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Catalytic Chelation Technique for the Removal of Heavy Metals in *Cosmos Caudatus Kunth* and *Solanum Lycopersicum*

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Abstract
The removal of heavy metals (Pb and Cd) from *Cosmos caudatus Kunth* and *Solanum lycopersicum* by chelation technique was conducted using three types of chelating agents, which are trisodium citrate, disodium oxalate and sodium acetate. The efficiency trend of chelating agent for the removal of heavy metals was follows the order of trisodium citrate > disodium oxalate > sodium acetate. Treatment using trisodium citrate was observed under optimized conditions which are 400 ppm of trisodium citrate and treatment time of 60 minutes at ambient temperature. The results showed the highest percentage heavy metals removal of *Cosmos caudatus Kunth* for Pb was 57.8%, and for Cd was 38.1% while, the removal of Pb for *Solanum lycopersicum* obtained was 41.8% and for Cd was 48.2%. The removal capacity of heavy metals was increased by using catalytic chelation technique in the presence of MgO/CaO (10:90)/Al_2O_3 catalyst. The 0.2% of catalyst loading gave percentage removal of Pb and Cd in *Cosmos caudatus Kunth* with 70.7% and 47.58%, respectively. Meanwhile, for *Solanum lycopersicum,* the removal of Pb was 47.3% and Cd 51.8%. Thus, this study successfully proven that the catalytic chelation technique has capability to enhance the removal of heavy metals in plants.
Keywords: Cosmos caudatus Kunth; Solanum lycopersicum; heavy metals; chelation; catalysts

1. Introduction

Vegetables are important components of human diet across the world both in terms of quantities consumed and nutritional value. However, these fruits could provide both essential and toxic metals over a wide range of concentrations (Diop, N., & Jaffee, S., 2005). Vegetables safety is a major public health concern worldwide. The increasing risk of contamination in fruits by pesticides, heavy metals, and toxins, the fruits safety issues have attracted the attention of research recently. Lead (Pb) and cadmium (Cd) head the priority list of hazardous substances of the Agency of Toxic Substances and Disease Registry (DT, O., AA, A., and OE, O., 2015). Table 1 indicates the maximum and guideline levels for the Pb and Cd contaminants in *Cosmos caudatus Kunth* and *Solanum lycopersicum* according to Codex International Food Standard and Malaysia Food Regulation 1985.

Table 1. Maximum and guideline levels for the study metals (lead and cadmium) contaminants in *Cosmos caudatus Kunth* and *Solanum lycopersicum* (Codex standard and Malaysia food regulation 1985)

Maximum Level (ML)	Lead (Pb) ppm	Cadmium (Cd) ppm
Codex Standard	0.1	0.05
Malaysia	2	1

This research highlighted on the efficiency of chelation and catalytic chelation technique in removing heavy metals in *Cosmos caudatus Kunth* and *Solanum lycopersicum*. Chelation technique introduced an effective and simple way to treat heavy metals poisoning compared to other methods that has been used in removing heavy metals. The chelating agent is the formation of ring-like structure that called as ‘chelate’ and the chelating agent will bind to the metal ion and form complexes before excreting out from the samples studied. Therefore, this present study focusing on Pb and Cd as these elements are environmental contaminants that can have serious risks to human health.

2. Materials and Methods

The purposes of this research were focused on the determination of Pb and Cd in *Cosmos caudatus Kunth* and *Solanum lycopersicum*, the effectiveness of three chelating agents includes trisodium citrate, sodium acetate and disodium oxalate in removing heavy metals in *Cosmos caudatus Kunth and Solanum lycopersicum* and application of catalytic chelation technique for enhancing the heavy metals removal.

2.1 Catalyst Preparation

Wetness impregnation method was used for the preparation of the catalyst. Firstly, a magnesium nitrate salts and calcium nitrate salts with ratio (10:90) were weight and dissolved in 5 mL of distilled water each. The catalyst solutions were then mixed together and the mixture was stirred for 30 minutes with a magnetic stirrer. The alumina was immersed in the catalyst solution for 1 hour after a solution produced a homogeneous mixture. The catalyst was then dried at room temperature before being aged at 90^{o}C in an oven overnight to remove water and provide a good coating of metal onto the exterior of the alumina. To remove impurities from precursor salts and excess water, the catalyst was calcined in the furnace at a rate of 5^{o}C/min from the furnace temperature up to 1000^{o}C and kept at this temperature for 5 hours in the presence of air.

2.2 Optimization Parameters

Three types of chelating agents used were trisodium citrate dehydrate, $C_6H_5O_7Na_3.2H_2O$, disodium oxalate, $Na_2C_2O_4$, sodium acetate trihydrate, $CH_3COONa.3H_2O$. Each salt (0.4 g) was dissolved and diluted to 1000 mL in volumetric flask (1000 mL) to prepare 400 ppm of chelating agent. The method was repeated by using 0.3 g, 0.5 g and 0.6 g to form 300 ppm, 500 ppm and 600 ppm respectively. Different treatment times involved which were 15 minutes, 30 minutes, 45 minutes and 60 minutes. Table 2 summarizes the treatment process of *Cosmos caudatus Kunth* and *Solanum lycopersicum* with chelating agents

Table 2. The treatment process of *Cosmos caudatus Kunth* and *Solanum lycopersicum* with chelating agents

Type of chelating agents	The concentration of chelating agents	Treatment times
Trisodium citrate Sodium acetate Disodium oxalate	300, 400, 500, 600 ppm	15 minutes, 30 minutes, 45 minutes and 60 minutes

2.3 Catalytic Chelation Technique

The catalytic chelation treatment has been conducted with the addition of 0.2 g, 0.4 g and 0.6 g of MgO/CaO (10:90)/Al_2O_3 catalyst in the sachet bag into the obtained optimum condition parameters for the removal of Pb and Cd in *Cosmos caudatus Kunth* and *Solanum lycopersicum*. 0.1 %, 0.2 % and 0.3 % of catalysts loading involved in this catalyst chelation treatment referred to 0.2, 0.4 and 0.6 g of MgO/CaO (10:90) Al_2O_3, respectively (DT, O., AA, A., and OE, O., 2015).

3. Results and discussion

The initial concentration of heavy metals in Cosmos Caudatus Kunth and Solanum lycopersicum were analysed by using Flame Atomic Absorption Spectroscopy (FAAS). Table 3 below shows the initial concentration of *Cosmos Caudatus Kunth and Solanum lycopersicum*. In general, *Cosmos Caudatus Kunth* had higher Pb (6.639 ppm) and Cd (0.058 ppm) contaminants compared to *Solanum lycopersicum*. However, both of them indicated that their heavy metals content exceeded the permissible limit stated by WHO and Malaysian Food Regulations 1985. Therefore, removal of heavy metals was significantly vital in order to provide safe vegetables to be consumed.

Table 3. The initial concentration of *Cosmos Caudatus Kunth and Solanum lycopersicum*

	Cosmos Caudatus Kunth		Solanum lycopersicum	
	Pb	Cd	Pb	Cd
*Initial concentration (ppm)	6.639	0.058	4.746	0.074

3.1 Effect of Type of Chelating Agents

In this section, three chelating agents were used to study the effect of different type of the chelating agents toward the effectiveness in removal of heavy metals from *Cosmos Caudatus Kunth and Solanum lycopersicum.* Type of chelating agent plays an important role for eliminating heavy metals as they have different properties. *Cosmos Caudatus Kunth and Solanum lycopersicum* were treated with 400 ppm of chelating agents at ambient temperature for 1 hour. The outcomes of treatment are shown in Figure 1.

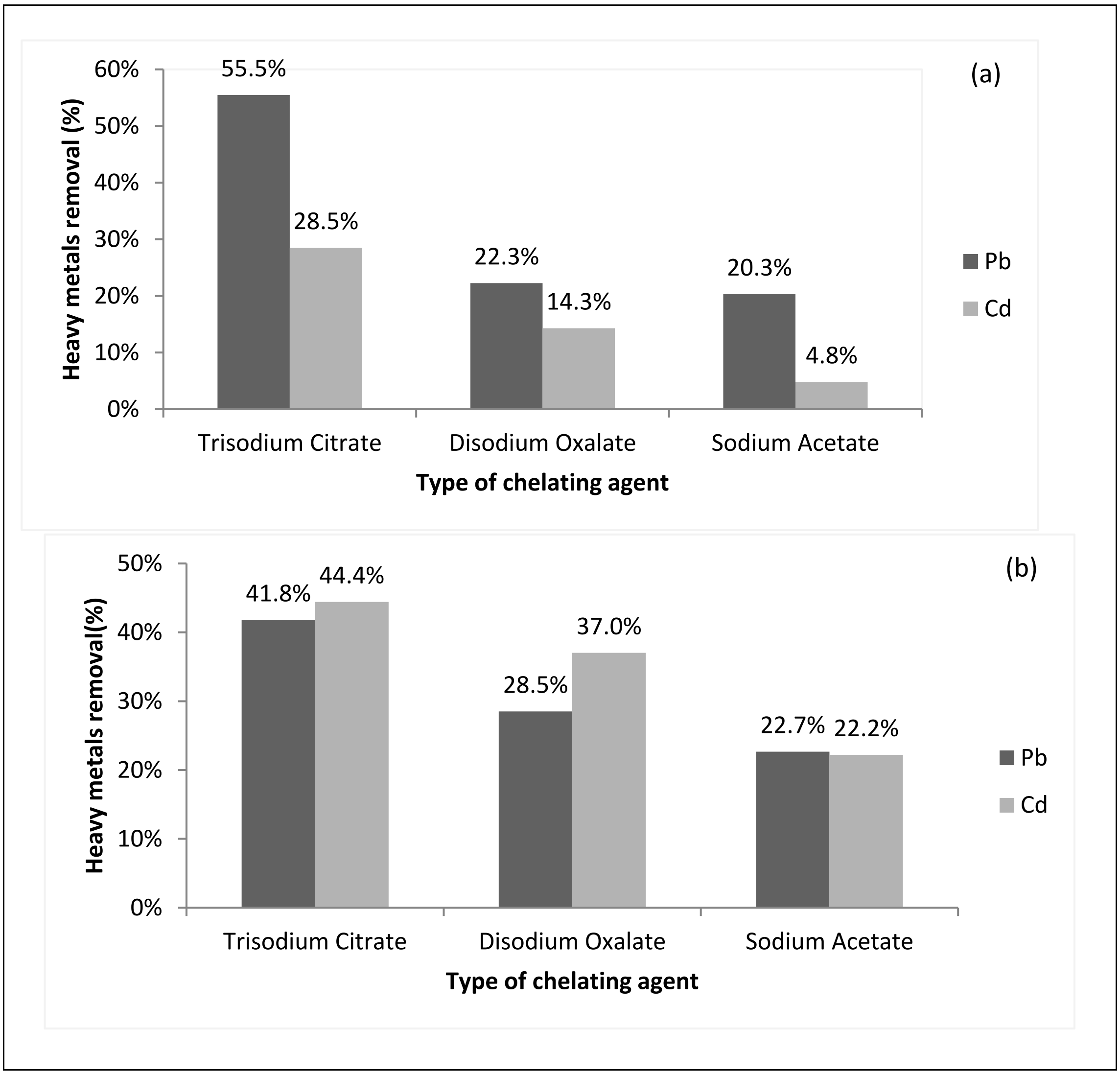

Figure 1. The percentage removal of Pb and Cd after treatment by using three different types of chelating agents (400 ppm) for 1 hour at ambient temperature from a) *Cosmos caudatus Kunth* and (b) *Solanum lycopersicum.*

Based on Figure 1, it showed that those chelating agents used have an ability to remove Pb and Cd from *Cosmos caudatus Kunth* and *Solanum lycopersicum.* The findings showed trisodium citrate recorded the highest percentage of heavy metals removal compared to disodium oxalate and sodium acetate. By treating with trisodium citrate, 55.5% of Pb and 28.5% of Cd were removed in *Cosmos Caudatus Kunth* while 41.8% of Pb and 44.4% of Cd were removed in *Solanum lycopersicum.* Besides, by using disodium oxalate, the Pb percentage removal was 22.3% and 28.5%, while for removal of Cd was 14.3% and 37.0% in *Cosmos caudatus Kunth* and and *Solanum lycopersicum* respectively. Meanwhile, sodium acetate gave lowest removal of heavy metals in the range of 5% - 23% from both *Cosmos caudatus Kunth* and *Solanum lycopersicum* over Pd and Cd.

From the Figure 1, it was evidently proved that trisodium citrate could chelate the highest amount of heavy metals from both *Cosmos caudatus Kunth* and *Solanum lycopersicum.* The chelating agents were able to make a bond with transition metal ions to form complex compound and thus metal ions can be excreted out from the samples (DT, O., AA, A., and OE, O., 2015). Removal of Pb was higher compared to Cd in both species because the stability constant of a complex can be quantitatively expressed in equilibrium equation values, which depend on the atomic structure of the chelated metals where Pb-complex 18.3 and Cd-complex was 16.4 (Samsudin, N. A. et al., 2012). The trend of type of chelating agents used to remove Pb and Cd was trisodium citrate > disodium oxalate > sodium acetate.

The highest removal of heavy metals from both species when using trisodium citrate because of a few reasons. It is observed that metal complexes of tridentate ligands forming from trisodium citrate are significantly more stable than the corresponding complexes as the increase in stability is called chelate effect. This results to a greater percentage of heavy metals removal from *Cosmos caudatus* Kunth and *Solanum lycopersicum.* Meanwhile, disodium oxalate and sodium acetate have low stability that caused the extracted metal ions being released back and retained in the organism (Hu, J., et al., 2013). The reaction pathway of trisodium citrate towards heavy metals was illustrated in Figure 2.

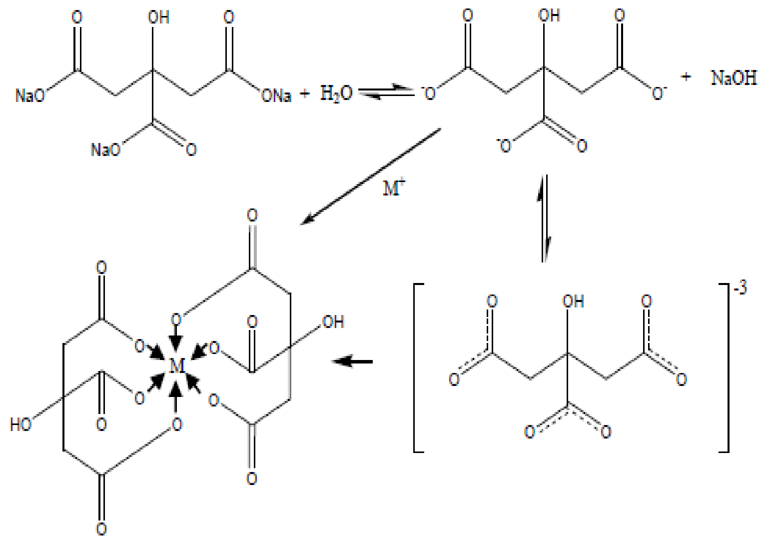

Figure 2. The proposed reaction pathway of chelation treatment towards heavy metals using trisodium citrate.

3.2 Effect of Chelating Agent Concentrations

Cosmos caudatus Kunth and *Solanum lycopersicum* were treated with trisodium citrate in various concentrations (300, 400, 500 and 600 ppm) for 1 hour in order to study the effect of concentration of chelating agents to the effectiveness removal of heavy metals. The percentage of Pb and Cd removal from *Cosmos caudatus Kunth* and *Solanum lycopersicum* are clearly shown in Figure 3.

From the Figure 3, there was an optimum concentration of trisodium for an effective removal of heavy metals from *Cosmos caudatus Kunth* and *Solanum lycopersicum.* The concentration was 400 ppm with highest percentage removal of Pb (57.4% and 41.0%) and Cd (38.1% and 48.2%), respectively . However, the results still not achieve the permissible limit set by WHO and Malaysian Food Regulations 1985. The higher the concentration of chelating agent, the higher removal of heavy metals would be, reaching an optimum percentage removal of heavy metals at 400 ppm for both species and percentage removal of heavy metals drop to some extent with further increasing the chelating agent concentration. The pattern was related to chemical equilibrium to Le Chartelier's principle that had been discussed by Azelee *et al* (Wan Azelee, I., 2014). At low concentration, the trisodium citrate was dissociated into sodium ion and citrates ions resulting efficient removal of heavy metal. As the concentration is too high, the dissociation of trisodium citrate generates large amount of citrate anions. The excess of citrate ion was reacted with water to produce citric acid to achieve equilibrium, thus the concentration of citrate ion drops due to lower heavy metals removal.

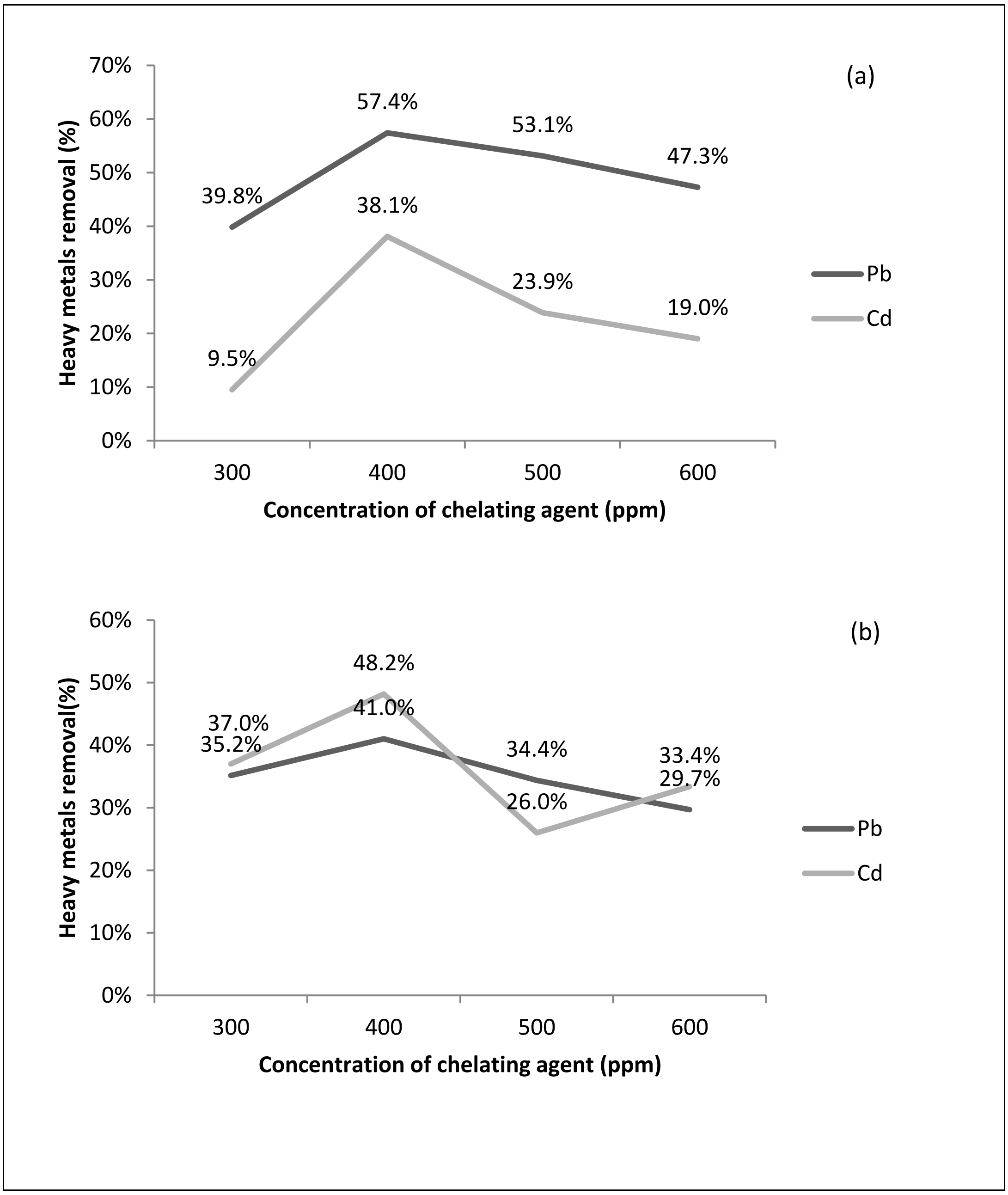

Figure 3. The percentage removal of Pb and Cd after treatment by using four different concentration of chelating agents of trisodium citrate in 1 hour at ambient temperature from (a) *Cosmos Caudatus Kunth* and (b) *Solanum lycopersicum.*

Le Chatelier's principle was not the only factor of decreasing in removal of heavy metals as the equilibrium constant is very small (K = 4.0 x 10−7) and only small amount of citrate ion would change into citric acid. The decreasing of percentage removal of heavy metals might be due to the competition of citrate ion itself as it would prefer to form a bond with themselves at a very high concentration.

3.3 Effect of Treatment Time

Treatment time for removing heavy metals is important as it will affect the percentage of heavy metals excretion. Figure 4 shows the quantitative results of percentage heavy metals that had been removed from *Cosmos caudatus Kunth* and *Solanum lycopersicum* for 15, 30, 45, and 60 minutes by using 400 ppm trisodium. From the results, the both plants show that 60 minutes give the highest percentage of heavy metals removal as for *Cosmos caudatus Kunth* the removal of heavy metals was 57.8% for Pb and 38.1% for Cd. Meanwhile, for *Solanum lycopersicum,* the removal of Pb was 41.8% and Cd was 48.2%. Further treatment time give higher excretion of heavy metals. The excretion of heavy metals at 60 minutes was still increasing showed that 60 minutes treatment time was still not in optimum time yet.

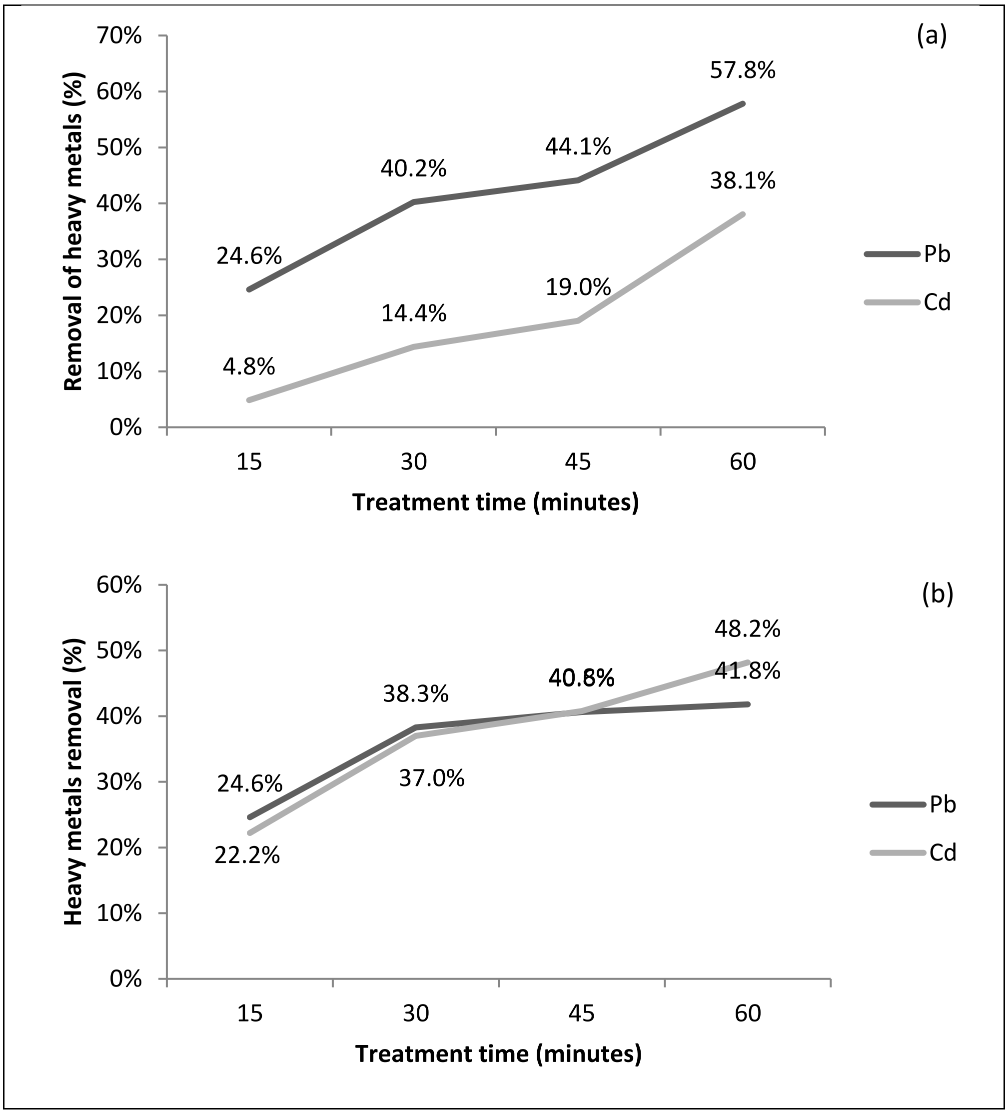

Figure 4. The removal percentage of heavy metals in (a) *Cosmos caudatus Kunth* and (b) *Solanum lycopersicum* after treatment at different reaction times using trisodium citrate (400 ppm) with stirring at ambient temperature.

3.4 Catalytic Chelation Activity

The previous sections showed that the chelation treatments were able to remove Pb and Cd from *Cosmos caudatus Kunth* and *Solanum lycopersicum.* In this section, the bimetallic oxide catalyst, MgO/CaO (10:90)/Al_2O_3 calcined at 1000 °C for 5 hours was added into the chelating solution. There are two benefits by using of bimetal oxides where they can act as adsorbents and provide more surface active sites that contributed to an increasing of heavy metal removal efficiency (Li, N. et al., 2015). In this section, 400 ppm of trisodium citrate with 60 minutes of reaction time was used to study the effect of catalyst in order to enhance the elimination of heavy metals. The results were presented in Figure 5.

Based on the Figure 5, when adding 0.1% of catalyst into 400 ppm of trisodium citrate at ambient temperature, 62.5% and 42.9% removal of Pb and Cd of *Cosmos caudatus Kunth* while, 48.2% and 44.1% removal for *Solanum lycopersicum* were detected respectively. The Pb and Cd results showed 70.7% and 47.6% of *Cosmos Caudatus Kunth* and 51.8% and 47.3% of *Solanum lycopersicum* after undergoing treatment of 0.2% of catalytic chelation technique. This is because higher active sites were provided on the surface of catalyst and adsorbents that can remove heavy metals from the *Cosmos Caudatus Kunth* and *Solanum lycopersicum*. On other hand, by adding 0.3% of catalyst, the percentage removal of Pb and Cd were slightly increased to 71.9%, 52.4% for *Cosmos Caudatus Kunth* and 53.1%, 51.8% for *Solanum lycopersicum*. From the data obtained above, 0.2% of catalyst dosage would be optimum for the removal of Pb and Cd from *Cosmos Caudatus Kunth* and *Solanum lycopersicum* as the increasing dosage beyond the optimum 0.2% gave slightly effect on the removal of heavy metal.

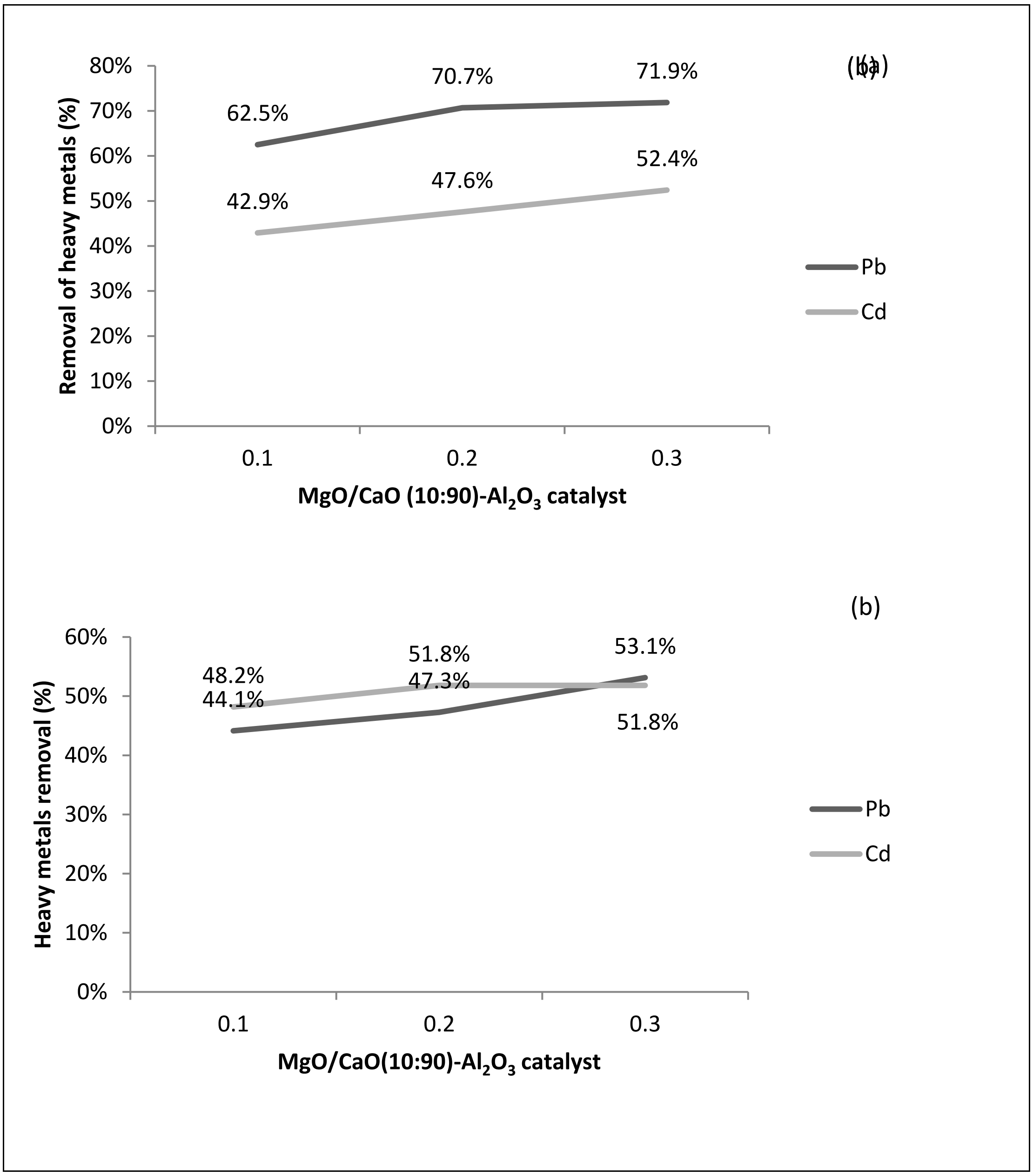

Figure 5. The percentage of Pb and Cd removed from *Cosmos Caudatus Kunth* and *Solanum lycopersicum* after treatment in 400 ppm trisodium citrate with three different percentages of MgO/CaO (10:90)/Al_2O_3 catalyst at ambient temperature in 60 minutes.

It was proven the catalyst has the ability to increase the removal of heavy metals from Cosmos Caudatus Kunth and Solanum lycopersicum. According to Langmuir Hinshelwood models, the reactant of trisodium citrate was adsorbed on the active sites of surface of the catalyst and dissociated into active species of sodium ions and citrate ions. The citrate will chelate with targeted metals ions presence in the sample to form complexes. Thus, it prevents trisodium citrate from back to citric acid as it was irreversible reaction due to the presence of catalyst. Later, the production of metal citrate compound and NaOH will be released into the solution leaving the catalyst alone. The catalyst will then proceed their catalytic activity with adsorbing new trisodium citrate compound on their surface. Thus, a cyclic catalytic chelation proceeds again (Ihsan Wan, A., R. et al., 2014).

4. Conclusion

In this study, the initial concentration of Pb and Cd were determined in the *Cosmos caudatus Kunth* and *Solanum lycopersicum*. The results for *Cosmos caudatus Kunth* was 6.639 ppm of Pb and 0.058 ppm of Cd while 4.746 ppm of Pb and 0.074 ppm of Cd contaminated in *Solanum lycopersicum* which exceed the permissible limit set by WHO and Malaysian Food Regulations 1985. The catalytic chelation technique at optimum conditions which was 400 ppm trisodium citrate for 60 minutes in the presence of catalyst of MgO/CaO (10:90) supported on Al_2O_3 was successfully removed the heavy metals from *Cosmos Caudatus Kunth* (Pb; 70.7%, Cd; 47.6%) and *Solanum lycopersicum* (Pb; 47.3%, Cd; 51.8%). It was proved in the presence of catalyst had improved the percentage of heavy metals removal and achieve the permissible limit.

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