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Simultaneous Removal of Lead, Cadmium, and Arsenic Ions from Bivalve Species Using Adsorption Method

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Abstract Bivalve such as blood cockle (*Tegillarca granosa*) feeds by filtering the suspended particle in water including heavy metals and eventually accumulate in the fleshes. Bivalve contaminated with heavy metals might be consumed by human which later could have been exposed to heavy metals toxicity. Therefore, this study was conducted to investigate the effectiveness of adsorption process towards the removal of lead (Pb), cadmium (Cd), and arsenic (As) ions from *T. granosa*. The findings found that the initial concentration of Pb and As in *T. granosa* exceeded the permissible limits set by WHO. To remove heavy metals from T. granosa, an adsorption procedure was carried out using lemon and mango peels as natural waste adsorbents. The presence of hydroxyl and carboxylic functional groups in mango and lemon peels was shown in FTIR spectra, which aided in the enhancement of the adsorption process. A series of tests were performed using various parameters such as dosage adsorbents, contact of time, and temperature of reaction. The highest removal percentages of Pb, Cd, and As in *T. granosa* using lemon peels were 59.65%, 88.89%, and 67.54% respectively. Meanwhile, the maximum removal from *T. granosa* using mango peels were 70.18% for Pb, 100% for Cd, and 84.71% for As. In conclusion, the adsorption process was effective in removing Pb, Cd, and As in *T. granosa*. Whereas both lemon peels and mango peels have ability to become effective naturals waste adsorbent in the adsorption process.

1. Introduction

Recently, the demand for seafood products has significantly increased due to awareness of their nutritional values and therapeutic benefits [1]. Amongst the seafood products, bivalve species have a pair of two-part hinged shells protecting soft-bodied such as clams, oysters, mussels, and scallops. Since bivalve species are also referred to as filter feeders, they obtain their food by filtering the majority of the suspended particles, including heavy metals, in the water that surrounds them. They are more likely to acquire heavy metals as a result. Unfortunately, people regularly consumed bivalves as part of their diet, potentially exposing them to heavy metal poisoning [2].Generally, the heavy metals found in the bivalve include arsenic (As), cadmium (Cd), chromium (Cr), copper (Cu), lead (Pb), nickel (Ni) and zinc (Zn) [3,4].

Metals can be categorized as potentially toxic (e. g As, Cd, Pb, mercury (Hg)) and essential (e. g Cu, Zn, iron (Fe), manganese (Mn)) [5]. Toxic metals could be harmful to the human when ingested even in a low concentration over a long period of time and eventually will cause acute and chronic poisoning and are carcinogenic to the human who eats the bivalve contaminated with heavy metals [5,6]. Hence, it is important to determine the concentration of the heavy metals in the bivalves as they reflect the heavy metal concentration in the coast [7]. It is also to ensure that heavy metals concentration in bivalves are under the permissible level set by guidelines such as World Health Organization (WHO) and Malaysia Food Regulation (MFR) 1985, so that they are safe to eat.

One of the effective ways to treat heavy metals poisoning from the bivalve is through the adsorption process [8]. Performing adsorption process will initiate a phenomenon in which a solution containing the adsorbate (heavy metals) will be adsorbed on the surface of the adsorbent [9]. In recent years, several studies have been conducted to develop newer, cheaper and more efficient absorbents to replace the commercial adsorbents (e. g activated carbon). Commercial adsorbents are widely used nowadays for their efficiency in removing heavy metals despite their high price [10].

The alternative adsorbents such as natural waste adsorbents have been introduced to fulfil the need for safe and economical methods as well as comparatively low-cost production compared to commercial adsorbents [11]. Thus, this study used lemon peels and mango peel as natural waste adsorbents to remove As, Pb, and Cd ions from blood cockle (*T. granosa*).

2. Methodology

This research was conducted to investigate the effectiveness of lemon peels and mango peels as natural waste adsorbents that are widely abundant in Malaysia to remove Pb, Cd, and As ions in blood cockle (*T.* granosa) using adsorption method.

2.1 Sample collection and preparation

Blood cockle (*T. granosa*) was purchased directly at a wet market in Kubang Kerian, Kelantan. The bivalves were quickly transported to School of Health Sciences's laboratory at Universiti Sains Malaysia Kubang Kerian, Kelantan. The bivalve was boiled to separate their shells and fleshes. In this study, only the fleshes with similar size and weight were used to represent the homogeneity of the sample. Then, the fleshes were washed using deionized water and stored in the refrigerator for further preparation for the analytical test.

2.2 Sample digestion and analytical test

T. granosa was weighed at 2.0 ± 0.5 g and digested using 8 mL of 65% v/v nitric acid, HNO_3 on a hot plate for approximately 30 minutes until clear solution was obtained. Then, the digested sample was allowed to cool at room temperature and then filtered. 1 mL of the filtered sample was diluted with deionized water in a volumetric flask. The filtered sample was analysed by using Flame Atomic Absorption Spectrometer (FAAS) and Graphite Atomic Absorption Spectrometer (GAAS) to detect and measure the concentration of heavy metals in *T. granosa*. The procedure was repeated after heavy metal removal process.

2.3 Preparation of natural adsorbents

Lemons and mangos were purchased from the market near Universiti Sains Malaysia Kubang Kerian, Kelantan and were peeled off to make the adsorbents. Both adsorbents were washed with deionized water in order to remove any contaminants. Next, the adsorbents were oven dried in the oven at 70 ºC for overnight. After the adsorbents dried, the adsorbents were ground into powder form and then preserved in a polyethylene container prior to treatment process. Lemon peels and mango peels were analysed with Fourier Transform Infrared (FTIR) spectroscopy to characterize the surface of the adsorbents. The FTIR absorbance data were collected between of wavenumber of 600 to 4000 cm^{-1}.

2.4 Removal of heavy metals

T. granosa sample of similar size was chosen and approximately weighed at 2.0 ± 0.50 g. 0.1 g of mango peels powder were mixed in 100 mL of deionized water producing 0.1 g dosage of mango peels adsorbents. Next, the sample was held in a sack and then soaked in a beaker containing 0.1 g dosage of mango peels. The solution was stirred for 30 minutes at 25 ºC. After that, the same method was repeated with different parameters as shown in Table 1.

Table 1. The treatment parameters for removal process

Parameters	Experiment Variables
Dosage of adsorbents	0.1 g, 0.2 g, 0.3 g
Contact of time	30 min, 50 min, 70 min
Type of adsorbents	Mango peels, Lemon peels

2.5 Statistical analysis for heavy metal concentration before and after removal process
To determine the percentage of heavy metals removed, the concentration of the metals was measured both before and after the adsorption procedure. The concentration of heavy metals in the samples was calculated.

Concentration of heavy metal (mg/kg):

$$= \frac{Intrument\ reading\ \left(\frac{mg}{L}\right)\ x\ volume\ of\ digested\ samples\ (L)\ x\ dilution\ factor}{Weight\ of\ digested\ samples\ (kg)} \quad \text{Eq. 1}$$

Meanwhile, the removal percentage of heavy metals from the samples was calculated based on Equation 2:

$$M\% = \frac{[M]initial - [M]after}{[M]initial}\ x\ 100\% \quad \text{Eq. 2}$$

Whereby,

M% = Percentage removal of heavy metals.
[M]initial = Initial concentration of heavy metals before the adsorption process in bivalves.
[M]after = Final concentration of heavy metals after the adsorption process in bivalves.

3. Results and Discussion

3.1 Characterization of natural waste adsorbents
Figure 1 shows the FTIR spectra of lemon peels and mango peels as natural waste adsorbents. The adsorption band ranged from 3660-2500 cm^{-1} and 1640-1620 cm^{-1} are the hydroxyl group (O-H) and carboxylic group (C=O), respectively. The intensity of the hydroxyl group in mango peels was slightly higher compared to lemon peels. According to Wu *et al.* [12], the hydroxyl group is very effective towards adsorption rate and highly efficient through the exchange with metal ions. Lemon peels showed significantly higher intensity of a carboxylic group than the mango peels. A study by Chang *et al.* [13] claimed that the carboxylic group contributes to high adsorption rate due to the presence of more negatively charged groups on its surface. Hence, lemon peels and mango peels could become effective natural waste adsorbents due to the presence of a high amount of oxygen-containing functional groups on the surface of adsorbents which lead to the enhancement of metal adsorption [14].

3.2 Initial concentration of heavy metals in T. granosa

Table 2 shows the initial concentration of Pb, Cd and As ions from *T. granosa* with the permissible limit set by WHO and MFR (1985) standard guidelines.

Table 2. The initial concentration of heavy metals in *T. granosa* and the permissible limit set by WHO and MFR (1985) standard guidelines

Sample / Heavy metal	Pb (mg/kg)	Cd (mg/kg)	As (mg/kg)
T. granosa	5.605	1.770	0.579
Permissible limits	WHO : 2.00	WHO : 2.00	WHO : 0.20
	MFR : 2.00	MFR : 1.00	MFR : 1.00

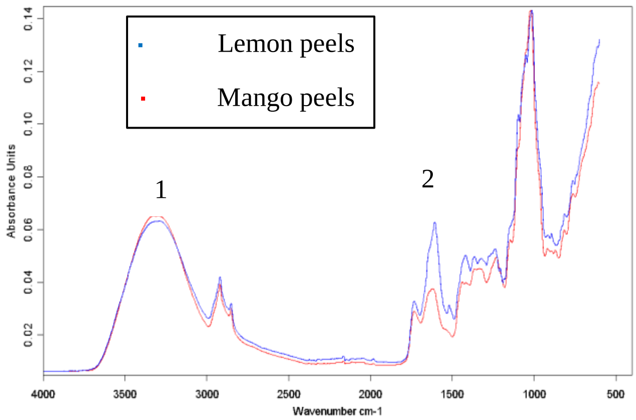

Figure 1. FTIR spectra of mango peels and lemon peels show several peaks; 1 (O-H group) and 2 (C=O group)

The initial contents of heavy metals in *T. granosa* were 5.605 mg/kg, 1.770 mg/kg, and 0.579 mg/kg for Pb, Cd, and As respectively. The concentration of Pb in *T. granosa* was higher than the permissible limit allows by WHO and MFR. The level of As in this sample was higher than guidelines limit set by WHO but yet lower than MFR. *T. granosa* recorded higher content of Cd than the recommended limit set by MFR. The hierarchy of heavy metals contents in *T. granosa* was Pb > Cd > As.

3.3 Effect on different dosage of adsorbents

Different dosage of adsorbents (lemon peels and mango peels) of 0.1 g, 0.2 g, and 0.3 g were prepared to test their effectiveness towards removal of heavy metal in *T. granosa.* Figure 2 illustrates the removal percentage of heavy metals from *T. granosa* by using lemon peels and mango peels, respectively.

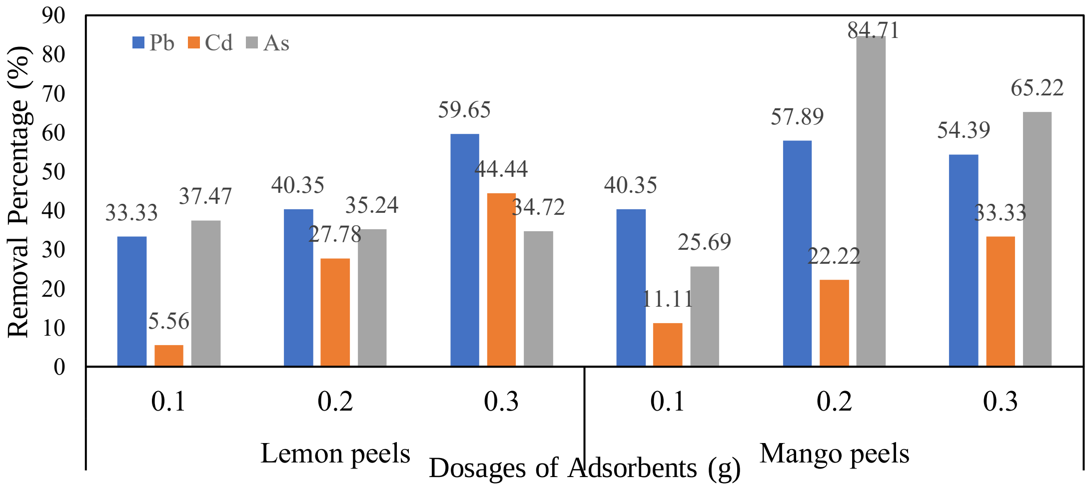

Figure 2. The removal percentage (%) of heavy metals from *T. granosa* after treatment using 0.1, 0.2, and 0.3 g of adsorbents dosages of lemon peels and mango peels, respectively for 30 min at 25 °C

For treatment by lemon peels, the result showed the maximum percentages removal of heavy metals were observed at 0.3 g of dosage where the percentage values up to 59.65% and 44.44% for Pb and Cd, respectively. The contents of heavy metals in *T. granosa* were reduced up to 2.290 mg/kg for Pb, 0.996 mg/kg for Cd, and 0.369 mg/kg for As. However, at the maximum removal percentage, the level of Pb in *T. granosa* still exceeded the permissible limit set by WHO and MFR, meanwhile Cd was successfully removed until it below the permissible limit set by WHO and MFR.

The maximum biosorption percentages of Pb and As after treatment using mango peels were observed at 0.2 g which were 57.89% and 84.71%, respectively. The concentration of Pb, Cd, and As after adsorption process were decreased up to 2.369 mg/kg, 1.194 mg/kg, and 0.089 mg/kg, respectively. Pb content in *T. granosa* was still beyond the permissible limit set by WHO and MFR meanwhile Cd level had been reduced below the permissible limit set by WHO. Whereas, As content in *T. granosa* was successfully to reduce below the recommended guidelines set by WHO and MFR. Both Pb and As showed a decrease pattern at 0.3 as they had achieved maximum adsorption at 0.2 g.

Based on the results, the removal percentage of heavy metals showed upward trend with the increases adsorbents dosages until the maximum adsorption capacity achieved. This pattern was supported by Hai Lin et al. [15], who asserted that when adsorbent doses rise, the number of accessible adsorption sites and their specific surface area eventually rise, leading to a higher removal percentage of heavy metal. Additionally, as adsorbent doses increased, the adsorption capacity dropped as well, which may be a result of overlapping adsorption sites brought on by adsorbent particle overpopulation [16]. The lemon peels and mango peels comprise of variety of functional groups such as carboxylic acid and hydroxyl group which acts as active binding sites for the adsorption of heavy metal ions. The presence of these functional were shown in the FTIR spectra. Higher dosages of the adsorbents resulted in higher surface area thus providing greater availability of the exchangeable binding sites for the heavy metal ions [17].

3.4 Effect on different contact of times

Different contact of times including 30, 50, and 70 mins were investigated for the removal of heavy metals from *T. granosa* by using lemon peels and mango pees as natural waste adsorbents. Figure 3 shows the removal percentage of heavy metals from *T. granosa* after the treatment using lemon peels and mango peels, respectively.

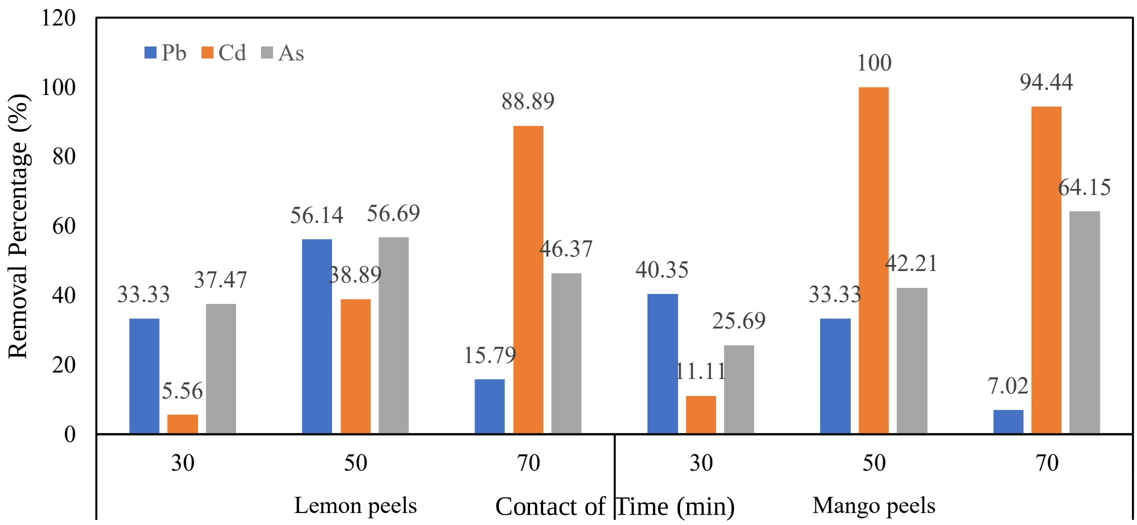

Figure 3. The removal percentage (%) of heavy metals from *T. granosa* after treatment using 0.1 g of lemon peels and mango peels, respectively for 30 min, 50 min, and 70 min at 25 °C

For treatment by lemon peels, the maximum removal percentages of Pb and As were observed at 50 min and Cd at 70 min in which the values were up 56.14%, 88.89%, and 56.69% for Pb, Cd and As, respectively. The concentration of Pb, Cd, and As in *T. granosa* were reduced up to 2.413 mg/kg, 0.197 mg/kg, and 0.246 mg/kg, respectively. The level of Cd in *T. granosa* was succeeded to reduce below the permissible limit set by WHO and MFR. However, Pb still exceeded the maximum limit allowed by WHO and MFR after treatment process.

The maximum percentage removal of Pb, Cd, and As after treatment using mango peels were observed up to 40.35%, 100%, and 64.15% respectively. Pb achieved maximum percentage removal at

30 min, Cd at 50 min whereas As at 70 min. The concentrations of Pb, Cd, and As in *T. granosa* after the adsorption were 3.390 mg/kg, 0 mg/kg, and 0.211 mg/kg respectively. The level of Cd was managed to be removed until it below the permissible limit set by WHO and MFR. Meanwhile, the level of Pb was still higher than the recommended levels allowed by WHO and MFR after the treatment process.

The removal of heavy metals were increased with the increased of contact of time until the adsorption reached the equilibrium point [18]. However, when the system reached the equilibrium point, there were slight decrease in the removal percentage of heavy metals due to the accumulation of metal ions species in the adsorbents [19]. The capacity of adsorption for each heavy metals were varied between the combination treatment of *T. granosa* using lemon peels and mango peels. These results suggested that affinity of lemon peels and mango peels for each heavy metal in the studied sample were different as each heavy metals obtained different values of removal percentage. The difference in the capacity of adsorption for heavy metals can be explained in term of difference in the ionic size of the heavy metals, the nature and distribution of active groups on the adsorbents [20].

3.5 Effect on different adsorbent types

Mango peels and lemon peels were the two types of natural waste adsorbents that were chosen to test their efficacy in removing heavy metals from T. granosa. Figure 4 shows the amount of heavy metals removed from T. granosa when lemon and mango peels were used as natural waste adsorbents.

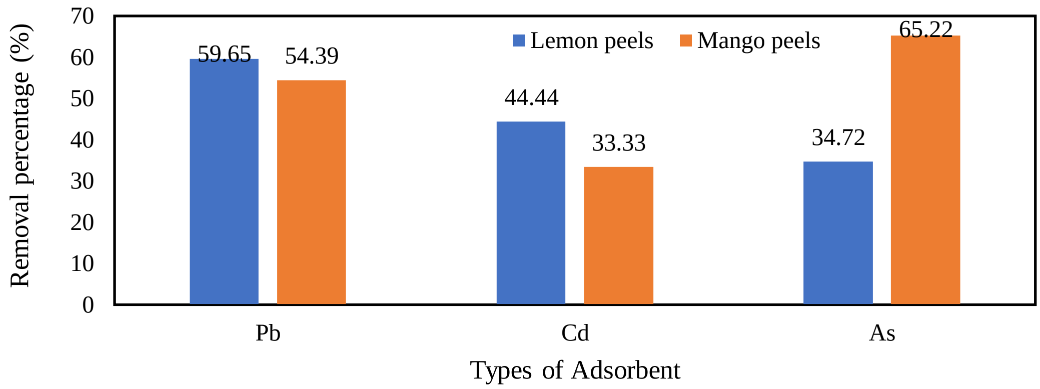

Figure 4. The removal percentage (%) of heavy metals from *T. granosa* after treatment using 0.3 g of lemon peels and mango peels for 30 min at 25 °C

According to Figure 4, lemon peels showed higher percentage removal of Pb (59.65%) and Cd (44.44%) compared to mango peels. However, it exhibited lower value for removal of As (34.72%) when comparing with treatment using mango peels in which the value was 65.22. In brief, lemon peels yielded higher removal percentage of As with value of 66.05%. Lemon peels were effective in removing Pb meanwhile mango peels were effective to reduce As. However, in overall adsorption process, statistical analysis showed there is no significant difference ($p > 0.05$) in term of effectiveness of adsorption between the lemon peels and mango peels in removing Pb, Cd, and As from *T. granosa*.

The difference in values for removal percentage of heavy metal may be due to the difference in the initial concentration of heavy metals [7]. At lower concentration, heavy metals ions present in the solution could interact with the binding sites of the adsorbents. Thus, heavy metals ions will be easier to be removed from the bivalves as compared with heavy metals ions that have higher initial concentration. An increase of the initial concentration of heavy metals will lead to increase in saturation of the adsorbents binding sites, causing low uptake of heavy metals ions by the adsorbents.

4. Conclusion

The concentration of Pb, Cd, and As in *T. granosa* was successfully determined by using FAAS and GAAS. The initial concentration of Pb, Cd, and As in *T. granosa* were 5.605 mg/kg, 1.770 mg/kg, and 0.579 mg/kg, respectively. Based on the FTIR spectra, lemon peels and mango peels have potential to become an effective natural waste adsorbents due to presence of hydroxyl and carboxylic functional groups which help to enhance the adsorption process. Hence, lemon peels and mango peels were effective to remove Pb, Cd, and As from *T. granosa*. There is no statistically significant difference between lemon peels and mango peels on the effectiveness in removing Pb, Cd, and As from *T. granosa*. In this study, the optimum absorption of *T. granosa* using lemon peels was obtained at 0.3 g for 70 min at 45°C which achieved 59.65% for Pb, 88.89% for Cd, and 67.54% for As. The highest removal percentage values for Pb, Cd, and As were 70.18, 100%, and 84.71% respectively using mango peels.

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