits the properties of RP may be greater than MP and WP, thus it has a higher adsorption rate of adsorbent and adsorbate binding energy than MP and WP during the experiment.

Nevertheless, the maximum adsorption capacity found in the Langmuir isotherm model is the theoretical adsorption capacity of the adsorbent at high pressures (>10 Pa) [61]. This result shows that in ambient conditions (<1 Pa) the rambutan peels have the highest adsorption capacity in this experiment, but at high-pressure certain peels would be better in adsorbing the heavy metals. For example, RP gives the highest removal efficiency for all heavy metals but the maximum adsorption capacity of RP maybe slightly smaller than MP in the copper adsorption as seen in Table 2.

For zinc adsorption on WP and copper adsorption on RP, the R^2 value is 0.7052 and 0.7157 respectively, which means the adsorption system is not compatible with Langmuir isotherm, but best fitting for Freundlich isotherm model. The R^2 value for both adsorption testing is slightly higher in Freundlich isotherm model which was 0.7554 (zinc by WP) and 0.7987 (copper by RP) respectively. This also means the adsorption system followed the isotherm models assumption, where the adsorption system assumes multilayer adsorption applied to the surface of the fruit peels. Fig. 5 shows the monolayer and multilayer adsorption model.

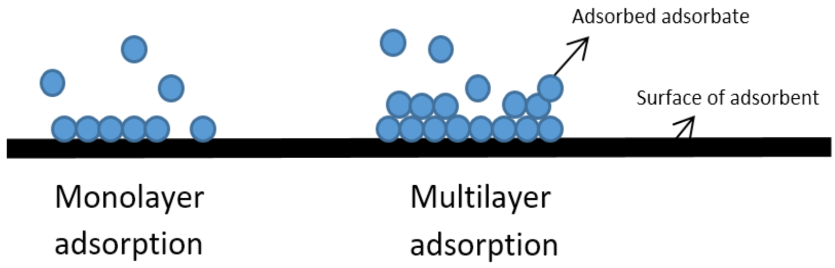


Fig. 5. Monolayer and multilayer adsorption model.

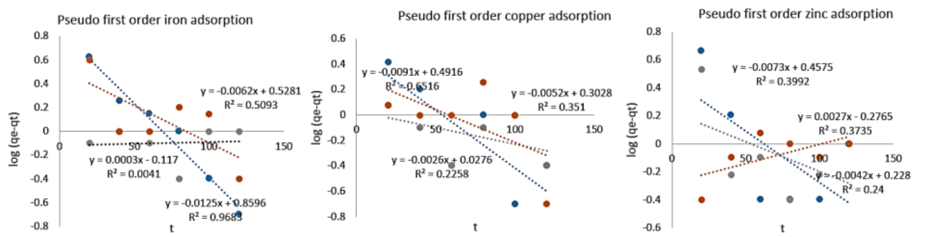
The monolayer adsorption revealed a unique adsorption phenomenon where a single layer of heavy metal ions occupies the adsorption site of the fruit peels. The adsorption process is rather simple where the adsorbent surface is homogenous with uniform adsorption energy [62]. For the multilayer adsorption, it is publicized that the adsorbent surface is heterogeneous with the adsorption energy distributed exponentially. The model demonstrates the ratio between the heavy metal ions to a given mass of fruit peels in the solute was not a constant at different solution concentrations and with the concept of stronger binding sites occupied first until the adsorption energy is decreased exponentially upon the completion of entire adsorption activity [63].

Based on Table 2, the n coefficient in the Freundlich isotherm model is the intensity of the adsorption, with the value of 1/n between 0 and 1 meaning the isotherm is favourable [64]. The 1/n value obtained from the experiment of zinc adsorbed by WP and copper adsorbed by RP was 0.4926 and 0.4954 respectively. This shows that the adsorption systems were favourable to the Freundlich isotherm. When the 1/n value is close to zero, it represents that the adsorption intensity of heavy metal onto the fruit peels become more heterogeneous [65]. Besides, the n value of the zinc by WP and copper by RP were 2.030045 and 2.01571 respectively which indicated that high adsorption intensity as the value of n is in the range of 2 to 10 [66].

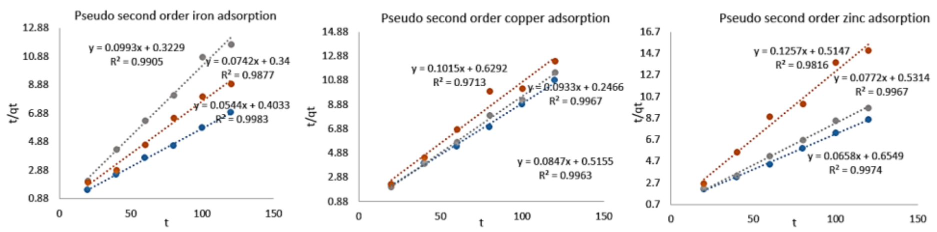
3.3. Adsorption kinetics analysis

Adsorption kinetics is an empirical model used to estimate the uptake rate of the adsorbate by the adsorbent. The basics graphical forms of all kinetics studies represent the underlying kinetics of the process [67]. To investigate the adsorption kinetics, the collected data were analysed by using Pseudo first order model, Pseudo second order model, Elovich model, and Intra-particle diffusion model. Figure 6 shows the Pseudo first order model, Pseudo second order model, Elovich model, and Intra-particle diffusion model of Iron, Copper, and Zinc metal ions adsorption by using RP (Blue line), MP (grey line), and WP (Orange line) respectively. The validity of these adsorption kinetics models can be further verified by linear plot of log (q_e–q_t) vs. t, (t/q_t) vs. t, q_t vs. ln (t), and q_t vs. $t_{0.5}$, respectively. The rate constant of adsorption kinetics models was presented in Table 3.

The magnitude of the regression coefficient R^2, as shown in Table 3 was used to validate the adsorption kinetics model for the heavy metal ions into the fruit peels [67]. The correlation coefficients of pseudo second order isotherm indicated the best fitting for all the heavy metal ions adsorption by different fruit peels because the R^2 showed higher than 0.97. A similar phenomenon and result have been identified by Devanathan et al. [68], Wong et al. [69], and Rind et al. [70] for the respective fruit peels in pollutants adsorption. In contrast, the application of the kinetic models such as the Pseudo first-order model, Elovich model, and Intra-particle diffusion models showed poor regression coefficients.



(a) (b) (c)



(d) (e) (f)

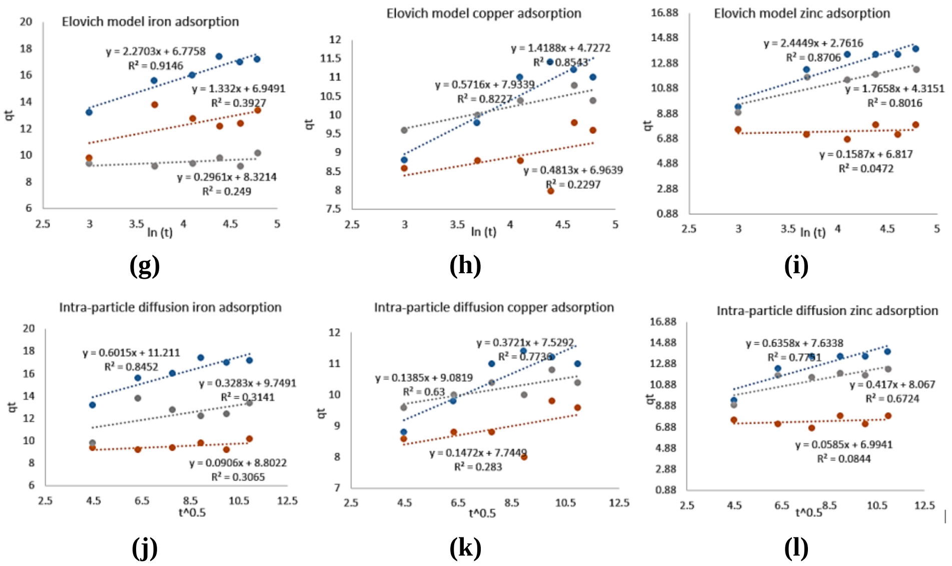


Fig. 6. The Pseudo first order (a, b, c), Pseudo second order (d, e, f), Elovich (g, h, i) and Intra-particle diffusion (j, k, l) isotherm of Iron, Copper, and Zinc metal ions adsorption by using RP (Blue line), MP (grey line), and WP (Orange line) respectively.

Table 3. Pseudo first order model, Pseudo second order model, Elovich model, and Intra-particle diffusion model result.

	Pseudo first order Model			Pseudo second order Model		
	K_1 (1/day)	q_e (mg/g)	R^2	k_2 (1/day)	q_e (mg/g)	R^2
Rambutan						
Iron	0.0287875	7.2376904	0.9683	0.007337863	18.382353	0.9983
Copper	0.0209573	3.1017015	0.6516	0.01391676	11.806375	0.9963
Zinc	0.0168119	2.8674774	0.3992	0.006611147	15.197568	0.9974
Mango						
Iron	-0.0006909	0.7638358	0.0041	0.030537287	10.070493	0.9905
Copper	0.0059878	1.0656142	0.2258	0.035299635	10.718114	0.9967
Zinc	0.0096726	1.6904409	0.24	0.011215356	12.953368	0.9967
Watermelon						
Iron	0.0142786	3.3736498	0.5093	0.016193059	13.477089	0.9877
Copper	0.0119756	2.0081678	0.351	0.01637357	9.8522167	0.9713
Zinc	-0.0062181	0.529054	0.3735	0.030698446	7.9554495	0.9816
	Elovich Model			**Intra-particle diffusion Model**		
	α	**β**	**R^2**	**k_{id}**	**C**	**R^2**
Rambutan						
Iron	44.900614	0.4404704	0.9146	0.6015	11.211	0.8452
Copper	39.71151354	0.704821	0.8543	0.3721	7.5292	0.7736
Zinc	7.565051634	0.4090147	0.8706	0.6358	7.6338	0.7751
Mango						
Iron	4.7486E+11	3.3772374	0.249	0.3283	9.7491	0.3141
Copper	609774.88	1.7494752	0.8227	0.1385	9.0819	0.63
Zinc	20.33436028	0.5663156	0.8016	0.417	8.067	0.6724
Watermelon						
Iron	245.6047691	0.7507508	0.3927	0.0906	8.8022	0.3065

Copper	925115.4222	2.0777062	0.2297	0.1472	7.7449	0.283
Zinc	7.1748E+17	6.3011972	0.0472	0.0585	6.9941	0.0844

For the Pseudo second-order reaction, it represented the chemisorption kinetics of heavy metal ion adsorption [71]. The good fit of the pseudo second-order model heavy metal ion onto the fruit peels suggests that the adsorption process was due to the external mass transfer [72]. Owing to the influence of pore and film diffusion, the adsorption capacity of RP was greater than MP and WP.

For iron metal ion adsorption, the calculated qe value from the pseudo-second-order reaction from highest to lowest are RP (18.382353 mg/g) > WP (13.477089 mg/g)> MP (10.070493 mg/g). For copper metal ions adsorption, the calculated q_e value from the pseudo second-order reaction from highest to lowest are RP (11.806375 mg/g)> MP (10.718114 mg/g) > WP (9.8522167 mg/g).

While for zinc metal ions adsorption, the calculated q_e value from the pseudo second-order reaction from highest to lowest is RP (15.197568 mg/g)> MP (12.953368 mg/g)> WP (7.9554495 mg/g). The sequence of the result obtained from the calculation is the similar to the experimental data. From the result obtained, it should be emphasized here that the chemical interaction between the heavy metal ions and the fruit peels is the dominant adsorption process in the study [73]. Nonetheless, the heavy metal ions adsorption may not only depend on the chemisorption but is probably involved in other binding mechanisms such as surface diffusion or the physisorption that may occur simultaneously in weak interaction during the adsorption process [74].

3.4. Contribution of knowledge

This work contributes its novelty in comparison to the other alternative heavy metal ions adsorption and a comparison of the maximum adsorption capacity of different fruit peels onto different heavy metal ions were discussed.

From previous studies, the range of different types of adsorbents with each experiment condition, isotherm model used, and source material, so an estimate of the adsorption capacity was gained by referencing various previous studies. None of the research was conducted by comparing the adsorption of the fruit peels using various heavy metal ions under the same experiment condition.

Based on the data collection in this study, there is a limited literature review on mango peels, rambutan peels, and watermelon rinds as an adsorbent for copper, iron, and zinc. These metal ions were selected in the study because one of the sources of some of these heavy metals is fertilizer and pesticides, making them common pollutants in rivers near agricultural industries.

As developing countries still mostly rely on the agricultural industry for their income, it is much more useful to target those heavy metals as the adsorbate since these alternative adsorbents will probably be used as a cheap alternative in developing countries rather than in advanced countries that are not lacking in funding.

4. Conclusions

Based on the result gained from the study, pretreated Fruit peels (rambutan peels, mango peels, and watermelon peels) had a significant effect on removing the iron, zinc, and copper ions. The recorded iron, copper, and zinc removal rates by rambutan peels were 87%, 55%, and 70%. Then, mango peels were adsorbed with

53% of iron, 52% of copper, and 59% of zinc. While the percentage removal of iron, copper and zinc by watermelon peels was 67%, 48%, and 38% respectively.

All of the heavy metal ions (iron, copper and zinc) adsorption on rambutan peels, mango peels, and watermelon peels were favourable to Langmuir isotherm, except for the zinc adsorption on watermelon peels and copper adsorption on rambutan peels where both were favourable to Freundlich isotherm. Besides, the study also clearly stated that all the heavy metal ions removed by different fruit peels match well with the pseudo-second-order model with high regression coefficient (R^2 >0.97).

The result indicated that chemisorption is the dominant adsorption process in the study. Finally, yet importantly, it can be concluded that RP, MP and WP were the suitable alternative adsorbent materials used to treat the heavy metal ions in the water.

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Nomenclatures

A_T	Temkin isotherm equilibrium binding constant, L/g
B	Sorption heat constant, J/mol
C	Interception constant for the intra-particle diffusion
Ce	The equilibrium concentration, mg/L
C_O	Initial concentration of solution, mg/L
k_1	The rate constant of Pseudo first order adsorption, min^{-1}
k_2	Rate constant of Pseudo second order adsorption, g/mg·min
kid	The rate constant for the Intraparticle diffusion, min^{-1}
k_L	Langmuir constant related to the energy of adsorption, L/mg
n	The constant for Freundlich adsorption intensity
q_e	Equilibrium capacity, mg/g
Qo	Maximum monolayer coverage capacity, mg/g
q_t	Amount of adsorbate adsorbed into adsorbent at time, mg/g
R^2	Regression coefficient
R_L	Dimensionless constant separation factor of equilibrium parameter
t	Reaction time, min^{-1}

Greek Symbols

α	Adsorption mechanism
β	Desorption constant of Elovich reaction, g/mg

Abbreviations

MP	Pretreated Mango Peels
RP	Pretreated Rambutan Peels
WP	Pretreated Watermelon Peels

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