Apiaceae Family Plants as Low-Cost Adsorbents for the Removal of Lead Ion from Water Environment

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Abstract. Adsorbents prepared from the three selected plants from Apiaceae family commonly known as parsley, coriander and culantro were observed to remove lead from aqueous solutions. Batch experiments were conducted to study the effect of dosage, pH, contact time and agitation speed at 10 mg L\(^{-1}\) initial Pb(II) concentration. Results revealed that three selected plants showed high adsorption capacity for removal of lead from aqueous solutions. The maximum biosorption of Pb\(^{2+}\) was found to be more than 97% with 1.0 g/l dosage for all three adsorbents under optimum pH of 3-5. The adsorption equilibrium was established after about 1 hr. The equilibrium adsorption capacity of parsley and coriander were found to fit well with the Langmuir isotherm whereas the Freundlich isotherm was better fit for culantro. The studies showed that the adsorbents can be used for removing lead ions from contaminated waters.

1. Introduction

Heavy metal pollution is an environmental problem of worldwide concern, among which lead (Pb) is one of the most common pollutants found in industrial effluents and is significantly toxic to human beings and ecological environments even at low concentrations [1]. It has the ability to accumulate in living organisms. Assimilation in the human body of relatively small amounts of Pb over a long period of time can lead to malfunctioning of certain organs and chronic toxicity.

According to World Health Organization (WHO) [2], the permissible limit of lead concentration in drinking water is 0.01 mg L\(^{-1}\) and according to Thailand Pollution Control Department (PCD) [3] is not more than 0.05 mg dm\(^{-3}\). Some of the methods for removal of heavy metals include chemical precipitation, ion exchange, electrodialysis, reverse osmosis and carbon adsorption. But these methods are often ineffective and/or very expensive for low concentrations of metals.

Since the last decade, biosorption or sorption of contaminants by sorbents of natural origin has gained important credibility due to its good performance and low cost of these complexing materials. Due to high uptake capacity and very cost effective source of raw materials, biosorption is a progression towards a perspective method [4].

In the present study, parsley (Petroselinum crispum), coriander (Coriandrum sativum), and culantro (Eryngium foetidum) plants from Apiaceae family were employed to investigate the biosorption of lead(II) from aqueous solution. Effect of different parameters such as dosage, pH, contact time and agitation speed on the removal process are studied. The experimental data obtained have been evaluated and fitted using adsorption isotherms.
2. Materials and Methods

2.1. Sample preparation
Coriander, culantro and parsley were bought from the local vegetable market Taladthai, Pathum Thani, Thailand. The plants were washed several times and dried vegetable under the sunlight. The dried materials were cut down, crushed and washed thoroughly with deionized water to remove any adhering dirt. Next, they were dried in an oven at 90 °C overnight. The dried plants were grounded and sieved through 250 mesh sieve size. The powdered plants were stored in an air tight container for further applications. Pb$^{2+}$ ion solution was prepared by dissolving Pb(NO$_3$)$_2$ in deionized water. The pH adjustments were done by adding 0.1 M NaOH and/or 0.1 M HNO$_3$ solutions.

2.2. Adsorption studies
All the experiments were carried out in Erlenmeyer flasks with 50 ml test solution at room temperature (25±2 °C). The effect of adsorbent dose (0.1, 0.5, 1, 2, 4 gm L$^{-1}$), pH (2-10), contact time (10, 20, 30, 40, 50, 60, 120, 180, 360 min) and agitation speed (100, 150, 200, 250, 300 rpm) were investigated at 10 mg L$^{-1}$ initial Pb(II) concentration. At the end of desired contact time, the samples were filtered by using syringe filters. Filtrates were then analyzed for residual lead concentration by using an Inductively Coupled Plasma (ICP) Spectrometer (Optima 8000, PerkinElmer, USA).

2.3. Data analysis
The adsorption at equilibrium, $q_e$ (mg g$^{-1}$), was calculated as in equation (1):

$$q_e = \frac{Co - Ce}{m} xV$$

Where, $C_o$ and $C_e$ are the initial and the final (equilibrium) Pb(II) concentration (mg L$^{-1}$) respectively; $V$ is the adsorbate volume (L); and $m$ is the mass of adsorbent used (g).

The percentage of lead ion removal was calculated as in equation (2):

$$\text{Removal (\%)} = \frac{Co - Ct}{Co} x100$$

Where, $C_o$ and $C_t$ are the initial and the final lead concentration (mg L$^{-1}$) at time $t$, respectively.

3. Results and Discussion

3.1. Effect of variable parameters

3.1.1. Effect of dosage.
The effect of adsorbent concentration on the lead removal efficiency is presented in figure 1. Parsley, coriander and culantro were found to have maximum removal efficiency of 96 %, 94 % and 97 % under pH 5, respectively, for 2.0 g/l dose at 10 mg L$^{-1}$ initial Pb(II) concentration. This is because the number of adsorption sites or surface area increases with the weight of adsorbent and hence results in a higher percent of lead removal at a high dose. However, the percent removal of three absorbents slightly decrease for 4.0 g/l dose. This is due to the fact that at higher adsorbent dose, the solution ion concentration drops to a lower value and the system reaches equilibrium [5].

3.1.2. Effect of pH.
From figure 2, it could be seen that for all the three adsorbents, lead adsorption decreased along with the increase in pH. Maximum adsorption of Pb$^{2+}$ in parsley, coriander and culantro were attained at pH 3 with 97 % removal. The increase in lead removal at low pH of 2 and 3 can be explained on the basis of a decrease in competition between proton and the lead cations for the same functional groups and by the decrease in positive charge at pH of 4 afterward the adsorbents which result in a lower electrostatic repulsion between the lead cations and the surface [6].
Effect of contact time  

Figure 3 shows a slowly increased adsorption rate of lead at the beginning until 60 min of contact time, thereafter, the adsorption rate became practically constant. The variation in the extent of adsorption may be due to the fact that initially all sites on the adsorbent surface were vacant and the solute concentration gradient was relatively high [6].

Effect of agitation speed  

The effect of agitation speed on lead removal by the given adsorbents is presented in figure 4. The speed of the reactor was increased, lead removal efficiency increased. It was observed that for parsley, coriander and culantro, maximum removal of 97%, 95% and 94%, respectively, were observed at 250 rpm. The removal was almost constant thereafter. However, the effective removal of Pb$^{2+}$ ions at 150 rpm were not much different from at 250 rpm.

Table 1 shows comparison of the adsorption efficiency of selected adsorbents with other plant materials. The removal capabilities for lead of low cost adsorbents depend on its initial concentration along with other factors as shown in table 1. Results from this study showed Pb(II) removal of more than 97% for all three species and are comparable to other studies.
Table 1. Comparison of the maximum adsorption capacity of lead (II) ion by various adsorbents from plant origin.

| Adsorbent            | pH  | Initial concentration | Dosages | Contact time | Pb²⁺ Removal % | Reference |
|----------------------|-----|-----------------------|---------|--------------|----------------|-----------|
| Soursop seeds        | 5   | 2.5 mg L⁻¹             | 1 gm    | 120 min      | 40.6           | [2]       |
| Banana Stalk         | 8   | 20 mg L⁻¹              | 0.90 gm | 152 min      | 96.41          |           |
| Coffee grounds       | Neutral | 0.5 mg L⁻¹         | 0.5 mg L⁻¹ | 1 hr         | 87.2           |           |
| Rice husk and Maize cobs | 2.5-6.5 | 25 mg L⁻¹            | 1.5 gm  | 120 min      | 98.5           |           |
| Parsley              | 5   | 10 mg L⁻¹              | 1 gm L⁻¹| 2 hr         | 97.88          | This study |
| Coriander            | 3   | 10 mg L⁻¹              | 1 gm L⁻¹| 2 hr         | 97.62          |           |
| Culantro             | 3   | 10 mg L⁻¹              | 1 gm L⁻¹| 2 hr         | 97.58          |           |

3.2. Adsorption Isotherms

3.2.1. Langmuir Adsorption Isotherm.
Langmuir isotherm is based on the monolayer sorption of Pb(II) on the surface of carbon sites and is represented linearly by the equation (3):

\[
\frac{C_e}{q_e} = \frac{1}{Q_0b} + \frac{C_e}{Q_0} \tag{3}
\]

A plot of \( \frac{C_e}{q_e} \) against \( C_e \) (figure 5) gave a straight line graph with a slope \( 1/Q_0 \) and intercept of \( 1/bQ_0 \). Values of \( Q_0 \) and \( b \) are calculated from the graph and reported in table 2. \( Q_0 \) and \( b \) are Langmuir constants related to adsorption capacity and energy of adsorption, respectively.

3.2.2. Freundlich Adsorption Isotherm.
Freundlich isotherm describes the heterogeneous surface energies by multilayer sorption and is expressed by the equation (4):

\[
\log q_e = \log K_f + \frac{1}{n} \log C_e \tag{4}
\]

where, \( K_f \) and \( n \) are the Freundlich constants incorporating the factors affecting the adsorption capacity and the degree of non-linearity between the solute concentration in the solution and the amount adsorbed at equilibrium respectively. Plots of \( \log q_e \) against \( \log C_e \) (figure 6) gave linear graphs with high \( R^2 \). Value of \( n > 1 \) indicates that the adsorption is favourable.

Table 2. Calculated Langmuir and Freundlich isotherm parameters.

| Adsorbents     | Langmuir constants | Freundlich constants |
|----------------|---------------------|----------------------|
|                | \( b \)     | \( Q_0 \)   | \( R^2 \) | \( N \) | \( K_f \) | \( R^2 \) |
| Parsley        | 1.022, 45.657 | 0.996, 2.462 | 0.999 | 19.984 | 0.859 |
| Coriander      | 0.392, 53.550 | 0.999, 1.875 | 0.993 | 14.601 | 0.957 |
| Culantro       | 0.411, 56.198 | 0.955, 1.882 | 0.993 | 15.906 | 0.971 |

Comparing the \( R^2 \) values of the two isotherms (table 2), the adsorption of parsley and coriander fitted well with the Langmuir model suggesting that the adsorption of Pb(II) onto these adsorbents is a mono-layer process and the adsorption behaviour is homogeneous rather than heterogeneous whereas culantro fitted well with Freundlich model since \( R^2 \) from Langmuir model was not close to unity, it could be conceivable that there might be some heterogeneity in the system [7].
4. Conclusions
The present investigation shows that parsley, coriander and culantro can be employed as a potential low-cost adsorbents for the removal of Pb$^{2+}$ ions from contaminated water because it can prepare without chemical and physical treatments. The Pb$^{2+}$ adsorption is found to be greatly dependent on the adsorbent mass and initial pH of the solution. Optimum lead removal was observed at 1.0 g/l dosage, pH value between 3-5, 150 rpm of agitation speed with 1 hr contact time. The equilibrium data were well described for parsley and coriander by the Langmuir isotherm model whereas culantro fitted well to Freundlich isotherm model. These results show that adsorbents which have a very low economical value may be used effectively for removal of Pb$^{2+}$ ions from aqueous systems for environmental protection purpose.

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6. References
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