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Biosorption ability of starfruit (*Averrhoa carambola* L.) in removing cadmium and lead in contaminated water samples

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Abstract

Starfruit (*Averrhoa carambola* L.) is a common fruit found in the tropics, particularly in the Philippines. Due to it having chelating agents in its fruit composition, the study determined the ability of unripe and ripe starfruits to filter heavy metals, cadmium Cd^{2+} (aq) and lead Pb^{2+} (aq), in contaminated water samples. Twenty water samples were prepared during the study, where ten samples were contaminated with Cd^{2+} (aq), and the other ten samples with Pb^{2+} (aq). 15% unripe starfruit solutions were introduced to five Cd^{2+}- and five Pb^{2+}-contaminated samples, and ripe starfruit solutions were introduced to the remaining samples. Findings revealed that both Cd^{2+} (aq) and Pb^{2+} (aq) were significantly reduced when the starfruit extract was introduced to the contaminated samples. It was also found out that the biosorption abilities of unripe and ripe starfruits were comparable with each other, and that starfruit filtered more Pb^{2+} (aq) than Cd^{2+} (aq). Thus, starfruit is capable of removing significant amounts of heavy metals, thereby indicating metal ion concentration reduction. Studies are recommended to investigate further this ability of starfruit.

Keywords: biosorption, starfruit, cadmium, lead, water contamination

Introduction

The Philippines is a country with about 20% of its income relying primarily on agriculture, horticulture, aquaculture and fishing (Habito and Briones, 2005) [11]. Agriculture, fisheries and other allied livelihood activities are primarily dependent on water to sustain the practices. When water is contaminated with pollutants and contaminants, heavy metals in particular, may lead to disastrous effects within the said practices (Verma and Dwivedi, 2013) [27]. Plants may be exposed to such contamination through uptake of water from the roots; animals eat these plants and may also accumulate metals within its tissue lining. Upon ingestion, several kinds of metals in certain doses, can exhibit toxic effects to human body (Jaishankar, Tseten, Anbalagan, Mathew and Beeregowda, 2014) [13]. As such, metal poisoning becomes a severe case of contamination, which may hamper the well-being of plants, animals and humans in general. Heavy metal contaminants can be removed from water sources through methods such as carbon filtration, chlorination, and specifically-designed filtration processes (Gunatilake, 2015) [10]. However, these methods are not that easily available for people (i.e. farmers and fishermen) who reside in rural regions. Due to this, many researchers study alternative means of removing heavy metals in water sources- using plant resources. Biosorption is one of these ways in removing such ions in water-contaminated sources (Abbas, Ismail, Mostafa and Sulaymon, 2014) [1]. The process involves the action of biomasses to passively absorb metal ions to its structure. Chelative agents are known to capably exhibit water-softening properties by forming precipitates with metal ions and allowing them to be extracted or absorbed. Chelating agents are substances whose molecules can rearrange the chemical composition of heavy metal ions by forming several bonds to each ion (Vandenbossche, Jimenez, Casetta and Traisnel, 2014) [26]. In cases of metal ion poisoining, these agents are used to help isolate such contaminants and to react them to form by-products which can be easily secreted (Ojuederie and Babalola, 2017) [16]. The study relies on this concept that metal ions tend to form complexes with certain forms of chelating agents. The reaction between these agents and metal ions may cause the former to either form products insoluble to water, allowing them to be relatively easy to remove, or to create complexes that may change their nature.

Due to ability of chelating agents in metal ion removal, various studies were conducted using plant parts as sources of such agents. Sulaymon, Mohammed and Al-Musawi (2013)[24] investigated the rate of absorption of various green and blue-green algal biomass in terms of lead, cadmium, copper and arsenic ions, and found out that Pb^{2+} (aq) were absorbed the most. Gaur, Kukreja, Yadav and Tiwari (2017)[8] assessed the phytoremediation potential of cilantro (*Coriander sativum* L.), and found out that the plant was effective in removing Pb^{2+} (aq) and As^{3+} (aq) in contaminated soil and water. Moreover, a review conducted by Sumiahadi and Acar (2018)[25] listed several crop plants such as cucumber (*Cucumis sativus* L.), lettuce (*Lactuca sativa* L.), radish (*Rapanus sativus* L.) and spinach (*Spinacia oleracea* L.), which have phytoremediation activities on heavy metals including Pb^{2+} (aq), Cu^{2+} (aq), Fe^{3+} (aq), As^{3+} (aq) and Cd^{2+} (aq). Furthermore, recent study by Go, Larrazabal, Sanchez and Ponce (2018)[9] observed the biosorptive nature of parsley (*Petroselinum crispum* Mill.), and their study findings revealed that Pb^{2+} (aq) was significantly reduced upon the introduction of the plant leaves.

One of the resources having promising chelating properties is starfruit (*Averrhoa carambola* L.). Balimbing, as called in the Central Philippines, is a plant native in the tropics, which has yellowish fruits containing edges running across the sides, that when cut, resemble a star-like shape (Dagupta, Chakraborty and Bala, 2013) [4]. Due to it containing elevated amounts of oxalic acid, $H_2C_2O_4$ (aq) (see Table 1), the fruit, which is generally edible, is usually looked down upon because of its toxicity in certain situations, especially to people who have urinary complications (de Oliveira and de Agular, 2015) [6]. However, using the fruit's $H_2C_2O_4$ (aq) as chelating agent in removing heavy metals could give a new light on the use of starfruit in the future.

Table 1: Oxalic acid content of starfruit

Authors	Unit	Content		
		Unripe	**Half-ripe**	**Ripe**
Soumya and Nair (2014) [23]	mg/mL	8.68^1 6.86^2		7.89^1 2.59^2
Manda, Vyas, Pandya and Singhal (2012) [15]	mg/g FW	0.039-0.679		
A Patil, D Patil, Phatak and Chandra (2010) [19]	mg/g FW (%FW)	6.30 (0.63)	8.53 (0.85)	10.40 (1.04)
Joseph and Mendonca (1989) [14]	mg/g FW	$5.90\text{-}10.90^1$ $1.40\text{-}1.69^2$	$5.40\text{-}7.00^1$ $0.89\text{-}1.82^2$ $0.08\text{-}0.73^3$	$3.79\text{-}4.10^1$ $0.22\text{-}0.97^2$
Wilson, Shaw and Knight (1982) [29]	g/100g DW			
Vines and Grierson (1966) [28]	mg/g FW (% total acid)	5.00 (40.00)		9.58 (73.70)

^{1} sour fruit, ^{2} sweet fruit, ^{3} different cultivars

The study sought to test the ability of starfruit to act as a metal ion filter in water-contaminated samples through determinaton of the starfruit's capability in reducing the amounts of Cd^{2+} (aq) and Pb^{2+} (aq) in contaminated samples. Comparison of the filterative abilities of the fruit on such heavy metals was also determined in the study. Results of the study may help in the development of alternative metal ion filters, and also increase availability of such filters in hardly accessible areas; hence, the conduct of the study.

Materials and Methods

The starfruits were collected as unripe and ripe fruits from a backyard in a Cebu city in Central Visayas, Philippines. The extracts of the fruits were collected by using a knife and cutting board to slice the fruit, then juicing the fruit to collect the liquid. The final composition ratio of starfruit extract used in the study was 15 mL extract per 85 mL water, or 15% starfruit aqueous solution.

Twenty samples of 250 mL distilled water were placed in beakers. Ten of these samples were contaminated with Cd^{2+} (aq) and the other ten with Pb^{2+} (aq). The Cd^{2+} and Pb^{2+} stock solutions with concentration level of 1000 ppm were prepared in order to contaminate the distilled water samples. Using a sterilized 50-mL volumetric pipette, the water samples were added with 1.25 mL of the stock metal ion solutions until each of the water samples reached a metal ion concentration of 50 ppm ± 5ppm.

Using another batch of sterilized 50-mL volumetric pipette, the contaminated samples were added with 100 mL of the 15% starfruit solution prepared, and allowed to react with the samples for a 30-minute durational period.

All the experimental samples were filtered through #42 filter papers to remove the starfruit residue, and dispose this residue. Using a micropipette, 5 mL from each of the remaining solutions of the samples were transferred to a sterilized beaker, and were prepared to be subjected into the atomic absorption spectrometry (AAS). 50 mL of distilled water was added into the beaker in order to meet the minimum volumetric requirements demanded by AAS. The samples were then measured through AAS, and the results were compared (through *t*-testing of dependent and independent samples, $\alpha=0.01$) with the standard starting concentrations in order to determine if there were any significant differences in contaminant concentrations.

Results and Discussions

Concentration of Cadmium and Lead during Pre- and Post-treatments

The concentrations of the heavy metals, Cd^{2+} (aq) and Pb^{2+} (aq), before and after the application of 15% starfruit solution are presented in Table 2 below.

Table 2: Pre- and post-treatment concentrations of Cd^{2+} (aq) and Pb^{2+} (aq)

Group	**Cd^{2+} (aq), Mean Concentration** (N=5 per group)		**Pb^{2+} (aq), Mean Concentration** (N=5 per group)	
	Pre-treatment	**Post-treatment**	**Pre-treatment**	**Post-treatment**
Unripe	46.31 ppm	25.25 ppm	46.31 ppm	7.82 ppm
Ripe	46.32 ppm	31.32 ppm	46.31 ppm	13.77 ppm

As shown in Table 2, the mean pre-treatment concentrations of Cd^{2+} (aq) and Pb^{2+} (aq) are almost the same in both the unripe and ripe starfruit groups, and are hence comparable. After the application of the respective starfruit solutions, there was a decrease in the heavy metal concentrations, and this may indicate the biosorptive properties of the starfruits.

Heavy Metal Reduction during Post-treatment

After introducing the 15% starfruit extract to the contaminated water samples, there was a reduction of Cd^{2+} (aq) and Pb^{2+} (aq) concentrations. Analysis of these concentrations is presented in Table 3 below.

Table 3: Heavy metal reduction during post-treatment

Group	Concentration Difference	SD	*t*-value	p-value
Unripe fruits				
Cd^{2+} (aq)	21.06 ppm	1.94	-24.26**	$p<0.01$
Pb^{2+} (aq)	38.50 ppm	1.11	-77.47**	$p<0.01$
Ripe fruits				
Cd^{2+} (aq)	15.08 ppm	1.91	-17.63**	$p<0.01$
Pb^{2+} (aq)	32.55 ppm	0.95	-76.94**	$p<0.01$

** highly significant

As presented in Table 3, there were significant reductions of Cd^{2+} (aq) and Pb^{2+} (aq) concentrations using the unripe starfruit concentration (t=-24.26, $p<0.01$; t=-77.47, $p<0.01$ respectively). Not only unripe fruits have significantly affected the post-treatment concentrations but also were the ripe starfruits. The ripe fruits had significant reductions in Cd^{2+} (aq) and Pb^{2+} (aq) concentrations (t=-17.63, $p<0.01$; t=-76.94, $p<0.01$ respectively). These reductions signify the ability of starfruits in removing the heavy metals in the contaminated water samples. This may be attributed to the activities of the $H_2C_2O_4$ (aq) content of the unripe and ripe starfruits.

Oxalic acid has a carboxyl group which plays an important role in metal biosorption (Shamim, 2018) [22]. In aqueous solutions, oxalic acid exists as its anionic form, the oxalate $C_2O_4^{2-}$ (aq)—a well-known chelating agent for heavy metals (Pan, Lei, Ko, Chao, Chiu, Lee and Lu, 2001) [17]. The equilibrium equation for oxalic acid-oxalate in aqueous solution is shown in the figure below.

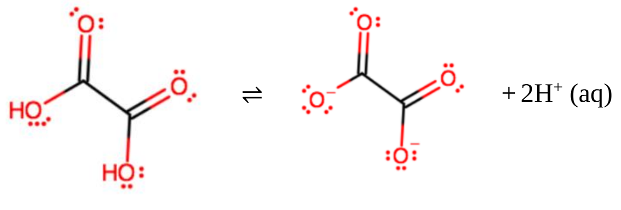
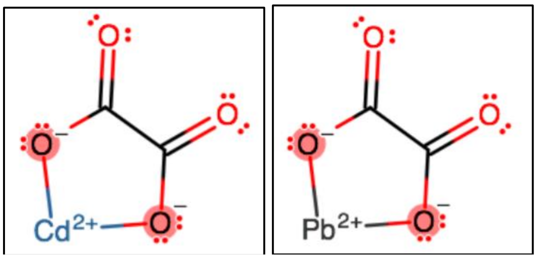


Fig 1: Chemical equilibrium of oxalic acid in aqueous solution

Oxalate chelating agents possess ligand-binding atoms with two possible coordinating linkages. The ligand-binding atoms of $C_2O_4^{2-}$ (aq) are the two oxygen atoms with more unshared electron pairs, where metal ions coordinate to form complex ring-like bidendate chelates, oxalate-Cd^{2+} and oxalate-Pb^{2+} complexes (Qahtani, 2017; Flora and Pachauri, 2010) [20, 7]. The formed bidendate complexes are presented in Figure 2.



(a) (b)

Fig 2: Structural formulas for (a) oxalate-Cd^{2+} and (b) oxalate-Pb^{2+} complexes

The formation of the oxalate-metal complexes prevents Cd^{2+} (aq) and Pb^{2+} (aq) from being free radicals, thereby increasing the affinity of the oxalate for the metals. Complex formation leads to surface sorption mechanisms such as precipitation, ion exchange and adsorption (Abbas, Ismail, Mostafa and Sulaymon, 2014; Papirio, Frunzo, Mattei, Ferraro, Race, D'Acunto, Pirozzi and Esposito, 2017) [1,18]. These mechanisms exhibit biosorption properties that form precipitates with Cd^{2+} (aq) and Pb^{2+} (aq) ions, allowing these metals to be extracted and removed. Due to these mechanisms, the unripe and ripe starfruits reduced significant concentrations of Cd^{2+} (aq) and Pb^{2+} (aq) in the contaminated water samples.

Comparison between Unripe and Ripe Starfruit Metal Ion Removal

The statistical comparison between the heavy metal concentration reduction between the unripe and ripe starfruit solutions is exposed in Table 4.

Table 4: Difference in the mean concentration reduction between unripe & ripe starfruits

Group	Mean Reduction	SD	Difference	*t*-value	p-value
Unripe	29.78 ppm	9.31	5.97	1.43^{ns}	$p>0.01$
Ripe	23.82 ppm	9.32			

^{ns} not significant

As exposed above, statistical comparison between the mean concentration reduction of heavy metals between unripe and ripe fruits resulted to a t-value equals to 1.43 and a p-value greater than 0.01, thereby indicating that there is no significant difference in the reduction of heavy metals between unripe and ripe fruits. This means that the reduction between unripe and ripe fruits is comparable, and thus, have similar heavy metal removal activities in contaminated water.

Comparison between Cd^{2+} (aq) and Pb^{2+} (aq) Reduction by Starfruit

Cd^{2+} (aq) and Pb^{2+} (aq) concentrations have both significantly reduced upon the introduction of 15% starfruit solution. The reduction of these two metals was compared, and the statistical results are presented in Table 5.

Table 5: Difference in the mean concentration reduction between Cd^{2+} and Pb^{2+}

Group	Mean Reduction	SD	Difference	*t*-value	P-value
Cd^{2+}	18.07 ppm	3.64	17.46	-11.26**	$p<0.01$
Pb^{2+}	35.53 ppm	3.28			

** highly significant

As presented above, there was a significant difference (t=-11.26, p<0.01) between the reduction of Cd^{2+} (aq) and Pb^{2+} (aq) when starfruit was introduced. This means that Pb^{2+} (aq) has been biosorbed in greater amounts than that of Cd^{2+} (aq), a finding similar to that of Sulaymon, Mohammed and Al-Musawi (2013) [24] when they investigated the absorption rates of various green and blue-green algal biomass. This could be due to the fact that Pb^{2+} (aq) has greater metal stability constant than that of Cd^{2+} (aq), thus Pb^{2+} (aq) competes more for the ligand-binding atoms of the chelating agent $C_2O_4^{2-}$ (aq) (Flora and Pachauri, 2010) [7]. This means that Pb^{2+} (aq) has higher ability to compete with protons or H^+ (aq) for organic binding sites than Cd^{2+} (aq) (Abdi and Kazemi, 2015) [3]. Heavier ions are preferred by the binding sites since these ions might have better fit with two distant functional groups (Davis, Volesky and Mucci, 2003; Haug and Smidsrød, 1965) [5, 12]. Thus, Pb^{2+} (aq) has more affinity to the chelating agent, and is eliminated more than Cd^{2+} (aq).

Percentage of Heavy Metal Biosorbed

To get the percentage of heavy metal absorbed, the following formula derived from the study of Seolatto, Silva Filho and Mota (2012) [21] was used:

$$\%\ \text{Biosorbed} = \left(\frac{C_i - C_{eq}}{C_i}\right) \cdot 100$$

Using this formula, the percentage of Cd^{2+} (aq) biosorbed by the unripe starfruit is 45.48% while the ripe starfruit is 32.38%. The % Pb^{2+} (aq) biosorbed by the unripe starfruit is 83.11% while the ripe starfruit is 70.27%. These results suggest that starfruits have high percentages of heavy metal biosorbed.

Conclusion and Future Directions

Starfruits have the potential ability to filter heavy metals in contaminated water samples. This may be attributed to the greater amounts of oxalic acid found in the fruit's composition, in which the chelating ability of the anionic form of the acid, $C_2O_4^{2-}$ (aq), allows the metal to be extracted and removed. Further investigations are recommended to study this biosorption ability of starfruit, taking into consideration the following aspects: adsorption, kinetic, isothermic and thermodynamic mechanims. Other parameters, such as increasing/decreasing the fruit's concentration, lengthening the exposure of the fruit to the contaminant, changing the pH of the solution, and examining the oxalic acid' structure during chelation process, may be investigated in order to have full understanding of how starfruit could help in the decontamination of heavy metal pollution in the environment.

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