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Demetallisation of Heavy Metals from Indian Mackerel (*R. kanagurta*) Fish

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Abstract. Fish especially Indian Mackerel (*R. kanagurta*) provides protein, essential fatty acids and essential metals that are needed in the human diet, however high concentration of essential metals will cause adverse health effect towards human. Thus, the removal of heavy metals such as lead (Pb) and copper (Cu) from *R. kanagurta* (Indian mackerel) by using different types of natural waste adsorbents was implemented in this study. Initial concentration of heavy metals (Pb, Cu) in Indian mackerel (*R. kanagurta*) fish were above the permissible limit set by World Health Organization and Malaysia Food Regulation 1985. Thus, in this study, corncob and eggshell were applied as natural waste adsorbents to enhance the demetallisation process.The result showed only the corncob able to efficiently remove all the heavy metals in Indian Mackerel (*R. kanagurta*) up to 78.31% compared to the eggshell, which yielded about 71.34%. Besides, this study proved that using corncob; the Cd metal found to be wholly removed from (R. *kanagurta*) which met the permissible limit set by WHO and MFR.

1. Introduction

Fish is one of the essential foods in the human diet because of its high nutritional quality [1]. Moreover, it can be considered as one of the vital sources of protein for millions of people worldwide [2]. It also contains the presence of fats, omega-3 fatty acids and vitamins with numerous minerals [3]. In recent years, world consumption of fish has simultaneously increased with the growing concern of their nutritional and therapeutic benefits [4]. According to the Food and Agriculture Organization (FAO), more than 60% of commercial landings are consumed as fresh fish, 12% of landings were processed for consumption which particularly dried, salted or smoked whereas 36% of landings were made for fish meal and fish sauce [5]. In 2016, Ahmad et al, [6] reported the ten most frequently consumed marine fish by Malaysian people in the following descending order: Indian mackerel, anchovy, yellowtail and

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yellow-stripe scads, tuna, sardines, torpedo scad, Indian and short-fin scads, pomfret, red snapper, and king mackerel.

Nowadays, rapid industrialisation and urbanisation have caused serious heavy metal contamination to the environment [7]. In fish, it is often at the higher level of the aquatic food chain, substantial amounts of heavy metals may accumulate in their soft and hard tissues [8]. Hence, it is important to determine the metal levels in fish tissues because they reflect the concentrations of metals found in water and sediments [9].

Heavy metals are elements that have atomic weights between 63.5 and 200.6, and a specific gravity greater than 5.0. Most of the heavy metals are dangerous to health or the environment. The main threats to human health from heavy metals are associated with the consumption of Pb, Cd, mercury (Hg) and arsenic (As) [10]. Previous studies showed that heavy metals could be removed from aquatic organisms via several methods which were destructive and non-destructive. For the destructive process, it was proven that heavy metals concentration in fish could be affected by processing or cooking methods.

On the other hand, the adsorption method is a relatively new process and is emerging as a potentially preferred alternative for the removal of heavy metals because it provides flexibility in design, high-quality treated effluent, reversible and can be reproduced [11]. To date, the removal of heavy metals in the fish sample using adsorption technique has not been comprehensively studied. Previous researchers stated that eggshell and corncob were the potential natural waste adsorbents for the removal of heavy metals in wastewater treatment [12,13]. Thus, in this study, the adsorption technique was used by applying eggshell and corncob as adsorbents to remove the heavy metals elements such as Pb, Cu and Cd in Indian mackerel (*R. kanagurta*) fish species.

2. Materials and Methods

2.1. Chemicals
All reagents such as nitric acid (HNO_3) and standard stock solution of Pb, Cd and Cu used in the study were analytical grade.

2.2. Sampling
The Indian mackerel (*R. kanagurta*) fish (Figure 1) was purchased directly (approximately 1 kg) at Tunjung market in Kota Bharu, Kelantan and carefully preserved with ice in clean polyethylene bags. The function of ice was to minimise the tissue decay and to maintain the moist condition during transportation. The fish was immediately transported to the laboratory at School of Health Sciences, Universiti Sains Malaysia, Kelantan, where the sample was washed using deionised water and then deep-frozen at -20°C while waiting for dissection and preparation for the analytical test.

Figure 1. Indian mackerel (*R. kanagurta*) fish species

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2.3. Preparation of Natural Waste Adsorbent
The two different natural adsorbents used in this study were corncobs and eggshells. Both of the eggshells and corncobs were purchased from the hypermarket near to USM Kubang Kerian and were consumed to be considered as waste prior to the removal process. These adsorbents were washed with tap water to remove any adhering dust and impurities from their surface and then rinsed with deionised water. The adsorbents were dried in the hot air oven at a temperature of 60˚C overnight until constant weight was obtained. After the drying process, they were converted to a mesh powder by grinding in a mechanical grinder and preserved in a polyethylene container before being used.

2.4. Removal of Heavy Metals from Indian Mackerel (R. kanagurta) Fish
Approximately 0.1 g mesh powder of corncob was dissolved in 100 mL deionised water to produce a concentration of 1000 ppm. Next, 6.0±0.05 g of Indian mackerel (*R. kanagurta*) fish was held in a sack and soaked in a beaker that contains 100 mL (1000 ppm) corncob solution, stirred using a magnetic stirrer for 1 hour at 36.50±0.50˚C. The procedures were repeated by applying different types of adsorbent (eggshell) with different concentrations (1000 ppm, 1500 ppm, 2000 ppm).

2.5 Heavy Metal Analysis
The muscle tissue of Indian mackerel (*R. kanagurta*) fish (approximately 6.0±0.05 g) was digested using 65% of HNO_3. The digestion was done until clear solutions were obtained, and the sample was allowed to cool at room temperature. Next, the solution was filtered using filter paper and then diluted to 50 mL with deionised water. The prepared sample was then analysed for Pb, and Cu content using flame atomic absorption spectroscopy (FAAS). The concentration of heavy metals before and after the removal process was presented in mg/kg.

2.6 Characterisation of Corncob
Based on the demetallisation process, only corncob worked well in removing the heavy metals in R. *kanagurta*) species compared to the eggshell. Thus, in this study, the functional groups present in the corncob before and after the treatment process were investigated by using Fourier-transform infrared spectroscopy (FT-IR). This FTIR result was used to describe the role of the functional group present with the enhancement of the demetallisation process. The FT-IR absorbance data were collected in the range of wave number 500-4000 cm^{-1}.

3. **Results and Discussion**

3.1 Initial Concentration
The data for the initial concentration of heavy metals (Pb, Cu and Cd) in the muscle tissue of the Indian mackerel (*R. kanagurta*) fish are listed in Table 1 with the permissible limit set by World Health Organization (WHO) and Malaysian Food Regulation (MFR) 1985. According to the data obtained, the concentrations of Pb, Cu and Cd in this fish species were higher than both permissible limits stated by WHO and MFR.

Table 1. The initial concentration of heavy metals in Indian mackerel (*R. kanagurta*) fish and the permissible limit set by WHO and MFR

Sample	**Pb (mg/kg) ± SD**	**Cu (mg/kg) ± SD**	**Cd (mg/kg) ± SD**
Indian mackerel (*R. kanagurta*)	26.02 ± 0.53	15.61 ± 0.52	6.39± 0.24
Permissible limits	WHO: 2.00	WHO: 1.00	WHO: 2.00
	MFR: 1.00	MFR: 1.00	MFR: 1.00

Some of the factors that influenced the heavy metal concentrations in different fish species were feeding habits and habitats of species, differences in aquatic environments, the chemical form of metal in the water, dissolved oxygen concentration unusual metabolic activity of the marine organisms [2,9]. Besides, differences in metal concentrations were probably due to the contribution of several factors such as age, geographical distribution, anthropogenic inputs and species-specific factors.

Non-essential heavy metals such as Pb Cd and have no known essential role in living organisms, and their bioaccumulation in fish can be toxic for humans, even at deficient concentrations [14]. Therefore, the removal of these heavy metals from fish and aquatic organisms was necessary to provide safe food for human consumption.

3.2. Demetallisation Process of Heavy Metals in Indian Mackerel (R. kanagurta) Fish

3.2.1. Effect of Different Adsorbent Types

Two different types of natural waste adsorbents (corncob and eggshell) were selected to investigate their effectiveness toward demetallization process. Figure 2 illustrates that corncob was used as adsorbent has the ability to remove Pb and Cu from Indian mackerel (*R. kanagurta*) fish.

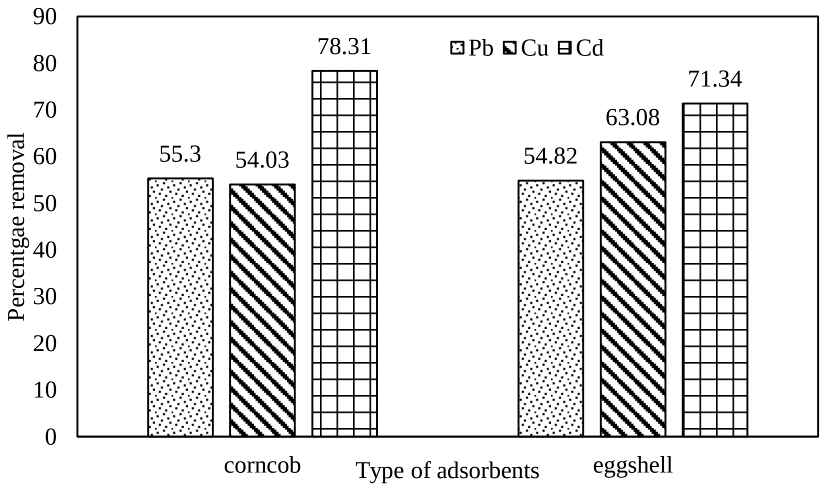

Figure 2. The removal percentage (%) of heavy metals from Indian mackerel (*R. Kanagurta*) fish after treatment using 1000 ppm of corncob and eggshell, respectively.

Based on the data showed, the corncob showed higher percentage removal of heavy metals such as Pb (55.3%) and Cd (78.31%) compared to eggshell even though it showed lower value for removal of Cu metal (54.03%) in Indian mackerel (*R. Kanagurta*) fish. Vaughan et al., [15] claimed that several active groups present in corncob such as hydroxyl, aldehydes, and carboxyl groups are capable of binding heavy metals by contributing an electron pair to constitute complexes with metal ions in aqueous solutions.

Besides, differences in the removal percentage of heavy metals intensities were due to the difference in the initial concentration of heavy metals. At lower concentration, all metals ions present in the solution could interact with the binding sites. Thus, the percentage of adsorption was higher compared to other metal ions that have higher initial concentration [16]. As the initial concentration of heavy metals increases, the saturation of the adsorbent sites will also increase, leading to low metal ions uptake by the adsorbents [17].

In contrast, eggshell yielded a lower percentage for the removal of Pb and Cd metals with values of 71.34% and 54.84%, respectively. Previous work claimed that lower amount of hydroxyl group on the eggshell surface led to the lower demetallisation process due to weak attraction between the hydroxyl group and heavy metals element in the fish species [18].

Using 1000 ppm of corncob, the concentration of each heavy metals Pb, Cu and Cd were still above permissible limit set by WHO and MFR by 11.76 mg/kg, 5.76 mg/kg and 1.83 mg/kg, respectively. Thus, in the next section, the concentrations of corncobs were varied to reduced the concentration of these metals below than permissible limits. Moreover, in the next section, the eggshell was excluded as the lower performance showed in the demetallisation process.

3.2.2. Effect of Different Concentrations of Adsorbent

In this study, different concentrations of corncob were prepared to test their effectiveness towards the demetallisation process. Figure 3 illustrates the removal percentage of heavy metals from Indian mackerel (*R. Kanagurta*) after treated with 1000, 1500 and 2000 ppm of the corncob.

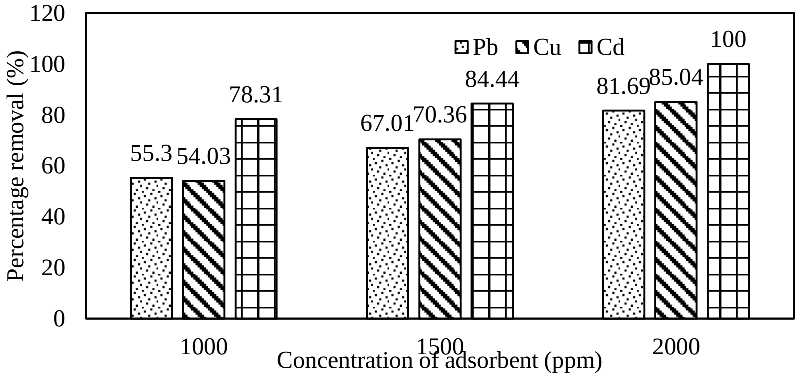

Figure 3. The removal percentage (%) of heavy metals from Indian mackerel (*R. Kanagurta*) fish after demetallization process using different concentrations of corncob (1000, 1500 and 2000 ppm).

According to Figure 3, increased concentration of corncob from 1000 to 2000 ppm, the percentage removal of all heavy metals also showed an increment up to 81.69% for Pb, 85.04% for Cu and 100% for Cd. This trend agreed by Lin et al, [19] who claimed that as the adsorbents concentrations increased, the number of available adsorption sites and specific surface area of sorbents eventually increased and this results to higher removal percentage of heavy metals. The Cd metal was successfully removed from this fish species. However, after treated with 2000 ppm of corncobs, the concentration for Pb and Cu were still above permissible limits with values of 4.76 mg/kg and 2.34 mg/kg, respectively.

3.3. Characterisation of the Potential Adsorbent

Pagnanelli et al. [15] reported that agricultural by-products are mainly composed of cellulose and lignin and usually contain some active functional groups, such as hydroxyl, carboxyl and ether groups The previous study claimed that the carboxylic and hydroxyl groups on the surface of the adsorbent play a vital role in the binding of heavy metal ions with the adsorbent, therefore, increasing the number of the carboxylic groups and hydroxylic groups should increase the binding capacity of the corncob as adsorbent.

In this research, the ability of the corncob to adsorb heavy metals was increased due to the higher intensity of carboxylic groups. Also, in Section 3.2.1., the demetallisation process showed that corncob has potential as an adsorbent for the removal of heavy metals in Indian mackerel (*R. Kanagurta*). Therefore, FTIR spectra for corncobs before and after the adsorption process are plotted in Figure 4.

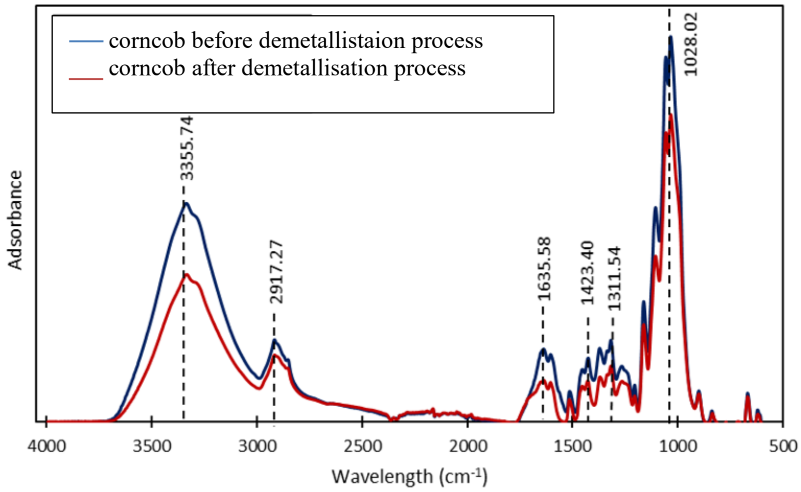

Figure 4. FTIR spectra of corncobs before and after adsorption process.

Figure 4 shows the spectral analysis of corncobs before and after demetallisation of heavy metals from Indian mackerel (R. Kanagurta) using adsorption process. The absorption band at 1635 cm^{-1} and 3355 cm^{-1} referred to the carboxylic (C=O) and hydroxyl groups (O–H), respectively. From the spectral analysis, it could be seen that there was a significant difference in the intensity of the carboxylic group and hydroxyl groups band before and after the demetallisation process using corncobs. The reduction in the intensity of the spectral for both groups after demetallisation process subjected to the adsorption the heavy metals ions adsorbed onto the active sites of corncobs. According to Leyva-Ramos et al. [20] the reduction showed that there was an interaction between the carboxylic site of corncobs with metal ions which are adsorbing on the carboxylic sites.

Conclusion

The heavy metals content (Pb, Cu and Cd) in Indian mackerel (*R. Kanagurta*) fish species recorded were above the limit set by WHO and MFR. The demetallisation process using adsorption technique using corncobs was successfully removed higher percentage removal of heavy metals from this fish species compared to the eggshell. Based on the FTIR spectra obtained in this study, the reduction of the carboxylic acid band proved the attraction between metals ions and active sites on the corncob which reduced the concentration of Pb, Cu and Cd metals in this fish species.

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