Calcareous and Gypsum Soils Lead Removal Using Two-Steps Washing

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Abstract

The soil washing technique is considered one of the quick and effective techniques for treating soil contaminated with heavy metals. In this study, EDTA-Na₂ and Oxalic were used as washing solutions to removing Pb from calcareous and gypsum soils contaminated with Pb only and with Pb in addition to the used engine oil. The soil samples were contaminated with different concentrations of Pb only using Pb(NO₃)₂ to soils sample for each concentration separately then the sample was divided into two equal parts. The first part represents the calcareous and gypsum soil samples contaminated with Pb. The second part was taken after air-dried, and then the used engine oil was added and homogenized well. Five parameters (pH, contact time, Pb concentrations, temperature, and liquid/solid ratio) were applied to test their effect on Pb removal. In general, the results of this study varied based on the effect of the variables.

Key words: Soil washing, Calcareous soil, Gypsum soil, EDTA-Na₂, Oxalic acid, pH.

1. Introduction

Heavy metals do not only constitute a threat to the aquatic and soil environment, crops, and the quality of the air, rather, they are a threat to human well-being and health, as they are one of the most stable and complex environmental pollutants, due to the difficulty of its metabolism, unlike most organic compounds that are easy to break down. Heavy metals resulting from human activities are familiar in industrial sites and can arise from the dust, spillage of raw materials, waste, end product, fuel ash, and fire [1]. A major pollution source of soil environment with heavy metals such as lead is emissions from traffic [2]. Besides mining activities, many heavy metals such as Cd, Ni, Pb, Zn, Cu, Cr, and As are released into the environment of soil, during coal production and combustion [3,4]. The movement of lead in the soil is controlled by various factors such as pH, organic matter, and lead forms. Lead accumulates significantly in the surface layer of the soil due to the high pH of the soil [5,6].

Numerous extensive researches on soil remediation techniques contaminated with metals and their safe use in agricultural production have been conducted in the past few decades. Contaminated soil remediation techniques of heavy metals include chemical, physical, and biological techniques [7]. Chemical techniques are used widely due to their simplified operation and efficiency [8]. Chemical techniques such as soil washing with different chemicals, are effective methods for treating contaminated soil [9]. Soil chelating agents commonly used for soil washing include EDTA, NTA, DTPA, and EDDS that form stable complexes with most heavy metals at a wide range of pH [10]. Organic acids such as oxalic acid and citric acid are considered biodegradable and environment-friendly low molecular weight organic acids [11,12], which may exert less adverse influences on soil quality, differently to inorganic acids, organic acids such as oxalic acid and citric acid can act as reducers and chelates of toxic metals [13]. Some organic acids may be released from plant roots and these can be used to mimic these roots during the extraction process [14].

2. Materials and Methods

2.1 Soil Sampling and Preparation

Soil sampling was done by choosing two types of soils from two agricultural lands (depth 0-30 cm), the first is calcareous collected from Babylon city and the second is gypsum from the Salahdin city. The collected soil samples were air-dried,
Soil Washing with Oxalic Acid then EDTA

The experiments were done by washing the soil samples with (0.05) M of oxalic acid and then with distilled water, air-dried, grinding, and sieved to pass through a sieve of 2 mm to remove debris and stones. Physiochemical properties of the prepared soil samples were analyzed (Table 3 and 4).

Table 1. Physio-chemical properties of calcareous and gypsum soils.

| Parameter | Unit     | Calcareous | Gypsum |
|-----------|----------|------------|--------|
| pH        | --       | 7.63       | 7.27   |
| EC        | dS.m⁻¹   | 2.29       | 4.17   |
| CEC       | Cmol.Kg⁻¹| 9.095      | 6.42   |
| OM        |          | 0.164      | 0.134  |
| CaCO₃     | %        | 34.11      | 22.74  |
| CaSO₄     |          | 0.067      | 31.08  |
| CO₂⁻      |          | Nil        | Nil    |
| HCO₃⁻     |          | 10         | 9      |
| Cl⁻       | meq.L⁻¹  | 8.46       | 5.64   |
| Mg²⁺      |          | 5.5        | 5      |
| Ca²⁺      |          | 3.5        | 7.5    |
| Na⁺       | mg.L⁻¹   | 33.7       | 29.6   |
| K⁺        |          | 10.6       | 14.0   |
| Pb        |          | 32.4       | 40.0   |

Table 2. Particle size distribution of calcareous and gypsum soils.

| Soil Type | Sand | Silt | Clay | Soil Texture      |
|-----------|------|------|------|-------------------|
| Calcareous| 49.2 | 15.2 | 35.6 | Sandy Clay        |
| Gypsum    | 47.2 | 19.6 | 33.6 | Sandy Clay Loam   |

2.2 Soil Contamination

To contaminate the calcareous (CS) and gypsum (GS) soils, first: with various concentrations of Pb only; second: with various concentrations of Pb in addition to used engine oil (CS-UEO, GS-UEO), the following two steps were followed. The first step: Concentrations (300-400-500-600) mg.L⁻¹ of Pb were added to the calcareous and gypsum soil samples each Concentration soil separately with continuous homogenization and left to air-dried then divide each sample of specific soil into two equal parts, first part represents the calcareous(CS) and gypsum(GS) soils contaminated with Pb only. The second step: The second part resulting from the previews contamination process was taken after air-dried, then the used engine oil (50) ml.kg⁻¹ was added and homogenized well. Both parts were kept in polyethylene containers and incubated for 20 days, and then they were air-dried, grinding, and sieved to pass through a 2 mm sieve for use in subsequent experiments.

2.3 Soil Washing Factors

Five factors were applied to test its effect on Pb removal which were pH (2, 4, 6 and 8), contact time (15, 30, 60, and 90 minutes), Pb concentrations (300, 400, 500, and 600 mg.L⁻¹), temperature (20, 40, 60, and 80 °C) and liquid/solid (L/S) ratio (5:1, 10:1, 15:1, and 30:1 ml.g⁻¹). All these parameters are applied at 180 rpm of shaking speed. When applying one parameter with different values, the other parameter will remain constant at pH EDTA-Na₂ - pH 4 or oxalic acid - pH 2, contact time 90 minutes, concentration Pb 400 mg.L⁻¹, temperature 20°C, and L/S ratio 10:1 ml.g⁻¹.

2.4 Soil Washing Experiments

Soil washing experiments were carried out to remove Pb from soils samples. Two experiments sets were conducted which including the use of EDTA-Na₂ and oxalic acid as washing agents. The first Soil Washing with EDTA-Na₂(E), then Oxalic Acid(O) - (E→O): It were done by washing the soil samples with (0.05) M of EDTA-Na₂ and then with distilled water, air-dried, grinding, and sieved to pass through a sieve of 2 mm and after that washed with (0.05) M of oxalic acid. The second Soil Washing with Oxalic Acid then EDTA-Na₂ - (O→E).

The experiments were done by washing the soil samples with (0.05) M of oxalic acid and then with distilled water, air-dried, grinding, and sieved to pass through a sieve of 2 mm and after that washed with (0.05) M of EDTA-Na₂. After the
experiments are completed, the filtrates were collected using Whatman No:42, then Pb was analyzed by the AAS Atomic Absorption Spectrometer.

3. Results and Discussion

3.1 Effect of pH

pH affects the removal of lead from the soil when removal solutions such as EDTA.Na₂ are used [15] because the increase in acidity increases the dissolution of ions present in the soil solution, which means that the removal efficiency will increase with decreasing pH values [16]. It was noted from Fig.1 that there were differences in the percentage of Pb removal from the soil with different pH values of EDTA.Na₂ solutions used in removal. The best removal rates were specifically at pH 4 and the lowest removal rates were at pH 6 for the removal solution [17]. Increasing the pH values of the solution used in the removal process reduces the removal efficiency, due to the formation of negative hydroxides of heavy metals that precipitate, which hinders their extraction from contaminated soil. The increase of H⁺ ions adsorbed on soil minerals may lead to the release of many ions in the soil solution, and this explains the high removal at low pH due to the dissolution of carbonate and sulfate minerals. The effect of pH on the effectiveness of lead removal in this study is consistent with the results of other researchers who studied the effect of pH on the mobility of heavy metals in soils [18].

3.2 Effect of Contact Time

The results of Fig. 2 showed a direct relationship between the contact time and removal percentage of lead, as the removal increases with the increase in the contact time reaching the highest value and then gradually decreases. These results are in agreement with the results of [19, 20] which showed that the removal increases rapidly at the beginning of the experiment and then gradually decreases until equilibrium state [21]. It can be explained that there are two stages for heavy metal adsorption. The first stage was the rapid adsorption for ions that bound weakly on the soil surfaces. As for the second stage, it is slow in removing ions because they are strongly associated with soil particles [22].
3.3 Effect of Pb Concentration

According to the results of Fig. 3 which showed that the Pb removal increased with an increase in their concentrations and then gradually decreases, the reason for the increased removal may be that soil susceptibility to adsorption was relatively reduced with the increase in the absorbed amount. The reason for this may be due to the slow adsorption of the element ions by the soil as a result of the formation of layers of lead ions around the soil particles with binding forces that decrease away from the surfaces of the particle [23]. Also, maybe due to the decrease in the electrostatic reaction between the charges of removal solution and Pb ions found on the active soil sites [24].

3.4 Effect of Temperature

The results (Fig. 4) explained that the removal efficiency increases with increasing temperature and then gradually decreases, these results are consistent with [25], where they were found that the raising of temperature strengthened the reaction capacity and consequently increased the removal efficiency, compared to extracting metal at the initial temperature (20 °C). The reason is may due to the increase in reaction kinetics within the removal solution reaching the equilibrium state. Also, both desorption and dissolution depend on temperature, which is among the processes that play an important role in removal efficiency [26].
3.5. Effect of L/S Ratio

The L/S is an important parameter for the application of soil washing. The increase in L/S indicates an increase in the washing solution ability to dissolve metal ions, as well as an increase in L/S means the increase the deionized water uses and this will lead to the use of more energy and equipment, therefore 10:1 ratio is preferred when washing the soil [26]. The results (Fig. 5) indicated that the percentage removal increased with an increase in the L/S ratio, where the highest removal was at the 30:1 ratio because more ions of washing reagents (EDTA, Na₂) are available at the higher L/S ratios. However, when considering the practical applications of this potential technology, higher L/S ratios will lead to more residual metal-bearing solutions for subsequent treatment [27].

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