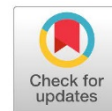


Research Article

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Evaluation of Empty Fava Beans Pods as Bioadsorbent for the Removal of Pb²⁺ from Aqueous Solutions Using Phytoadsorption Technique

Salaheddin A. Sharif^{1,*}, Widad S. El-Mugrbi², Hamed A. M. N. El-Moghrabi³, Mohamed A. B. Mostafa⁴, Adel Alsharkasi⁵, Reham B. A.-H. Al Hussein⁶, and Khadija A. Abubakr⁷

*Corresponding author:
s.sharif@uob.edu.ly
Mercury Research Group, Department of Chemistry, Faculty of Arts and Science, University of Benghazi, Ghemines, Libya.

² Department of Botany, Faculty of Arts and Science, University of Benghazi, Ghemines, Libya.

³ Department of Botany, Faculty of Arts and Science, University of Benghazi, Ghemines, Libya.

⁴ Department of Chemistry, Faculty of Science, Tobruk University, Tobruk, Libya.

⁵ Department of Statistics, Faculty of Science, University of Benghazi, Benghazi, Libya.

⁶ Department of Biology, Faculty of Education, University of Benghazi, Ghemines, Libya.

⁷ Department of Biology, Faculty of Education, University of Benghazi, Ghemines, Libya.

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Abstract

Environmental contamination with toxic heavy metals is a global concern. Cleaning up heavy metals from contaminated aquatic systems forces a lot of challenges. Phytoremediation processes are the interesting safe techniques that were focused by scientists and governments during the last decades for the up-taking of toxic heavy metals from ecosystems. Consequently, phytoadsorption approach was applied in this research using dry empty pods of fava beans (*Vicia faba* L.) to evaluate their potential for the removal of toxic lead heavy metal from its aqueous solutions. We have developed a green and simple method to remove lead ions (Pb²⁺) from their aquatic system. The obtained results have showed that the 350–1000-μm biomass particles of fava beans pods were able to take up lead ions at highly rated removal percentages and high adsorption capacity using 100-ml, 100-ppm solutions at room temperature and neutral pH. For example, the highest removal percentage of lead ions was 66.8% with an absorption capacity of 3.34 mg/g using 2.0 g at a shaking rate of 200 OSC/min after 30 min. On the other hand, the removal percentage of lead ions using 0.1 g of fava beans pods biomass was 36.8 % with the highest absorption capacity of 36.8 mg/g at a shaking rate of 800 OSC/min at the same period of time. Therefore, the empty fava beans (*Vicia faba* L.) pods can be used as potential phytoadsorbents for the removal of lead and other heavy metals from the contaminated aquatic ecosystems.

Keywords: Phytosorption; Dry Empty Fava Beans Pods; Lead Heavy Metal; Aqueous Solutions.

INTRODUCTION

Environmental pollution refers to any negative changes in the ecological balance of the earth's components; land, water and air. These changes can lead to serious phenomena such as climate change which causes major difficulties to the life of all creatures. For example, it can end up with



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health risks to humans, animals, and plants. The anthropogenic activities and natural sources are among the main reasons for this contamination. Chemicals, in particular toxic heavy metals, are the most dangerous contaminants to ecosystems, living organisms and therefore to humans (Prasad & Freitas, 2000; Briggs, 2003; Rajakaruna et al., 2006; Zaynab et al., 2022). Heavy metals are elements that have high atomic weights with densities greater than 5 g/cm^3 . They are non-biodegradable materials in the environment. Generally, they are found in two groups; essential metals, which have important roles for the biological systems, such as iron (Fe), zinc (Zn), manganese (Mn), cobalt (Co), and copper (Cu). The second type is non-essential metals; which do not have any biological roles but also have toxic effects even at low concentrations, such as arsenic (As), lead (Pb), cadmium (Cd), mercury (Hg) (Chen, 2012; Appenroth, 2010). Volcanic eruptions, forest fires, rock weathering, wind-borne soil particles, and sea-salt sprays represent the natural sources of heavy metals that can be released into the ecosystems. On the other hand, human activities such as domestic wastewater, industrial processes, paints, batteries and textile industry, industrial discharges, agricultural processes, pesticides, fertilizing, mining, and vehicle emissions are the second source of heavy metals (Briggs, 2003; Xiong et al., 2016). The release of heavy metals into the lands and water is a serious threat to agricultural processes and pure groundwater. Exposure to toxic metals can cause a wide variety of diseases and disorders in human, animals and plants. Soft tissues, the brain and nervous system, liver, kidney, and lungs are the most affected organs that can be damaged by exposure to toxic heavy metals, chronically and acutely. Additionally, Alzheimer's disease (AD), Parkinson's disease (PD), Huntington's disease (HD), amyotrophic lateral sclerosis (ALS), Minamata disease, and ataxias are the most well-known neurodegenerative diseases and disorders related to toxic heavy metals (Jaishankar et al., 2014; Breydo & Uversky, 2011).

Generally, the type of heavy metal, its chemical form, dosage, duration and mean of metal exposure, and its solubility in water are the main reasons for heavy metal toxicity. Moreover, accumulation, biomagnification, and resistance to degradation or elimination in live systems are significant factors that lead to an increase the metal toxicity (Abeed et al., 2022; Ibrahim et al., 2021). Due to the toxic effect of heavy metals in all ecosystems, humans, animals and plants, a lot of efforts to diminish the contamination by heavy metals particularly in the aquatic areas have been afforded. Looking for green solutions such as decontamination or remediation processes for the treatment of water has become a challenge (Ibrahim et al., 2021; Sekhar et al., 2003). The removal of toxic heavy metals from aquatic systems can be achieved using traditional methods such as mechanical, physical or chemical processes. The traditional methods that can be used for removing heavy metals from water are precipitation, ion exchange, membrane processes, evaporation, chemical oxidation or reduction, solvent extraction, chemical fixation, chemical alteration/complexation, capping, membrane filtration, electrochemical treatment technologies, floatation, coagulation, and flocculation (Sekhar et al., 2003; Abdel-Halim et al., 2003; Qadeer & Akhtar, 2005). On the other hand, there are modern methods that have received a lot of attention from governments and international organizations. These methods are based on the functionalization of the biological material and biotechnology. The most interesting approaches are called bioremediation processes (Prasad & Freitas, 2000; Sekhar et al., 2003; Mueller et al., 2009).

The bioremediation process is defined as a simple, innovative, effective, and potentially green technique that utilizes plants, animals or microorganisms to clean up all types of contaminated ecosystems. It is well-known as phytoremediation in the case of using plants as a cleaner (plant-based environmental remediation), or zooremediation for the use of animals. If microorganisms were used in the bioremediation process, then it is known as a microbial remediation (Mueller et al., 2009; Sharif et al., 2023; Sharif et al., 2023). phytoremediation is a cost-effective, efficient, sustainable and green technology that uses plant species to clean up contaminated ecosystems from pollutants to

improve the environment and make it more sustainable (Sharif et al., 2023; Sharif et al., 2023; Ibeanusi et al., 2009; Erdei et al., 2005). Removal of heavy metals from ecosystems (soil or water) by plants using the phytoremediation technology was divided into seven mechanisms depending on the state of the plant. If the plant was alive, there are six mechanisms which are phytoextraction, phytostabilization, phytodegradation, phytovolatilization, phytostimulation (rhizodegradation), and phytofiltration (rhizofiltration). Whereas, it is named as a phytosorption mechanism if the plant is dead. This technique can be further classified into two types; phytoabsorption and phytoadsorption (Sharif et al., 2023; Wao et al., 2014; Karman et al., 2015).

Phytoadsorption technology is a relatively new, green, simple, and efficient approach that uses the dead cell biomass of plants for the removal of pollutants, in particular toxic heavy metals, from aqueous solutions or industrial wastewaters. Furthermore, it is an inexpensive, sustainable, potential, and profitable process. There is a wide variety of available natural materials such as agri-food wastes (AFW) that were used as adsorbents in the adsorption process (Redha, 2020; Amuda et al., 2007; Hashem, 2007; Shin & Rowell, 2005). The phytoadsorption process was defined as a biological physicochemical interaction between the biomass of plants and the pollutants to remove them from their medium by either physical or chemical adsorption. While the plant biomass, in the physical adsorption mechanism, uses the physical attractions (hydrogen bonding or Van der Waals attractions), it uses the chemical bonding (ionic bonds, and covalent bonds) in the chemical adsorption process on the surface of natural material. There are many factors that play significant roles in the phytoadsorption efficiency. These factors are pH, temperature, contact time, biomass dosage, initial metal concentration, presence of another cation, and chemical modifications of biosorbents. This technique was widely used for removing heavy metals from their aquatic systems onto the surface of dead plant particles (Redha, 2020; Rahman & Sathasivam, 2015; Salim et al., 2021; Dubey et al., 2014; Etorki et al., 2014).

In this study, we aimed to assess the potential of dry empty fava bean pods as phytoadsorbent for the removal of lead heavy metal ions from their aqueous solutions using the phytoadsorption technique.

MATERIALS AND METHODS

Sample Preparation

Lead Metal (Pb^{2+})

A 100-ppm lead metal ions solution was prepared by dissolving lead nitrate, $\text{Pb}(\text{NO}_3)_2$, in distilled water. This concentration was used in all experiments thereafter.

Biomass of Empty Fava Beans Pods

Fresh fava beans were collected from the local market, in Benghazi city, Libya. The fava bean pods were emptied from seeds, washed with water, and dried in a dark place for 2 months. Next, they were ground and an amount of 350–1000- μm particles were sieved with two sieves. The dry particles were then stored in a dark and dry place for the next steps.

Phytoadsorption Experiments and Analysis of Samples

All experiment procedures and samples analyses were carried out according to standard methods (Sharif et al., 2023; Sharif et al., 2023). Different amounts of empty fava beanspod particles, 2.0, 1.0, 0.50, or 0.10 g, were separately added to 100 mL of the 100-ppm lead nitrate solution of each sample in a 500-mL container (polyethylene bottle). Then, they were shaken well using an instrumental shaker (Flask Shaker SF1) at various shaking rates of 200, 400, 600, and 800 OSC/min for

30 minutes. All experiments were conducted at room temperature and a neutral pH. All bottles of the lead-fava beans powder mixtures were left for 24 hours to allow the solid matter to precipitate. Next, the precipitated mixtures were filtered using the Whatman filter papers No 1. The filtrates were then diluted to 1 ppm and acidified with nitric acid (0.5 mL of 60% HNO₃) at a rough pH of 3, and stored in the refrigerator for the next steps. Concentrations of the remained lead metal ions in all filtrates were detected using the flame atomic absorption spectroscopic (FAAS) instrument (Model: Perkin Elemer 500) at a room temperature of 24 °C and a pH of solutions at 2.5–3.6. Eventually, the removal percentage (%) of lead ions and the adsorption capacity q_e (mg/g) were calculated. The adsorption capacity of each sample after equilibrium was calculated by the mass balance relationship equation as follows

$$q_e = (C_i - C_d) V/W$$

where C_i is the initial concentration of lead ion solution (mg/L), C_d is the detected concentration of filtrate solutions (mg/L), V is the volume of the solution (L) and W is the mass of adsorbate (g).

RESULTS AND DISCUSSION

All investigated samples showed that the empty fava bean pods, which are used as bioadsorbent, with a size of 350–1000 µm were efficiently able to remove significant amounts of lead ions from their aqueous solutions. This depends on many studied factors such as loaded biomass, and shaking rate at a contact time of 30 minutes. These observations were due to the high affinity of biomass surface to adsorb the lead ions.

Shaking Rate: 200 OSC/min

Various amounts of biomass loading (2.0, 1.0, 0.5, and 0.1 g) were investigated during 30 minutes of shaking. Generally, there was a fluctuation in the observed removal percentages of lead ions (Table 1, Figure 1). For example, the removal percentage of lead ions using 2.0 g of fava bean pods was 66.8% after 30 minutes of shaking (entry 1). This result represents the highest removal percentage within all samples. The adsorption capacity of this experiment was 3.34 mg/g. Next, the removal percentage decreased to 21.4% with an adsorption capacity of 2.14 mg/g due to the use of 1.0 g of biomass at the same period of time (entry 2). This represents the least adsorption capacity of all conducted samples. Unexpectedly, although the loading of the dry fava beans pods was decreased to 0.5 g the removal percentage of lead ions was raised to 44.9% with a significant increase in the adsorption capacity with 9.98 mg/g (entry 3). Eventually, by decreasing the biomass loading to 0.1 g, the removal percentage of lead ions decreased to 18.8% with a remarkable increase in the adsorption capacity of dry fava bean particles to 18.8 mg/g (entry 4).

Shaking Rate: 400 OSC/min

Similarly, different amounts of biomass (2.0, 1.0, 0.5, and 0.1 g) were investigated during the same interval time of shaking (30 minutes). The observed results of these experiments showed the same pattern of the removal percentages (Table 1, Figure 1). For instance, the removal percentage of lead ions by using 2.0 g of the dry fava beans pods was 56.6% after 30 minutes of shaking (entry 5). This result represents the highest removal percentage within this group. The adsorption capacity of this experiment was 2.83 mg/g. Next, the removal percentage decreased to 38.6% with an adsorption capacity of 3.86 mg/g due to the use of 1.0 g of biomass at the same period of time (entry 6). Afterward, when the loading of the dry fava beans pods was decreased to 0.5 g, the removal percentage of lead ions was raised to 47.1% with a significant increase in the adsorption capacity to 9.42 mg/g (entry 7). At the lowest amount of biomass loading with 0.1 g, the removal percentage of lead ions decreased to 26.3% with a remarkable increase in the adsorption capacity of dry fava

beans particles into 26.3 mg/g (entry 8). These results were consistence with the previous observations of the 200 OSC/min shaking-experiments.

Shaking Rate: 600 OSC/min

Using the same amounts of dry fava bean particles (2.0, 1.0, 0.5, and 0.1 g), four experiments were conducted at the same period of time (30 minutes). The observed results in these experiments showed a gradual decrease in the removal percentages of lead ions with the decreased load of dead biomass (Table 1, Figure 1). For example, the Pb-removal percentage using 2.0 g of the dry fava beans pods was 54.9% after 30 minutes of shaking (entry 9). This result represents the highest removal percentage within this group as expected. The adsorption capacity of this experiment was 2.75 mg/g. Next, the removal percentage decreased to 37.6% with an adsorption capacity of 3.76 mg/g due to the use of 1.0 g of biomass at the same period of time (entry 10). Interestingly, when the loading of the dry fava beans pods was decreased to 0.5g the removal percentage of lead ions was decreased to 29.6% with a significant increase in the adsorption capacity of 5.92 mg/g (entry 11). Consistently, at the lowest loading of biomass (0.1 g), the removal percentage of lead ions decreased to 28.7% with a remarkable increase in the adsorption capacity of dry fava bean particles into 28.7 mg/g (entry 12).

Shaking Rate: 800 OSC/min

Similarly, the same amounts of biomass (2.0, 1.0, 0.5, and 0.1 g) were also investigated for the highest shaking rate during the same contact time (30 minutes). The observed results of these samples showed the same pattern of the removal percentages of all the previous experiments (Table 1, Figure 1). For example, the removal percentage of lead ions using 2.0 g of the dry fava beans pods was 53.1% after 30 minutes of shaking (entry 13). The adsorption capacity of this experiment was 2.66 mg/g. Next, the removal percentage decreased to 40.8% with an adsorption capacity of 4.08 mg/g due to the use of 1.0 g of the biomass at the same period of time (entry 14). Next, with 0.5 g loading of the dry fava beans pods the removal percentage of lead ions increased to 48.6% with an increase in the adsorption capacity of 9.72 mg/g (entry 15). Finally, at the lowest loading of fava beans biomass, 0.1 g, the Pb-removal percentage decreased to 36.8% (entry 16). The calculated adsorption capacity of dry fava bean particles using this amount of material was 36.8 mg/g. This result represents the highest adsorption capacity within all conducted experiments.

Table: (1). The removal percentage of Pb²⁺ (%) and adsorption capacity, q_e , (mg/g) after shaking using dry empty fava beans pods.

Entry	Biomass (g)	Shaking Rate(OSC/min)	Pb Detected (ppm)	Pb Detected(%)	Pb Removal (%)	Adsorption Capacity (mg/g)
1	2.0	200	33.2	33.2	66.8	3.34
2	1.0	200	78.6	78.6	21.4	2.14
3	0.5	200	55.1	55.1	44.9	8.98
4	0.1	200	81.2	81.2	18.8	18.8
5	2.0	400	43.4	43.4	56.6	2.83
6	1.0	400	61.4	61.4	38.6	3.86
7	0.5	400	52.9	52.9	47.1	9.42
8	0.1	400	73.7	73.7	26.3	26.3
9	2.0	600	45.1	45.1	54.9	2.75
10	1.0	600	62.4	62.4	37.6	3.76
11	0.5	600	70.4	70.4	29.6	5.92
12	0.1	600	71.3	71.3	28.7	28.7
13	2.0	800	46.9	46.9	53.1	2.66
14	1.0	800	59.2	59.2	40.8	4.08
15	0.5	800	51.4	51.4	48.6	9.72
16	0.1	800	63.2	63.2	36.8	36.8

Conditions: Pb²⁺ concentration = 100 ppm. Particle size of dry empty fava beans pods: 350–1000 μ m. Contact time: 30 min. Bottle volume: 500 mL. Sample volume: 100 mL.

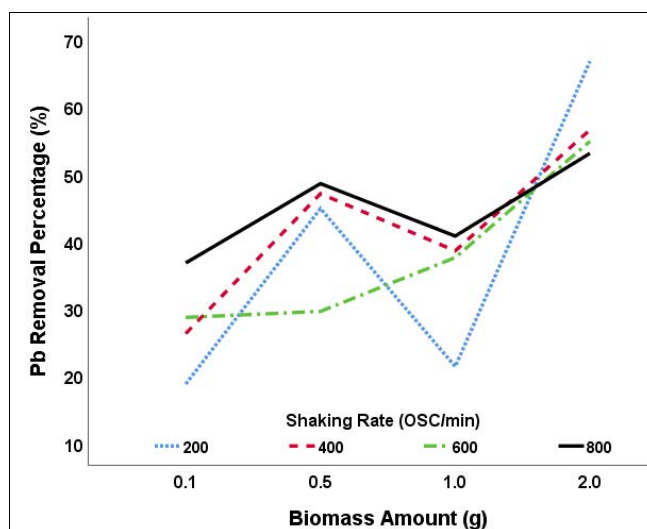


Figure: (1). The removal percentage of Pb^{2+} (%) after shaking using dry empty fava beans pods.

Adsorption Capacity of Fava Beans Pods

The adsorption capacity, q_e , of dry fava bean pods for the removal of lead ions from their aqueous solutions was gradually decreased from using 0.1 to 2.0 g of the biomass (Figure 2). It was observed that the shaking rate of 800 OSC/min afforded the highest adsorption capacity of the 0.1 g ground fava bean pods. Then the adsorption was sharply decreased due to using 0.5 g of the dry biomass, followed by a gradual decrease in the capacity with increasing the amount of bioadsorbent that was used. Similarly, the applied shaking rates have shown that the pattern of adsorption capacity of the dry particles of fava bean pods was in inverse proportion with the biomass loading.

To our knowledge, this work is the third attempted report for the investigation of the dry empty fava beans pods as bioadsorbent for the removal of lead ions from aqueous solution (Naji et al., 2019; Sánchez-Ponce et al., 2022). According to Naji, the removal percentage of lead ions from their 100 mL synthetic wastewater solution using 1 g of the dry fava bean pods ($<1000 \mu m$) was around 68, 70, and 80% after 1, 2, and 4 hours of shaking (125 OSC/min), respectively, at pH 5. [30] Recently, it was reported that the removal percentage of Pb^{2+} using 0.5 g of empty broad beans pods ($<125 \mu m$) was 91.5% with an adsorption capacity of 15.62 mg/g from 50 mL, 1 ppm of lead ions solution after 24 hours of shaking using an orbital laboratory shaker (200 rpm). However, these observations were not optimized during that study (Sánchez-Ponce et al., 2022).

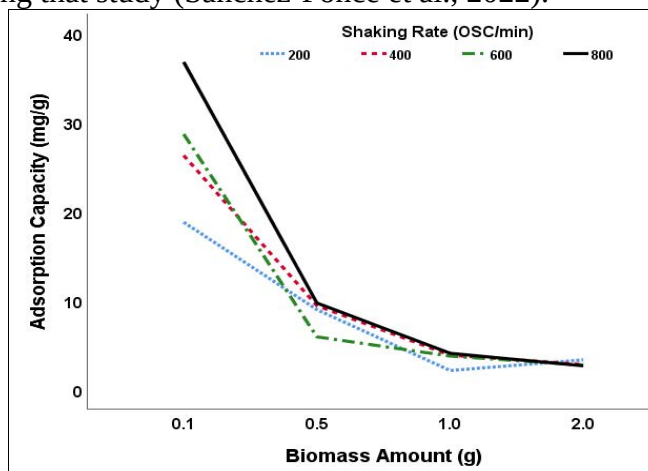


Figure: (2). The adsorption capacity, q_e , (mg/g) of dry empty fava beans pods for the removal of Pb^{2+} .

CONCLUSION

Contamination of aquatic systems with heavy metals has become a dangerous threat to humans, animals and plants. Removal of these pollutants required continuous developments of green technologies. Recently, the phytoadsorption process has been proved as a well-known, green, potential and sustainable approach for the removal of heavy metals using a wide variety of natural materials plants. The obtained data from the designed experiments have shown that the dead biomass of empty fava bean pods can be used as efficient phytoadsorbents for the removal of lead heavy metal ions from their aqueous solutions at low concentrations.

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