

Research article

## Assessment of lead desorption from pomelo peel biosorbent after water treatment

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### Abstract

Biosorption, using fruit peel, can now provide an efficient process for toxic lead removal from wastewater treatment. However, the lead adsorbed on the biomass surface could potentially desorb back into solution and re-contaminate water systems. This current work evaluated the amounts of lead desorption from pomelo peel based on two widely used techniques: chemical extraction and column leaching. The efficiency of lead adsorption from solution treated by pomelo peel was  $8.80 \pm 0.27$  g Pb/kg biomass (approximately 94.7% removal). Lead desorption was evaluated using two common eluents: 0.01 M  $\text{Ca}(\text{NO}_3)_2$  and 0.04 M EDTA (a chelating agent) solutions. Under batch kinetic chemical extraction, the amounts of lead desorption were  $0.17 \pm 0.01$  g Pb/kg obtained using  $\text{Ca}(\text{NO}_3)_2$  and  $10.16 \pm 0.55$  g Pb/kg obtained using EDTA (1.80% and 115.0%, respectively, desorption of the adsorbed Pb) with up to 3 d equilibration. For the column leaching study, the amounts of lead desorption were  $6.60 \pm 0.56$  g Pb/kg obtained with  $\text{Ca}(\text{NO}_3)_2$  and  $9.42 \pm 0.24$  g Pb/kg obtained with EDTA (75.0% and 107.1% desorption, respectively). The relative advantages and disadvantages of the two types of assessment were considered. The results indicated that the disposal of contaminated solid waste resulting from water treatment is a serious issue in waste management. Such disposal represents a potential risk for lead metal mobilization and transfer to other compartments of the environment such as soil, plants or underground water.

### Introduction

There are many sources of water pollution, involving both direct and indirect contamination sources and nowadays, waste water streams containing heavy metals are produced as a result of various industrial activities (Hassaan et al., 2016). Several different chemical treatment techniques have been employed for the removal of these toxic metals from waste streams before being released into nearby rivers, such as chemical precipitation, electrolysis techniques, and the use of activated carbon and the application of carbon nanotubes (Ahmaruzzaman and Gupta, 2011; Fu and Wang, 2011; Gupta and Salch, 2013). In addition, in recent years, research attention has been directed towards some biological methods for the cleanup of metals from industrial effluents including using algae, bacteria, fungi and fruit peels (Pagnanelli et al., 2003; Vijayaraghavan and Yun, 2008; Vilar et al., 2009; Gupta et al., 2015). The use of several biosorbents for heavy metal removal has been widely applied because of lower

costs and their eco-friendly nature compared to other chemical adsorbents (Gupta et al., 2015). The binding between metals and biomass has been described as depending on the functional groups contained in the cell walls or the biopolymers of dead microorganisms (Gupta et al., 2015).

It has been documented that pomelo peel has a high efficiency for lead removal from contaminated water resulting in up to 90% metal adsorption (Phatsarapongkul and Pung, 2014). This could be due to the fact that the peel contains mainly cellulose and a high percentage of pectins. These compounds contain several functional groups (amino, carboxyl, hydroxyl) which could play an important role in metal binding (Schiewer and Patil, 2008; Saikaew et al., 2009). However, the metal adsorbed onto the surface of such material could potentially desorb and be released back into water systems. On this basis, the disposal of the biosorbent after metal adsorption should be of concern, since it could eventually cause secondary contamination by metal desorption under natural conditions.

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In relation to metal desorption studies, most previous work has focused on chelated-assisted biosorbent washing, or strong acid washing for metal removal. The complete metal removal and recovery process is beneficial as it regenerates the biomass which is then able to be used in a continuous sorption-desorption cycle system, thus being cheap and reusable and the reagents commonly used to remove the metal from the peel surface are strong acid (HCl or HNO<sub>3</sub>) or EDTA (chelating agent) (Lasheen et al., 2012). From the point of view of environmental risk assessments related to solids wastes, metal desorption is one of the most important issues in ecology, agriculture and environmental management. The mobility, bioavailability and toxicity of metals depend strongly on their chemical form and type of binding (McLaughlin et al., 2000). Thus, analytical techniques and leaching procedures for distinguishing different forms of metals are required.

The biosorption process has been defined as the sorption of metal ions by chemical functional groups on the biomass surface. Desorption of metal ions from the sorbent should be metal-selective and economically feasible (Pagnanelli et al., 2003). In general, metal desorption from soil/solid surfaces are investigated using chemical extraction such as a single extraction reaching an equilibrium state and this technique has been successfully applied to estimate the metal bioavailability, potential mobility and transport of elements in natural environments. However, single extraction methods alone have limitations as the results are dependent on the extraction parameters such as the type, concentration, pH of reagent, sample/extractant ratio, extraction time and temperature, method of shaking and phase separation (McLaughlin et al., 2000). The effect of extraction conditions as potential sources of irreproducibility, have been investigated previously (Quevauviller, 1998). Despite the fact that single extractions are widely applied for the study of many solid materials such as soil, sediment and contaminated sites, further information on metal availability can be assessed using time dependent approaches.

An alternative leaching method that is operationally defined for determining metal available forms from soil/solid materials is column configuration. Such a column leaching procedure provides time dependent information on the physicochemical lability of the lead bound by surfaces, depending on the strength of eluents used. Within such columns, the mobilization mechanism is close to those situations found in the field as related to rainfall or other natural conditions (Jean-Soro et al., 2012).

For the disposal of biological waste produced by water treatment, it is of considerable interest to study metal desorption from the solid waste. There has been no previous report examining this phenomenon. The purpose of this current work was to evaluate the leaching of lead from pomelo peel used to remove metal from waste water which after disposal as solid waste could become a source for recontamination. The metal desorption experiments were performed using two different approaches: time dependent single extraction and leaching column extraction. This study also considered the effects of different types of chemical extractant, namely calcium nitrate Ca(NO<sub>3</sub>)<sub>2</sub> and EDTA as a chelating agent.

## Materials and Methods

### Biomass: pomelo peel

#### Preparation of pomelo peel

The pomelo peel (using only the white part) was dried at 45°C in an oven for 48 hr. The dried peel was then ground and passed through

a 2.0 mm stainless steel sieve. The peel was then dried again at 45°C in an oven until the weight was constant before storing in desiccators prior to laboratory analysis.

#### Adsorption process of Pb(II) by pomelo peel

Stock solution of 1,000 mg/L Pb(II) was purchased from Merck Chemicals (Darmstadt, Germany). A 100 mg/L Pb(II) solution was then prepared from the stock solution and the pH of the solution was adjusted to 4.0. Biosorption of Pb(II) was determined by shaking 100 mL of 100 mg/L Pb(II) with 2.0 g of dried pomelo peel in a 250 mL Erlenmeyer flask at 25°C for 1.5 hr with shaking at 150 revolutions per minute (rpm). The pomelo peel was then removed using centrifugation at 5,000 rpm for 10 min and then filtered through Whatman filter paper No.42. The Pb-adsorbed pomelo peel was then dried at 55°C in an oven and stored in a dessicator prior to the desorption study.

#### Reagents and standards

All chemical used were of analytical reagent grade and obtained from Merck (Darmstadt, Germany) and Univar Chemicals (NSW, Australia and Auckland, New Zealand). High purity water was used throughout with a metered resistivity; 18 MΩ. The adsorption and desorption processes were carried out using an end-to-end optical shaker (OS10 IKA; GFL, Burgwedel, Germany). The concentrations of lead in the supernatants/extracts were analyzed by flame atomic absorption spectrometer (FAAS; SpectAA/220FS; Varian, Mulgrave, Australia). The calibration standards Pb(II) were prepared by dilution of a 1,000 mg/L Pb(NO<sub>3</sub>)<sub>2</sub> solution (Univar; NSW, Australia) to 1, 3, 5, 7 and 9 mg/L with deionized water (DI) to obtain the calibration graph of  $y = 0.0347x \pm 0.0187$ , with a coefficient of linear regression of 0.9995.

#### Total lead in solid waste samples

Weighed solid waste samples (0.2500 g) were transferred to glass vessels together with 10.00 mL concentrated HNO<sub>3</sub>. The glass tubes were then placed in a water bath at 90 °C for 2 hr. After cooling, the digested clear solutions were made up to volume in 50 mL volumetric flasks. The lead concentration in the digested solutions was then determined using FAAS.

#### Determination of lead desorption

##### Time-dependent study procedure

A 0.25 g solid waste sample was weighed into a 50 mL centrifuge tube and 25.00 mL of extractant was added. At time intervals of 1 min, 5 min, 10 min, 30 min, 1 hr, 3 hr, 1 d, 2 d and 3 d at ambient temperature, triplicate samples were removed from the shaker. The extracts were separated using centrifugation at 4,000 rpm for 10 min and the supernatant was decanted and filtered through a Whatman No.1 filter paper for FAAS measurement. Filtrates were kept in polyethylene (PE) bottles and stored in a (4°C) prior to FAAS analysis.

##### Leaching column set-up

Glass columns with a radius of 2.5 cm and 30 cm length were used for the leaching experiments. Solid waste samples (2.3 g) were weighed into beakers and 30 mL of water added. The samples were equilibrated for 15 min and then packed into the glass columns. The extractants were applied to the top of the columns using a peristaltic pump at a constant flow rate of 1.0 mL/min. Subfractions were collected at volume intervals of 15 mL at the end of the column and kept in PE bottles. The final collected volume of each sample was 200 mL. The eluted samples were stored in a refrigerator (4°C) prior FAAS analysis.

## Results and Discussion

### Lead adsorption by pomelo peel

The raw waste material used in this work was the dried pomelo peel after adsorption of Pb from an aqueous standard solution (100 mg/L Pb<sup>2+</sup>). There was a considerable loss of weight of the peel during drying after adsorption (down to 50% of the initial weight of the pomelo peel prior to the adsorption process). Table 1 shows the total lead concentration found in the pomelo peel biosorbent determined using the acid digestion method. The quantity of lead was  $8.80 \pm 0.27$  g Pb/kg ( $94.7 \pm 0.83$  % removal). The % recovery of acid digestions was satisfactory at  $110.1 \pm 5.6$ . The adsorption efficiency found in this work was similar to that reported previously (Saikae et al., 2009). The results clearly indicated that pomelo peel has a high efficiency for lead removal from aqueous solutions. The Pb-treated dried solid waste was used throughout the lead desorption studies.

**Table 1** Characteristic of lead adsorption on pomelo peel solid waste

Parameter	Pomelo waste (n = 3)
Initial concentration of Pb (II) (mg/L)	100.00
Original amount of peel for adsorption (g)	2.0
Percentage Pb removed from solution <sup>a</sup>	$94.7 \pm 0.8$
Lead adsorbed by peel <sup>b</sup> (g Pb/kg)	$8.80 \pm 0.27$

<sup>a</sup> based on Pb concentration remaining in solution after adsorption

<sup>b</sup> determined by acid digestion. There was a substantial reduction in peel weight during drying after adsorption.

### Lead desorption study

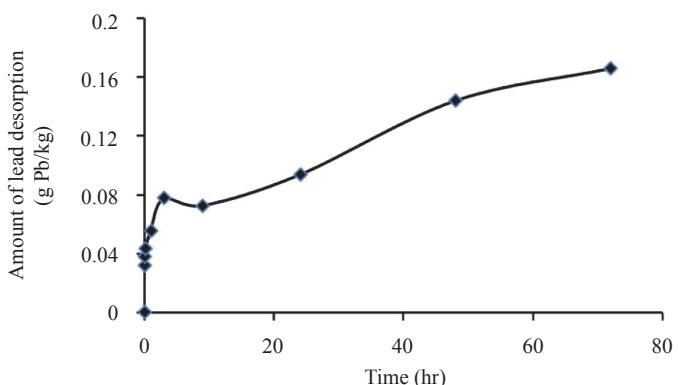
To study the lead desorption from the solid waste, single extractions were used to assess the potential for lead desorption at several different times. In this way, the experimental data provided information regarding the bioavailability of the adsorbed Pb. Using the single extraction method, the potential for metal removal from solid material generally depends on the nature of the extractant used which can potentially affect metal dissolution (Quevauviller, 1998; McLaughlin et al., 2000). In this work, two extractants of different strengths were used to examine lead availability from the solid waste. First, calcium nitrate was selected as a non-persistent chemical as it is a mild extractant for metal desorption whereby metals are easily extracted by cation-exchange and it is used for example to determine exchangeable phases in soil sequential extraction schemes; previous reports have used Ca(NO<sub>3</sub>)<sub>2</sub> to extract metals associated with soil/solid surfaces and is considered to be readily bio-available (Hogg et al., 1993; Gray et al., 1998; McLaughlin et al., 2000).

The other extractant used in this work was EDTA. It was chosen as a chelating agent for lead dissolution. EDTA is most commonly used because of its strong complexing ability for heavy metals leached from soil/solid materials (Elliotte and Brown, 1989; Hogg et al., 1993; Gray et al., 1998; Tongtavee et al., 2005). In general, both extractants are commonly applied for studying the availability of metals bound by soil/solid materials. In this work, lead desorption studies were performed under the batch extraction system as a function of time as shown in Figs. 1 and 2.

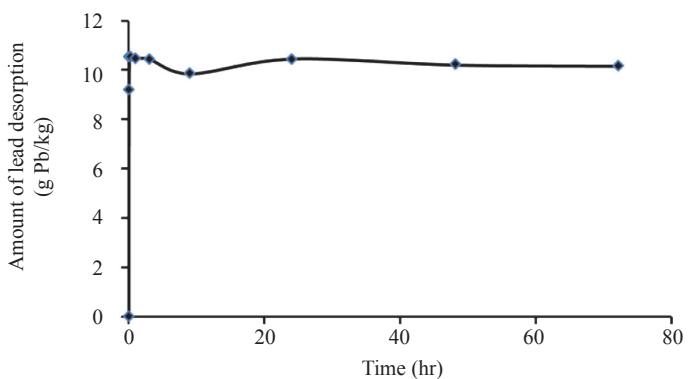
Fig. 1 shows the influence of Ca(NO<sub>3</sub>)<sub>2</sub> on lead desorption behavior. It can be seen that the amount of lead extracted by Ca(NO<sub>3</sub>)<sub>2</sub> initially increased steeply with extraction time and then more gradually after the first few hours. Although, the extraction of Pb did not reach a maximum concentration by the end of the experiment

(after 3 d), the amount of adsorbed Pb desorbed was relatively small ( $0.17 \pm 0.01$  g Pb/kg solid waste). The reasons for this may have been related to lead adsorption phenomena. It has been reported that the adsorption of metal on pomelo peel is by chemi-sorption (Langmuir equation-monolayer) suggesting that adsorbed films do not exceed one molecule in thickness (Schiewer and Balaria, 2009). According to this concept, lead desorption will be determined by the relative bonding strength for Pb between the peel surface and the chemical extractant. The experimental results demonstrated that the Pb-EDTA complex caused desorption at a much faster rate than by using Pb-Ca ion exchange. The lead extraction time using EDTA was very fast, increasing rapidly and appearing to reach a plateau after 5 min as shown in Fig. 2. This was probably because of the strong complex formation between lead and EDTA. The amount of extractable lead was nearly  $10.16 \pm 0.55$  g Pb/kg. Laboratory studies have shown that 0.04 M EDTA can provide high efficiency in removing heavy metals from contaminated soils (Jean-Soro et al., 2012; Marzouk et al., 2013). The results showed that EDTA can form complexes with all the lead bound to external carboxyl groups of cellulose.

The results of this study confirmed that the type of extractant affects the lead desorption behavior from contaminated solid materials.



**Fig. 1** Pb desorption from pomelo peel into Ca(NO<sub>3</sub>)<sub>2</sub> (batch desorption)



**Fig. 2** Pb desorption from pomelo peel into EDTA (batch desorption)

### Lead desorption using leaching columns

In a further attempt to assess lead desorption lead desorption was examined using leaching columns. Since in the batch single extraction method, the desorbed species are not removed from the solution, the amounts of lead extracted usually depend on the solid/extractant ratio. Under the column leaching procedure, the rates of heavy metal desorption/dissolution may become a more important factor than under batch extraction conditions; yet few studies have addressed this aspect (Sneddon et al., 2006; Lasheen et al., 2012). The eluent flows through the solid waste packing in the column with a constant flow rate, simulating natural rainfall passing through the waste on land.

In the leaching experiment, the amounts of lead desorption obtained were evaluated as the cumulative leaching of lead versus the collected subfraction at constant volume intervals. The shapes of cumulative leached Pb curves obtained from the two eluents are shown in Fig. 3.

As can be seen from Fig. 3, the cumulative removal of Pb gradually increased with time, although lead leaching using  $\text{Ca}(\text{NO}_3)_2$  was slightly slower compared with EDTA desorption. Leaching with  $\text{Ca}(\text{NO}_3)_2$  reached a maximum at a total leaching volume of 120 mL which accounted for approximately 75.0% of the Pb present on the peel. This relatively rapid leaching of Pb by  $\text{Ca}(\text{NO}_3)_2$  suggests that lead metal is most likely exchangeable or weakly bound to the pomelo peel surface. This portion could be estimated as readily dissolved Pb, which is potentially harmful to plants and animals.

Pb elution using EDTA in the continuous leaching mode was more rapid than with  $\text{Ca}(\text{NO}_3)_2$  and released  $9.42 \pm 0.24$  g Pb/kg. This represents 107.09% of the total Pb adsorbed by the pomelo peel. The over estimation of the Pb desorbed was probably caused by the considerable dilution of high concentrations of Pb-EDTA in the early eluent subfractions required prior to measurement using FAAS. These results can be interpreted as showing that all the Pb absorbed by the pomelo peel could be potentially re-desorbed and thus could be defined as potentially available to the environment.

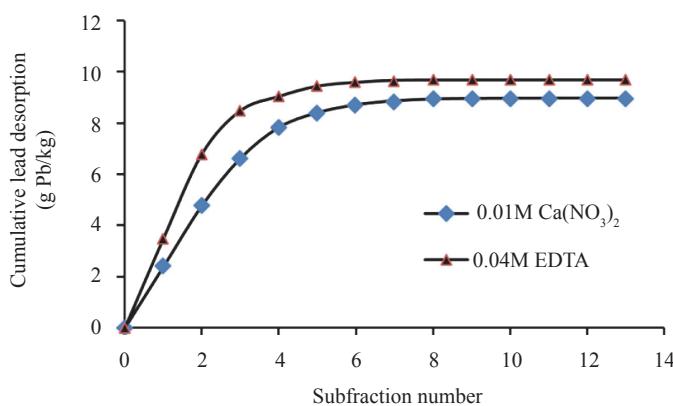


Fig. 3 Comparison of cumulative lead desorption obtained by column leaching using the two eluents

### Comparison of available Pb determined by different methods

Both batch extraction and column techniques were used to investigate lead desorption and to assess lead availability. Table 2 shows a comparison of the available lead obtained from the two different approaches. For the batch extraction experiment, the results indicated that the amounts of the available Pb extract ranged widely from 1.8% to 115% of the total Pb adsorbed by the pomelo peel. For the column leaching study, the amounts of lead desorbed were obtained by summation of the amounts in each individual subfraction of each eluent. As shown in Table 2, the amount of Pb extracted using  $\text{Ca}(\text{NO}_3)_2$  obtained with batch extraction was much lower than that obtained using column leaching. In the case of the batch system, an exchangeable equilibrium was essentially developed between the Pb and Ca whereas in the leaching system the Pb desorbed by exchange with Ca is removed from the system stimulating further desorption from the peel. The Pb derived using  $\text{Ca}(\text{NO}_3)_2$  extraction corresponds to the instantaneously exchangeable Pb ions. This pool must be considered as the pool of Pb ions directly available for plants and living organisms.

Table 2 Comparison of amounts of lead desorption obtained using two different approaches

Parameter	0.01 M $\text{Ca}(\text{NO}_3)_2$	0.04 M EDTA
Total concentration of lead (g Pb/kg)	$8.80 \pm 0.27$	$8.80 \pm 0.27$
Maximum leaching days (Single extraction method)	>3 days	5 mins
Lead desorption (g Pb/kg) (Single extraction method)	$0.17 \pm 0.01$ (1.80%)	$10.16 \pm 0.55$ (115.0%)
Lead desorption (g Pb/kg) (Column leaching method)	$6.60 \pm 0.56$ (75.0%)	$9.42 \pm 0.24$ (107.1%)

EDTA = chelating agent.

In contrast to the  $\text{Ca}(\text{NO}_3)_2$  data, there was no substantial difference in the removal of Pb using EDTA with the two different extracting methods since the Pb-EDTA complex is stronger than any chemi-sorption between Pb and the carbonyl group on the peel. The amount of Pb extracted using EDTA represented nearly 100% of the total Pb found in the solid waste. The data for the EDTA eluent could be interpreted further as showing that all the Pb adsorbed is potentially toxic to the soil/water system, but may contain some strongly bound Pb that may not be so easily leached under normal environmental conditions compared with the Pb extracted using  $\text{Ca}(\text{NO}_3)_2$ .

The current study assessed alternative methods for determining potential Pb mobility from pomelo peel used to remove Pb from contaminated water. The effectiveness of the selected extractants was discussed and confirmed. Extraction capacity depended on the nature of the adsorption binding mechanism and the biomass weight. The experimental evidence demonstrated that the desorbed lead was greatly dependent on the nature of the eluent used.

The choice between batch single extraction or column leaching procedures depends on the aim of the determination. Batch single extraction can represent a valuable tool to assess lead (and related elements of interest) release as well as the suitability of extractants for estimating potential mobility. It remains the method of choice in routine analysis due to being faster and easier to apply, particularly when many samples have to be processed. In contrast, column leaching would be too time consuming and requires additional equipment for routine use. On the other hand, the column technique has proved to be

a very useful tool for predicting the behavior of the contaminated peel in a nonequilibrium, more natural system.

These results are relevant to the potential impact of lead toxicity resulting from the dissolution/mobilization of Pb from solid waste such as pomelo peel. The disposal of contaminated solid waste resulting from water treatment is a serious issue because of the potential for secondary contamination. The major risk resulting from the continuous mobilization of metals may be the contamination of soils, rivers and sediments. Slow or fast metal mobilization under changing environmental conditions can cause serious problems for living organisms.

### Conflict of Interest

The authors declare that there are no conflicts of interest.

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