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Aluminum Corrosion in Vegetable Solutions- a Contribution to Dietary Intake

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The increased aluminum concentrations in the human body have been a huge concern due to its health effects. Aluminum utensils are believed to be the primary source of the aluminum metal to humans. In the present work, leaching of aluminum from aluminum utensils in different food solutions was examined. Three aluminum utensils of different origins were chosen from the local market. Different vegetables (green cabbage, red cabbage, and eggplants) were used to prepare different food solutions. Two techniques for analysis were used, weight loss (W_L) measurement and environmental scanning electron microscopy (ESEM). The results clearly indicate that the leaching of aluminum from the aluminum utensils, through the cooking process of each vegetable, participated a lot to the daily human intake of aluminum. The amount of leaching was found to be high in the food solutions after the cooking process. According to the World Health Organization (WHO), the obtained values are considered above their limitation values which might lead to several health effects.

Keywords: Aluminum leaching, green cabbage, red cabbage, eggplant, toxicity

1. INTRODUCTION

Aluminum is the third most common element found on Earth. It is an excellent heat conductor, but also a fairly soft metal that leaches more molecules into food than harder metals used in cookware. As a soft metal, it is prone to scratching and it warps easily at high temperatures. A major health drawback of aluminum is that it is a reactive material, which would react with acidic and alkaline food. The reaction causes food to have an off-metallic taste and changes its color, making it appear with an unattractively grey shade. More importantly, food cooked in aluminum can react with the metal to form aluminum salts. Despite that it can be found in food and medicine, aluminum is considered toxic to humans and could cause several diseases. Some studies state, although not yet proven, that the excessive aluminum levels in the body could contribute in causing Alzheimer's disease [1]. Aluminum cookware, apart from other sources of dietary aluminum, is considered to be a potential source of this metal to human beings. Manufacturers have addressed aluminum leaching by anodizing the cookware. Through anodization, chemical baths are used to increase the thickness of the oxide layer making it harder, more durable, and less likely to corrode and leach; provided the surface has not been damaged. Although it is more difficult to damage the surface of anodized versus non-anodized aluminum, surface damage might still occur. A key purchasing consideration is that not all anodized aluminum cookware, available in the market, use this material on the interior surface that come in contact with food. Instead of that, manufacturers use the heat transferring properties of the anodized aluminum on the exterior of the cookware and a different non-sticking material on the interior of the cookware (with other potential of toxicity problems much greater than the anodized aluminum). From an environmental perspective, aluminum cannot be destroyed in the environment; it can only change form [2].

Studies of all forms of human intake of aluminum, including that from food, has been prompted due to concerns over the possible environmental aluminum exposure and Alzheimer's disease relationship. Apart from the sources of dietary aluminum, aluminum cookware is considered to be a possible source of aluminum to humans. Many experiments were conducted to study the leaching effects with different foods, beverages and water in connection with pH variation. Unfortunately, there were many results disagreeing in the leached aluminum levels. This might be due to several factors, such as non-systematic and non-uniform experimental designs and conditions. In this work, the human intake values of aluminum will be evaluated precisely by standardizing the aluminum sample sizes, using real life cooking conditions, emphasizing the aluminum chemistry role in various cooking solution media, and applying strict analytical control in the estimation of aluminum [3].

Aluminum leaching in red and green cabbage as well as in eggplants is discussed in this study. The pigments in red cabbage are called anthocyanin. Anthocyanin change color in response to changes in acidity or pH. Red cabbage juice is purplish-red under acidic conditions, but changes to a blue-green color under alkaline conditions [4]. Although it has been reported that they act as powerful antioxidants, their rate to scavenge free radicals is not clear. These anthocyanins are also found in tomatoes.

Eggplant is consumed throughout the world, and varies in color, shape, and size. It is a good source of vitamins C, K and B6, panothenic acid, magnesium and many other nutrients [5]. It is reported that eggplants have a high content of phenolic compounds [6]. Predominant among these is chlorogenic acid, which lab research suggests that it may block the formation of cancer, such as liver and colon cancers. Powerful compounds in eggplant skin can help halt cancer proliferation.

Eggplant is one of the top ten vegetables in terms of oxygen radical absorbance capacity due to a novel source of anthocyanin, which is a major phenol in eggplant and is the most important antioxidant with a variety of physiological functions such as anti-mutagenesis, anticancer, and vision improvement. The anthocyanin concentration in eggplant fruit peel is higher than those in other such as potato, tomato, and pepper. Anthocyanin is an important pigment for the coloration in plants. There are some correlations between the fruit color and phenolic contents; eggplants have a great variation (3-20 times) in contents and proportions of phenols. There is even no anthocyanin in green and white eggplant accessions. Peel color is a complex trait, which has been subjected by several classical genetic analyses [7-12].

The leaching of aluminum from three aluminum cookware (Indian, Chinese, and Qatari) in different food solutions which contain green cabbage, red cabbage, and eggplant are studied in this present work.

2. MATERIALS AND METHODS

2.1. Materials

Three kinds of aluminum cookware, from different origins, are chosen from the local market.

The cookware origins are from India, China, and Qatar. The cookware are cut into small rectangular shapes with dimensions of 1x1.2 cm, and each has a small hole of 1 mm diameter at one end in order to hang them in the vegetable food solutions. The vegetables used are green cabbage, red cabbage and eggplant.

The following food solutions are prepared from these vegetables, drinking water, salt, and tomato juice:

- Green Cabbage:

150 g green cabbage + 300 ml drinking water + 3 g salt
300 g green cabbage + 300 ml drinking water + 3 g salt
300 g green cabbage + 150 ml drinking water + 3 g salt + 150 ml tomato juice

- Red Cabbage:

100 g red cabbage + 200 ml drinking water + 3 g salt
100 g red cabbage + 200 ml drinking water + 3 g salt + 100 ml tomato juice

- Eggplant:

150 g eggplant + 300 ml drinking water + 3 g salt
150 g eggplant + 150 ml drinking water + 3 g salt + 150 ml tomato juice

2.2. Methods

2.2.1. Weight loss (W_L) method

In this work, the weight loss method (W_L) is used to study the leaching of aluminum into the different vegetable food solutions at their boiling temperatures. The aluminum specimens are cleaned by distilled water and acetone, dried, and weighed using a four-digit sensitive balance. After boiling the samples for 20 minutes, the aluminum samples are then cleaned by distilled water followed by acetone and reweighed again. The pH values of the solutions are also measured before and after the experiment.

To assure consistency, all the experiments are performed in duplicates.

2.2.2. Environmental scanning electron microscopy (ESEM)

The samples are analyzed, before and after the experiment, using environmental scanning electron microscopy (ESEM) which is connected with an energy dispersive x-ray (EDX). This test gives an indication about leaching of the metals compared to the initial condition.

3. RESULTS AND DISCUSSION

The report of WHO (World Health Organization) in 1989 states that the provisional tolerance weekly intake (PTWI) is 7 mg of aluminum / kg of body weight. This means that for an average 50 kg body weight person, the daily intake of 50 mg of aluminum is tolerated. However such recommendation is generally based on the data available from short term toxicity studies [13]. This value therefore is subject to revision as and when data become available from chronic toxicity studies. It is also subject to examining the applicability of such recommendations especially in populations where widespread deficiencies of other minerals such as calcium and iron are common. In fact, recent evidence does suggest that aluminum absorption is greatly influenced by nutrients such as iron, calcium and zinc.

By cooking red cabbage samples in different acidic cooking solutions, it is determined that the aluminum leaching rate increases as the pH value decreases. The aluminum leaching rate is found to be 5.1 mg of aluminum per 100 g of red cabbage cooked in lemon juice at a pH of 2.6; while those cooked in tomato sauce is found to be 2.7 ±0.2 mg of aluminum per 100 g of tomato sauce with sugar and 4.9 ±0.2 mg of aluminum per 100 g of tomato sauce without sugar. Furthermore, similar values are found using the same samples stored for 48 hours in the refrigerator; these values are 2.8 ±0.2 mg of aluminum per 100 g of tomato sauce with sugar and 5.0 ±0.2 mg of aluminum per 100 g of tomato sauce without sugar [14].

In our study, it is noted that the leaching of aluminum occurred from all cookware in all the food solutions during a 20 minutes exposure.

The corrosion rates are calculated by dividing the weight loss, in each experiment, by the sample area and the 20 minutes exposure time. The calculated aluminum intake per person is based on the assumption that family composed of three members use aluminum utensils of 20 cm diameter and 18 cm height. The area exposed to the food will be around 1440 cm^2.

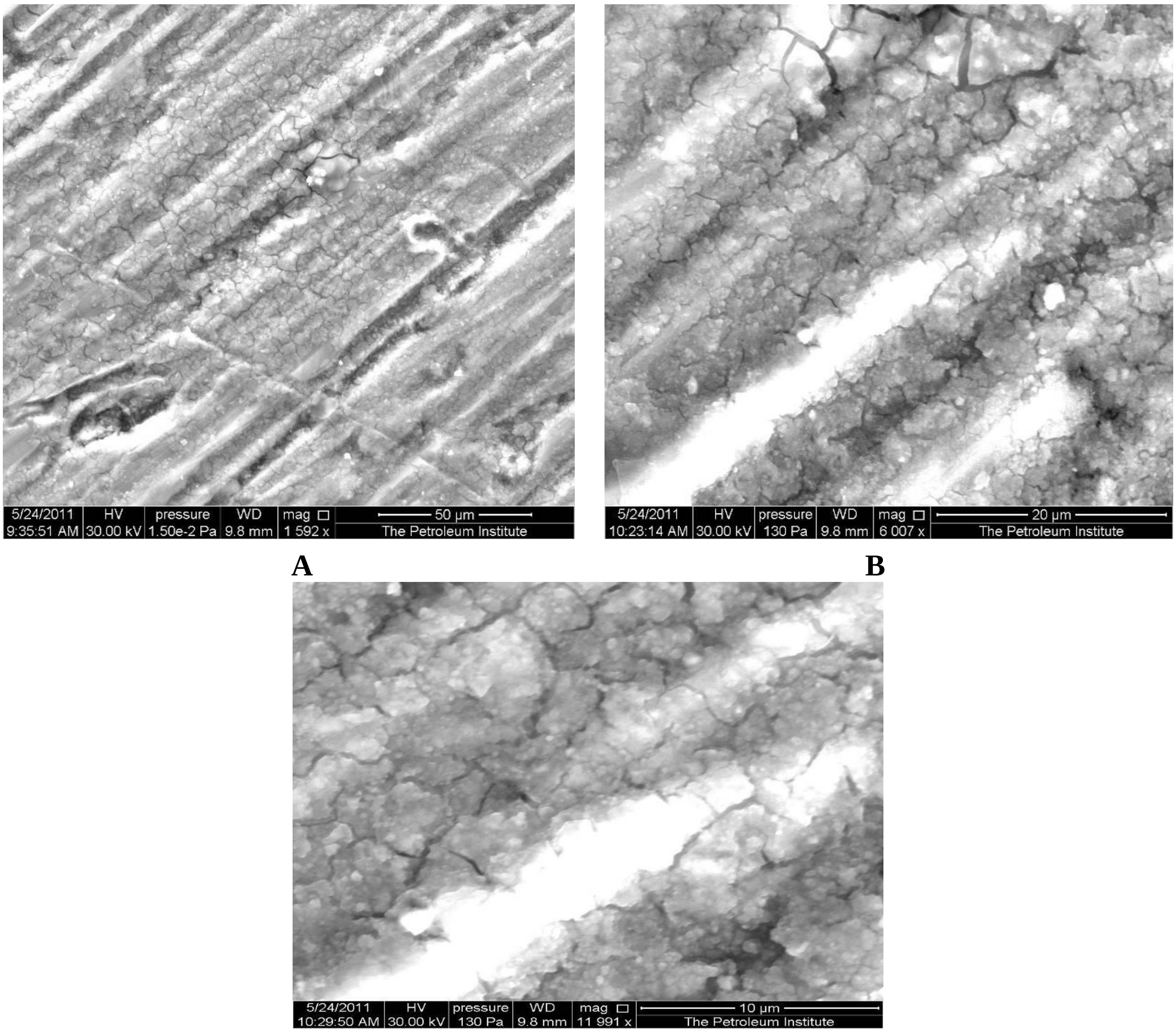
3.1. Green Cabbage

Neelam reported that green vegetable preparations contribute greatly to the total daily aluminum intakes [15]. This statement is confirmed in this work.

The aluminum leaching in the Chinese, Qatari and Indian cookware samples using green cabbage food solution are shown in Table (1).

Table 1. Aluminum leaching rate of three cookware samples of different origins used to cook a food solution for 20 minutes at boiling temperature

Sample origin	Solution composition	Initial pH value	Final pH value	Weight loss (mg)	Corrosion rate (mg/cm^2.hr.10^{-2})	Aluminum intake (mg/person)
China	150g of green cabbage + 300ml of drinking water + 3g of salt	6	6	0.2	25.2	40.4
Qatar		6	6	0.1	12.6	20.2
India		6	5.8	0.3	37.8	60.6



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Figures 1 A-C. ESEM images of the Indian aluminum sample after exposure to green cabbage solution at boiling temperature for 20 minutes.

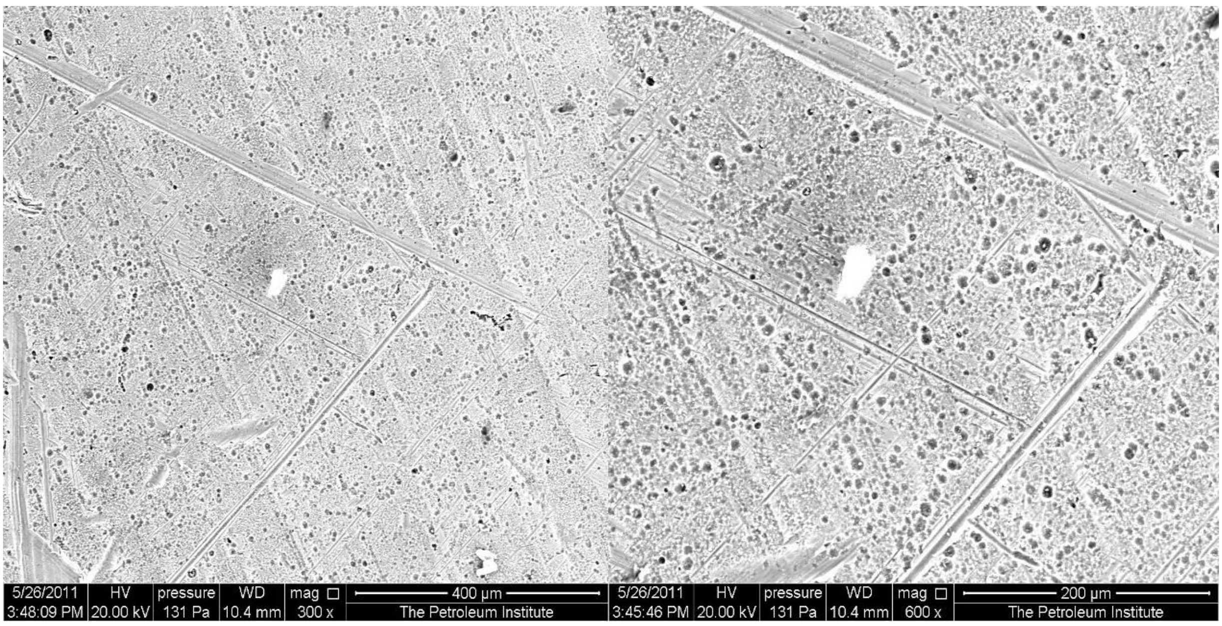
Comparing the three samples, leaching of aluminum is highest for the Indian sample which is further investigated by ESEM. Figure (1) shows different magnifications of the Indian sample emphasizing grains and grain boundaries which indicate that the outer layer of aluminum oxide is almost dissolved in the food solution. It shows the uniform thinning of a metal without any localized attack.

The effect of changing the concentration of the food solution and the addition of tomato juice on the leaching process is shown in Table (2). The addition of 150 ml of tomato juice reduces leaching.

Table 2. Aluminum corrosion rate of the Indian cookware sample in different green cabbage food solution for 20 minutes at boiling temperature.

Solution number	Solution composition	Cabbage solution concentration	Weight loss (mg)	Corrosion rate (mg/cm^2.hr.10^{-2})	Aluminum intake (mg/person)
1	150g of green cabbage + 300ml of drinking water + 3g of salt	33.1 %	0.3	37.8	60.6
2	300g of green cabbage + 300ml of drinking water + 3g of salt	49.8 %	0.2	25.2	40.4
3	300g of green cabbage + 150ml of drinking water + 3g of salt +150ml of tomato juice	49.8 %	0.1	12.6	20.2

Figures (2 A-C) are showing pitting corrosion on the surface of the Indian aluminum sample after immersion in solution (2) (Table (2)).



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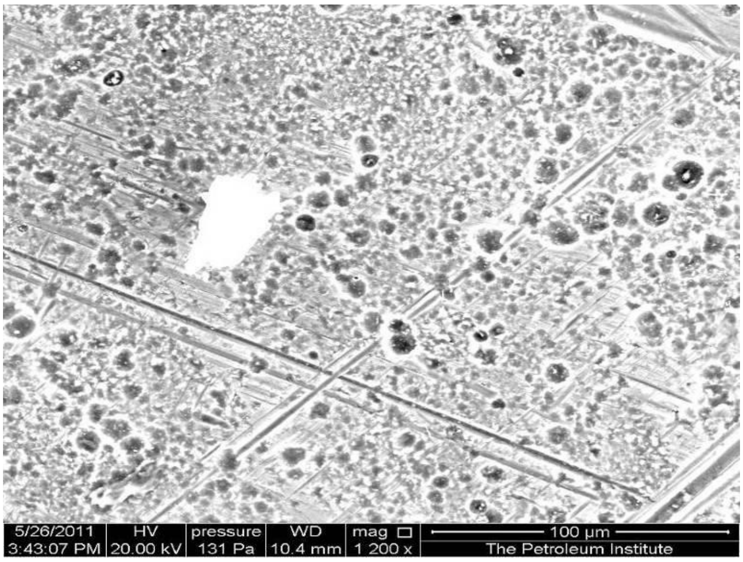

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Figures 2 A-C. ESEM images of the Indian aluminum sample after exposure to the concentrated green cabbage solution at boiling temperature for 20 minutes.

This could be the reason behind the reduction in the leaching rate at high green cabbage concentrations. The surface of the metal is almost covered by the vegetable, leaving small area exposed to the solution, this leads to the formation of pitting. It is a form of localized corrosion of metal surface where small areas corrode preferentially leading to the formation of cavities or pits, and the bulk of the surface remains unattacked. Aluminum is susceptible to this form of corrosion. It occurs with only a small weight loss on the entire surface. The reduction of the corrosion in the presence of tomato juice is due to the same reason.

The reduction of the leaching rate by the addition of tomato juice to the cabbage is in agreement with previous works [14, 16].

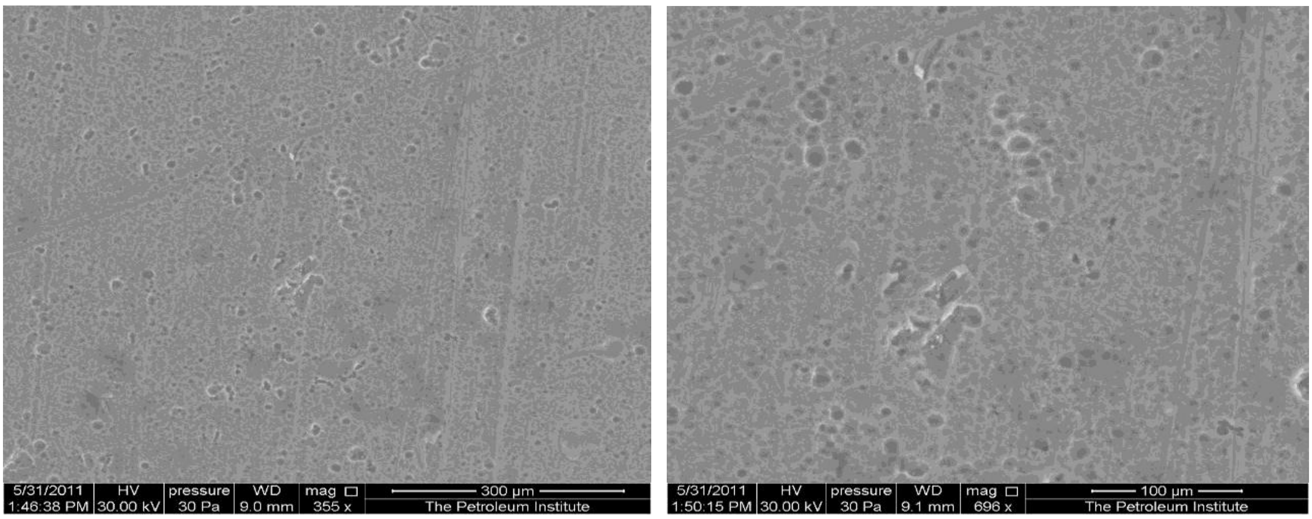
3.2. Red Cabbage

The leaching of the Indian and Chinese samples in red cabbage solutions are shown in Table (3). The leaching of the Chinese sample in the red cabbage food solution is double the one in the green cabbage food solution (Table (1)), while the Indian sample shows no difference in both the red and green food solutions.

From these results, it is clear that adding tomato juice to the red cabbage food solution has no effect on the leaching of the Indian sample (40 mg aluminum / person, with and without tomato juice). The addition of tomato juice to the green cabbage food solution shows lower leaching rate value than the addition of tomato juice to the red cabbage food solution using the same Indian sample (Tables (2) & (3)); the aluminum intake value is 20.2 mg / person from the green cabbage while it is 40.4 mg / person from the red cabbage. The Chinese sample shows an increase while using red cabbage food solution than using green cabbage food solution. The aluminum intake value in the red cabbage food solution containing tomato juice and the one without is 40 mg / person (Table (3)).

Table 3. Aluminum corrosion rate of the two cookware samples of different origins in red cabbage food solution of different concentrations after cooking for 20 minutes at boiling temperature.

Solution number	Sample origin	Solution composition	Cabbage solution concentration	Initial pH value	Final pH value	Weight loss (mg)	Corrosion rate ($mg/cm^2.hr.10^{-2}$)	Aluminum intake (person/mg)
1	China	100g of red cabbage + 200ml of drinking water + 3g of salt	33.1 %	6	5.9	0.4	50.4	80.8
2	India	100g of red cabbage + 200ml of drinking water + 3g of salt	33.1 %	6.4	6	0.2	25.2	40.4
3	India	100g of red cabbage + 200ml of drinking water + 3g of salt + 100ml of tomato juice	25.0 %	4.7	5	0.2	25.2	40.4



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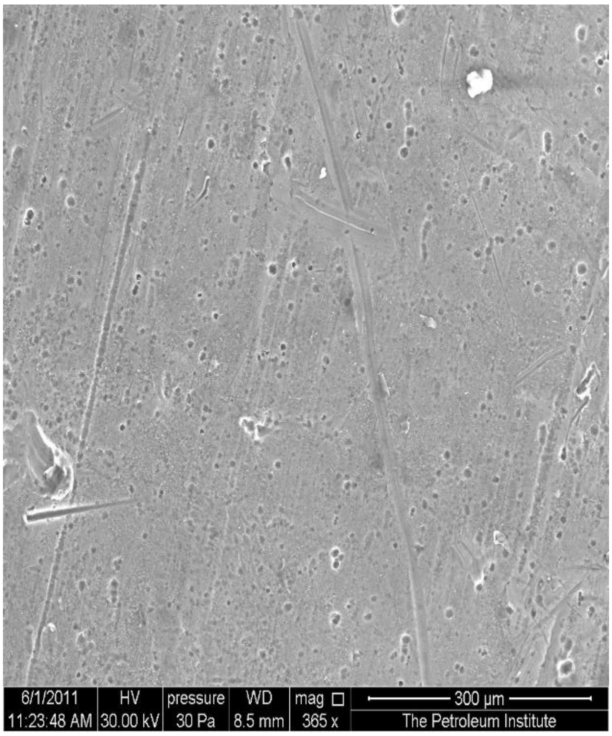
Figures 3 A-C. ESEM images of the Indian aluminum sample after exposure to red cabbage solution at boiling temperature for 20 minutes.



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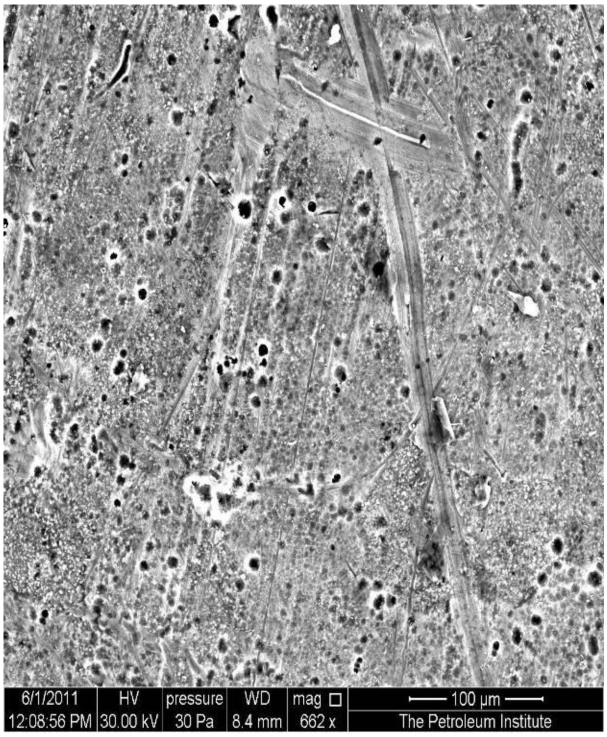

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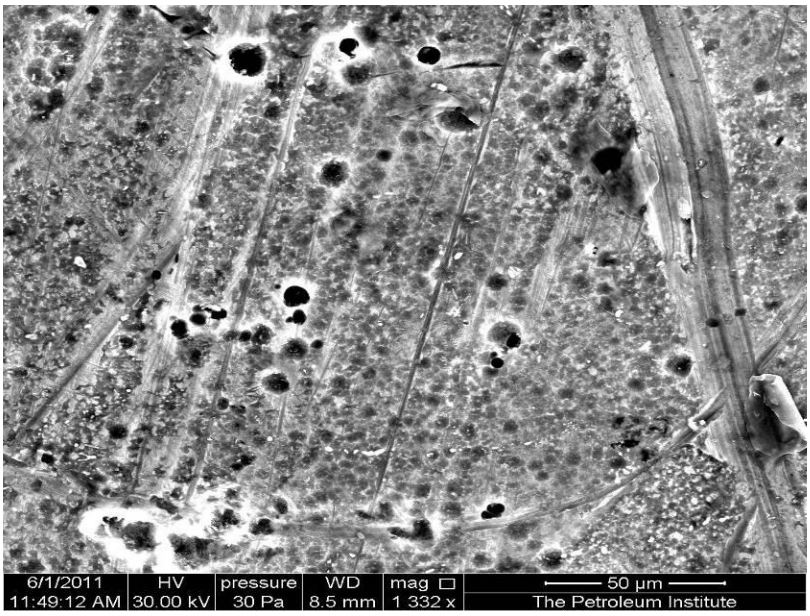

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Figures 4 A-C. ESEM images of the Indian sample after exposure to red cabbage with tomato juice solution at boiling temperature for 20 minutes

Figures (3 A-C) show the morphology of the Indian sample after the exposure to solution (2), and Figures (4 A-C) show the morphology of an Indian sample after the exposure to solution (3).

The two samples show some pitting on the entire surface; this could be the reason for the low leaching rate values compared to other materials.

For the Chinese aluminum sample, the leaching rate is found to be very high (80 mg / person for 20 minutes cooking time). It is reported that red cabbage samples cooked with different additives show that low pH increases the aluminum leaching rate [16]. While Verissimoa et al. report that other factors besides pH are important in the leaching of aluminum to the food solutions [14]. Possible sources of interference can arise either from the chemical manipulation or from the food itself. It is reported that red cabbage contains almost twice vitamin C as green cabbages. Red cabbages are always richer in anthocyanins depending on the pH [17].

Figure (6) summarizes the date for all the two types of cabbage solutions and the two different aluminum materials, Indian and Chinese:

- Chinese aluminum samples leached twice more in green cabbage solution than in red cabbage solution. This could be due to the presence of riboflavins which act as oxidizing agents because of their ability to accept a pair of hydrogen atoms.
- Indian aluminum samples leach less in red cabbage solution but show pitting on the surface while they leach more in the green cabbage solution and severe general corrosion occurs.
- When tomato juice is added to the Indian samples in both green cabbage and red cabbage solutions, leaching rate is not high but there is evidence that pitting occurs.

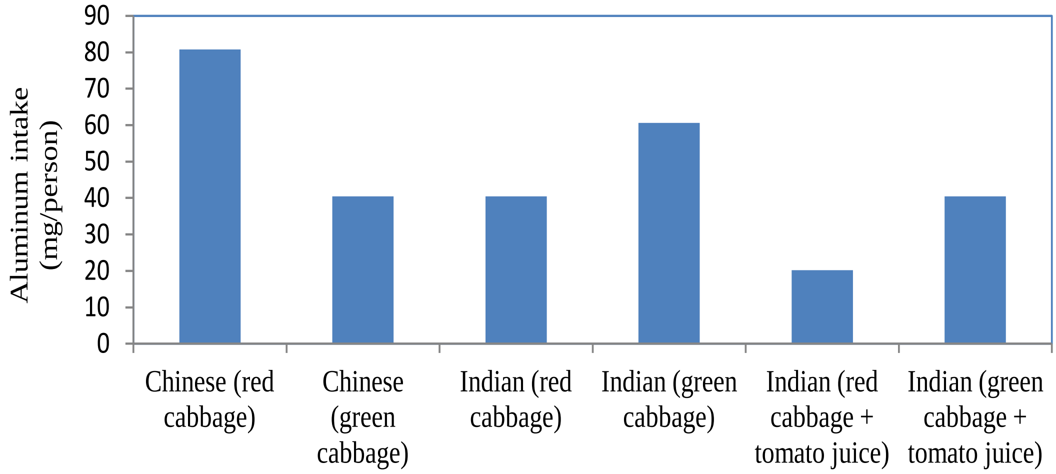


Figure 6. Leaching of Chinese & Indian aluminum sample in different green & red cabbage solutions at boiling temperature for 20 minutes

3.3. Eggplant

The leaching of Chinese and Indian samples in a food solution of peeled and unpeeled eggplants is shown in Table (4). In peeled eggplant solution the leaching is low compared to all previous work done using other vegetables. The aluminum intake value is found to be 20 mg / person for both the Indian and Chinese samples. The addition of 150 ml of tomato juice to the eggplant food solution stopped the leaching for 20 minutes test period. This is because the mode of damage has changed from general corrosion to localized corrosion, like pitting. The duration period is so short, that losses in weight due to the initiation of pitting corrosion is almost negligible. For this reason another series of tests are performed for a period of two hours. The results show that there is leaching with the addition of tomato juice. The aluminum intake value is found to be 20mg/person.

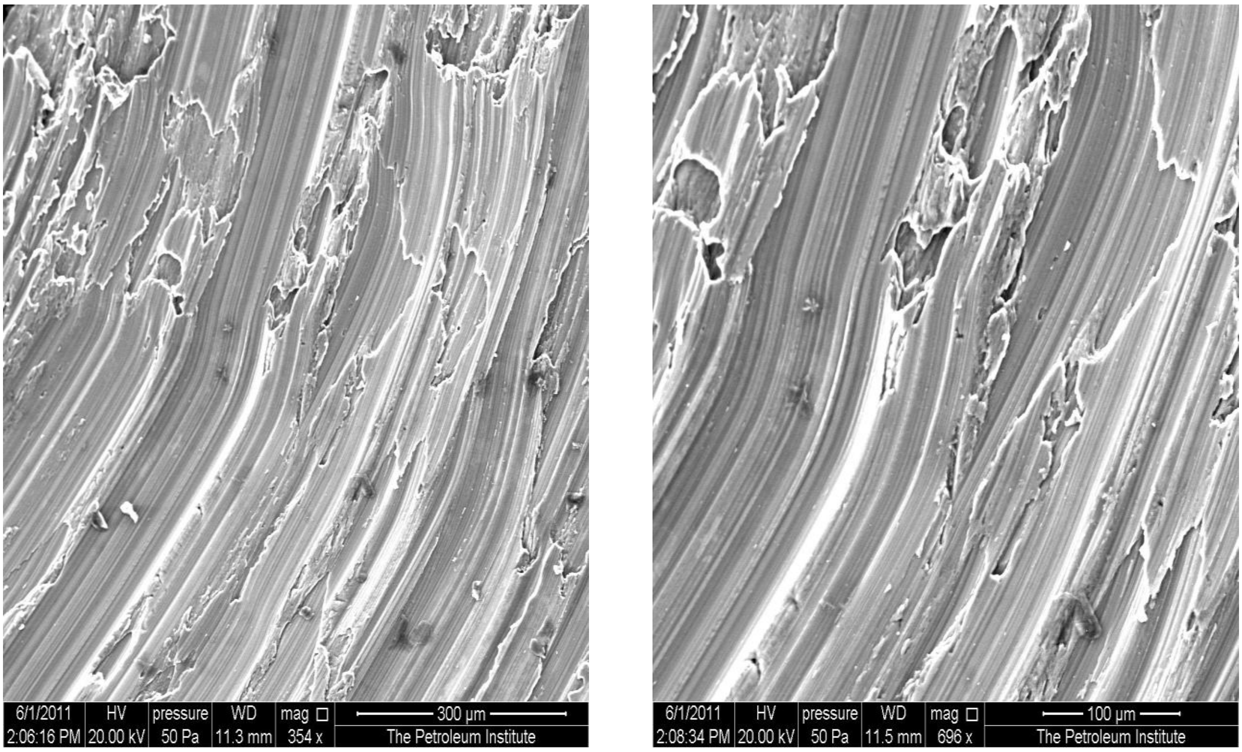
In comparison between the food solution prepared using unpeeled and peeled eggplant, the leaching of Indian sample is four times the peeled one. The aluminum intake value is 80 mg / person compared to 20 mg / person, respectively. As a result, unpeeled eggplants cause more leaching than the peeled eggplants. This is again attributed to the presence of riboflavin with its oxidizing ability.

Table 4. Leaching of different aluminum cookware (from two different origins) in eggplant food solution with eggplant percentage of 33.1% using drinking water for 20 minutes at boiling temperature.

Sample origin	Solution composition	Initial pH value	Final pH value	Weight loss (mg)	Corrosion rate ($mg/cm^2.hr.10^{-2}$)	Aluminum intake (mg/person)
China	150g of peeled eggplants + 300ml of drinking water + 3g of salt	5.9	5.7	0.1	12.6	20.2
India	150g of peeled eggplants + 300ml of drinking water + 3g of salt	5.9	5.7	0.1	12.6	20.2
India	150g of unpeeled eggplants + 300ml of drinking water + 3g of salt	6.4	6.9	0.4	50.4	80.8
India	150g of peeled eggplants + 150ml of drinking water + 3g of salt + 150ml of tomato juice	-	-	0	0	0

Figure (5) shows the surface morphology of the Indian sample after the exposure to the unpeeled eggplant solution for 20 minutes. The high leaching value in the unpeeled eggplant solution, compared to the peeled one, could be due to fact that the eggplant skin contains vitamin C and other acids as mentioned earlier [5].

In addition to that, there is not much previous work done by others regarding the leaching of aluminum in eggplant food solution.



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Figures 5 A-B. ESEM images of the Indian sample after exposure to peeled eggplant solution at boiling temperature for 20 minutes

All the above results are conducted within a cooking time of 20 minutes only, so cooking for a longer time increases the aluminum intake values. The increase in the exposure time to 40 minutes enhances the leaching by a factor of four compared to the 20 minutes exposure, for a general corrosion mode.

4. CONCLUSION

The results of the present work clearly indicate that the use of aluminum utensils in cooking green cabbage, red cabbage, and eggplant contribute significantly to the total daily intake of aluminum. Increasing the concentration of green cabbage in the food solution from 33 wt % to 50 wt % causes a decrease in the leaching of aluminum into the food solution. This is due to the change in the nature of the reaction between the aluminum and the solution. Uniform corrosion occurs in low concentration, while pitting occurs at high concentration. The increase in aluminum levels in unpeeled eggplant food solutions range between factors of 3-5 compared with the level in peeled eggplant solution. Finally, increasing the cooking time enhances the leaching of aluminum in all the food solutions used in this work.

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