# Removal of Pb (II) from Aqueous Solutions Using Waste Tea Leaves

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## ABSTRACT

**Background:** The presence of lead in natural waters has become an important issue around the world. Lead has been identified as a highly toxic metal that can cause severe environmental and public health problems and its decontamination is of utmost importance. The aim of this work was to evaluate the adsorption of lead (Pb(II)) on waste tea leaves as a cheap purification method.

**Methods:** In this experimental study, prepared waste tea leaves were used as adsorbent for the removal of Pb (II) from aqueous solutions. Adsorption experiments were carried out as batch studies at different contact time, pH, amount of adsorbent, initial metal concentration and temperature.

**Results:** The results showed that maximum removal efficiency was observed at pH 6. Also the adsorption of Pb (II) ions increased with decreasing initial metal concentration. The Langmuir isotherm model fits well with the equilibrium adsorption isotherm data and its calculated maximum monolayer adsorption capacity was 166.6 mg $g^{-1}$ at a temperature of 25±0.1˚C. The kinetic data obtained have been analyzed using pseudo-first-order and pseudo-second-order models. The best fitted kinetic model was found to be pseudo-second-order.

**Conclusion:** The results suggest that tea wastes could be employed as cheap material for the removal of lead from aqueous solutions.

**Keywords**: Chemical Water Pollution, Lead, Tea, Water Purification.

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## INTRODUCTION

Lead in the natural environment arises from both natural and anthropogenic sources, and is detrimental to human health and all living things [1]. All lead compounds are considered cumulative poisons. Recently, increasing interest has been focused on removing Pb(II) ions from drinking water due to its supreme toxicity to our health [2]. Drinking water contaminated with Pb(II) ions for long term, even if in a very low concentration, could lead to a wide spectrum of health problems, such as nausea, convulsions, coma, renal failure, cancer and subtle effects on metabolism and intelligence [3,4]. The maximum allowable lead concentration in drinking water has been set at 15 ppb by the US Environmental Protection Agency (2002).

A number of methods have been examined for the removal of lead from water, such as: precipitation, coagulation, adsorption, ultrafiltration, reverse osmosis, and membrane separation [5-7]. Among them adsorption is recognized as an effective and economic method for heavy metals removal [8,9].

Activated carbon is the most commonly used adsorbent for removal of metals from waste waters. However, its widespread application is restricted due to the high cost and difficult disposal. Most of the recent research activities evaluate the properties of various low-cost adsorbents that could have potential applications [10,11].

Agricultural waste materials are widely used as adsorbents for the removal of different chemicals. These include rice husk, peanut shells, corn cobs, saw dust, coir dust, barks and dried tree leaves, tea and coffee wastes, rice and wheat bran [12,13]. Some studies have demonstrated the ability of tea wastes to remove synthetic dyes and some types of heavy metal ions from water [14-16].

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In the present work, the waste tea leaves were used as an adsorbent for the removal of Pb(II) ions from aqueous solutions. Our adsorption studies included kinetics and equilibrium. The effects of pH, contact time, the amount of tea wastes and temperature on the adsorption efficiency were studied too.

## MATERIALS AND METHODS

### *Instruments*

Pb(II) concentrations were measured using an inductively coupled plasma mass spectrometer (Verian710-Es Australia). All pH measurements were conducted with a 780 pH-meter (Metrohm, Switzerland) with combined glace-calomel electrode.

### *Reagents and Materials*

$Pb(NO_3)_2$, hydrochloric acid (HCl) and sodium hydroxide (NaOH) with the highest purity available were purchased from Merck (Darmstadt, Germany). Double-distilled water was used in all experiments. Stock solution (1000 mg $L^{-1}$) of Pb(II) was prepared by dissolving $Pb(NO_3)_2$ in double-distilled water. The solutions of different initial concentrations were prepared by diluting the stock solution in appropriate proportions.

### *Preparation of the Tea Wastes*

Waste tea leaves were prepared from black tea (Golestan Breakfast Tea, Golestan Company, Iran) widely available in Iranian markets. After brewing, the tea waste was washed and then rinsed with double-distilled water. After drying at 85°C, it was grounded and sieved (mesh size 10). In order to preserve, it was kept in plastic stopper bottle containers, and to minimize contact with humidity, all these bottles were preserved in desiccators before the time of use. We assessed the physical and chemical properties of adsorbent [17] which are presented in Table 1.

**Table 1.** Physical and chemical properties of tea wastes.

| Value<br>Tea wastes | Parameter |
|---|---|
| 10.5 | Humid (%) |
| 0.353 | Density (g $cm^{-3}$) |
| 81 | Dissolved material (%) |
| 108 | Solution particles total (mg $l^{-1}$) |
| 85 | Organic matters (%) |
| 2.85 | Ash content (%) |
| 6 | $pH_{ZPC}$ |

### *Batch Adsorption Experiments*

Two grams of waste tea leaves were added to 100 mL of Pb(II) solution (100-800 mg $L^{-1}$), and the pH of the solution was adjusted at 6 with 0.1 mol $L^{-1}$ HCl and/or 0.1 mol $L^{-1}$ NaOH solutions and then the mixture was agitated using a magnetic stirrer with a stirring speed of 160 r.$min^{-1}$ for 60 min. Subsequently, the tea wastes with adsorbed Pb(II) were separated from the mixture using Whatman filter paper with a pore diameter of 42µm. The concentration of the Pb(II) ions which remained in the solution were determined by inductively coupled plasma mass spectrometry (Verian710-Es Australia) and the concentration of the Pb(II) ions remained in the adsorbent phase ($q_e$, mg $g^{-1}$) were calculated using Eq. (1):

$$q_e = \frac{(c_o - c_e)V}{W} \quad (1)$$

Where $C_0$ and $C_e$ (mg $L^{-1}$) are the initial and equilibrium metal concentrations in solution, respectively, V (L) is the volume of solution and W (g) is the weight of adsorbent.

Finally, metal removal efficiency was calculated using Eq. (2):

$$R(\%) = \frac{C_o - C_e}{C_o} \times 100 \quad (2)$$

Where $C_0$ and $C_e$ (mg $L^{-1}$) were the initial and final metal concentrations [18].

## RESULTS

The experimental conditions that could affect the adsorption of Pb(II), including: the solution pH, initial metal concentration, adsorbent dose, contact time and temperature were optimized.

The effect of the solution pH on the adsorption of Pb(II) ions onto tea wastes was assessed at different values, ranging from 1 to 8, with a stirring time of 60 min. In these experiments, the initial metal concentration and the amount of adsorbent were set at 100 mg $L^{-1}$ and 2 g, respectively, for all batch tests in this experiment. Figure 2, represents the results of the effect of the solution pH on the removal efficiency of Pb(II) ions and as it shows, removal of Pb(II) increased from 42.8 to 92.5% when the pH increased from 1 to 6. Also the zero point charge ($pH_{ZPC}$) for the tea wastes was determined around pH=5 (Figure 1).

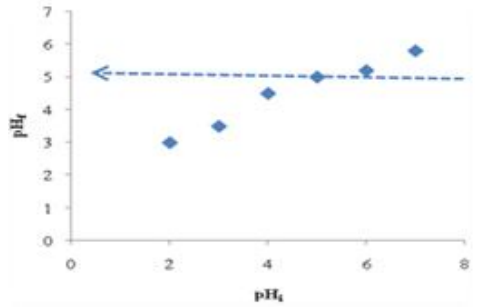


**Figure 1.** Determination of the point of zero charge of the tea wastes.

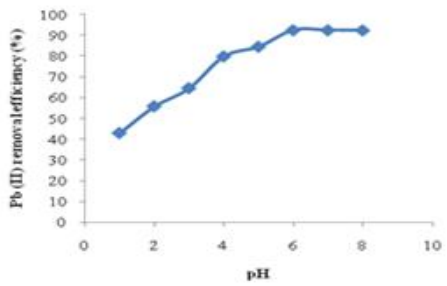


**Figure 2.** Effect of pH solution on the removal of Pb(II) from aqueous solution by waste tea leaves. (Pb(II) concentration 100 mg $l^{-1}$, contact time 60 min, adsorbent 2 g, temperature 25±1 °C).

The effect of adsorbent quantity for removal was investigated by adding various amounts of adsorbent in the range 1–5 g at a temperature of 25±0.1°C. The results are shown in Figure 3 and indicated that addition of 2 g of adsorbent was enough for maximum separation of Pb(II) ions.

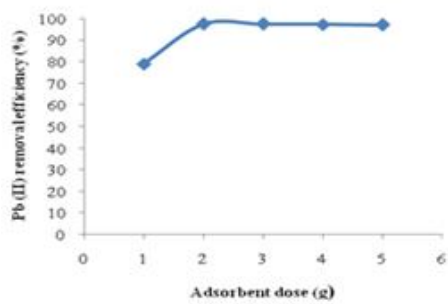


**Figure 3.** Effect of adsorbent quantity on the removal of Pb(II) from aqueous solution by tea wastes (pH=6, initial Pb(II) concentration 100 mg $l^{-1}$, contact time 60 min, temperature 25±1 °C).

The effect of contact time on the adsorption of Pb(II) was studied to determine the time taken by tea wastes to remove 100 mg $L^{-1}$ metal solution at pH 6. The results are shown in Figure 4. It can be seen that after about 60 min, almost all the Pb(II) ions were adsorbed.

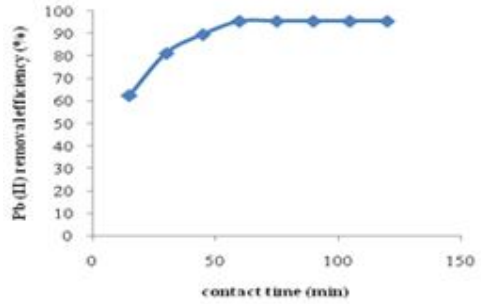


**Figure 4.** Effect of contact time on the removal of Pb(II) from aqueous solution by tea wastes (pH=6, initial Pb(II) concentration 100 mg $l^{-1}$, adsorbent dose 2 g, temperature 25±1 °C).

The removal percentage for adsorption of Pb(II)) ions using tea wastes was studied by varying lead ion concentrations from (100, 200, 300, 400, 600, 700 and 800 $mgL^{-1}$) while keeping adsorbent quantity, pH, temperature and contact time constant. The results are shown in Figure 5. From the experiments it is deducted that the removal efficiency decreased with increase in initial metal ion concentration.

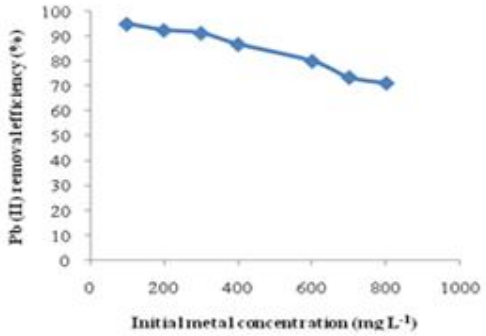


**Figure 5.** Effect of initial metal concentration on the removal of Pb(II) from aqueous solution by tea wastes (pH=6, contact time 60 min, adsorbent 2 g, temperature 25±1 °C).

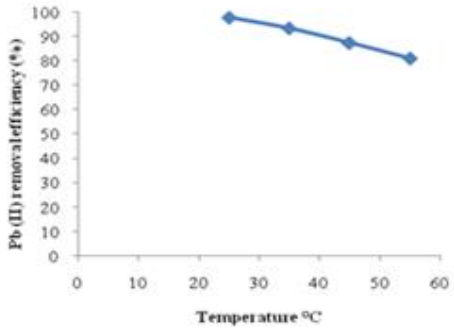


**Figure 6.** Effect of temperature on the removal of Pb(II) from aqueous solution by tea wastes (pH=6, initial Pb(II) concentrations 100 mg $l^{-1}$, contact time 60 min, adsorbent 2 g).

The effect of different temperature (25–55 °C) on the adsorption of Pb(II) ions using tea wastes was studied at constant pH 6 and 100 mg $L^{-1}$ of initial metal concentration. The results are shown in Figure 6. It is evident that 25°C is the optimal temperature for adsorption.

In order to examine the mechanism and rate-controlling steps in the overall adsorption process, pseudo-first-order and pseudo-second-order kinetics models were adopted to investigate the adsorption process. The linear plots of pseudo-first-order and pseudo-second-order models for Pb(II) ions adsorption onto tea wastes are shown in Figure 7. The kinetic parameters obtained are summarized in Table 2.

The equilibrium data collected in present study was tested by applying different isotherm models like Langmuir and Freundlich. The linear fittings for two isotherm models are shown in Figure 8, and the obtained isotherm parameters are summarized in Table 3.

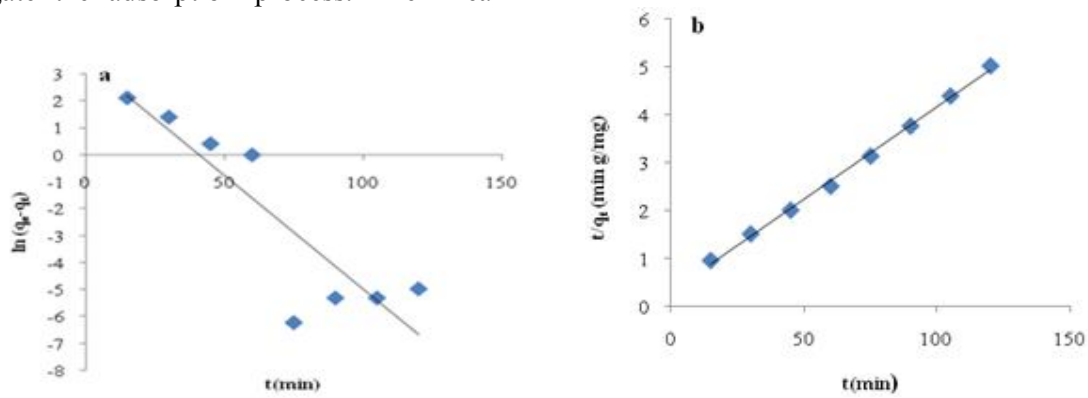


**Figure 7.** (a) Pseudo-first-order and (b) pseudo-second-order kinetics plots of Pb(II) adsorption onto tea wastes.

**Table 2.** Pseudo-first order and pseudo-second order kinetic model parameters for adsorption of Pb(II) onto tea wastes.

| | | Pseudo-first-order kinetic model | | | | Pseudo-second-order kinetic model | | |
|---|---|---|---|---|---|---|---|---|
| | $C_0$(mg $L^{-1}$) | $q_e$ exp(mg $g^{-1}$) | $q_{e1}$(mg $g^{-1}$) | $k_1$ ($min^{-1}$) | $R^2$ | $q_{e2}$ (mg $g^{-1}$) | $k_2$ (g $mg^{-1}$ $min^{-1}$) | $R^2$ |
| Pb (II) | 100 | 23.8 | 32 | 0.084 | 0.781 | 26.31 | 0.004 | 0.997 |

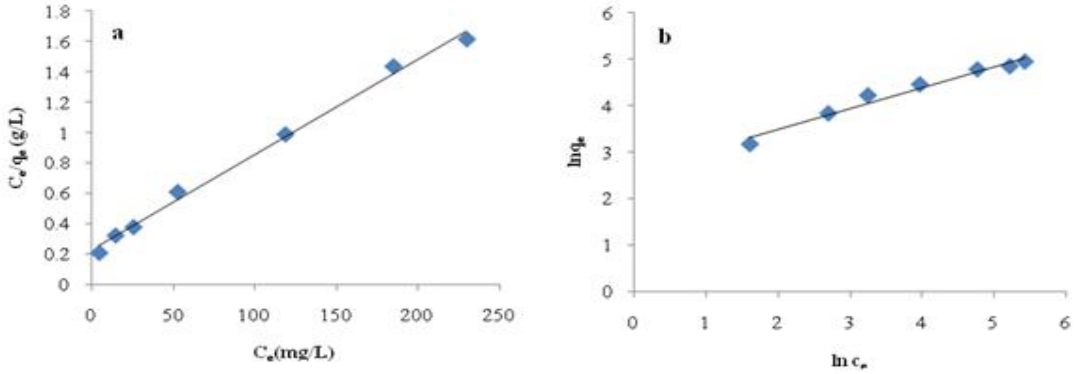


**Figure 8.** (a) Langmuir and (b) Freundlich isotherms for Pb(II) adsorption onto tea wastes.

**Table 3.** Isotherm parameters of adsorption of Pb(II) onto tea wastes.

| | Langmuir | | | Freundlich | | |
|---|---|---|---|---|---|---|
| | b (L $mg^{-1}$) | $q_m$ (mg $g^{-1}$) | $R^2$ | $K_f$ ($mg^{1-(1/n)}$ $L^{1/n}$ $g^{-1}$) | n | $R^2$ |
| **Pb (II)** | 0.026 | 166.6 | 0.994 | 13.30 | 2.217 | 0.970 |

## DISCUSSION

Solution pH is an important parameter that affects adsorption of metal ions. As the results showed, the adsorption capacity increased by increasing pH and reached maximum at pH 6, and remained nearly constant at higher pHs (Figure 2). At lower pH ($<pH_{zpc}$), the number of positively charged sites on the surface of the tea wastes increase, which does not favor the adsorption of Pb(II) ions due to electrostatic repulsion. Besides, excess $H^+$ ions compete with Pb(II) ions for the adsorption sites of tea wastes and decrease metal adsorption. At higher pHs, Pb(II) was precipitated in the form of hydroxides; therefore, the effects of pHs higher than 8 were not investigated. Similar results were obtained by various authors for the adsorption of Pb(II) on various adsorbents [19.20].Adsorbent quantity is another important parameter that determines the capacity of an adsorbent for a given initial concentration of adsorbate. As in Figure 3 is seen, an increase in the amount of adsorbent from 1 to 2 g resulted in an increase in Pb(II) adsorption from 79.2 to 97.5 %, which suggests that there is an increase in the number of adsorption sites with the increase in tea wastes. Further increases in quantity did not affect removal efficiency and 2 g was the optimal amount. Similar phenomenon was observed for the adsorption of Zn(II) onto graphene oxide [21].

Optimizing the effect of time in adsorption systems is necessary to develop cost effective procedures. Figure 4 show the effect of contact time on the adsorption of Pb(II) ions by tea wastes. As it can be seen, removal was rapid at the initial stages and gradually decreases with the progress of adsorption until reaching equilibrium at about 60 min. At the initial contact time due to high amounts of available adsorbent surface the rate of adsorption was fast. The lesser efficiency of adsorption after a lapse of time could be due to two reasons. First, occupying the sites reduced the availability of active surface sites on the adsorbent. Second, the remaining vacant surface sites were difficult to be occupied due to repulsive force of the adsorbed metal ions on the solid and bulk phase. Similar results were observed by Guoa who investigated the effect of contact time on removal of Pb(II) from aqueous solution by magnetic graphene composite and indicated that adsorption increases with increasing contact time [22].

The adsorption capacity is dependent on the initial metal ion concentration. As seen in Figure 5, the Pb(II) ions adsorption at various concentrations reveal that the removal percentage diminishes with increases in the initial metal concentrations, while the actual amount of adsorbed Pb(II) ions per unit mass of adsorbent increases, which shows a significant relationship between the adsorption efficiency and initial metal concentration. At lower metal concentrations, more vacant sites are available for adsorption which result in an increase in the concentration gradient and rate of Pb(II) ions diffusion to adsorbent. At high concentration of metal, the available sites of adsorbent become fewer and hence the removal percentage of these Pb(II) ions decreases. Fei Q and Bei W also reported the similar results [23].

Temperature is an important parameter that affects adsorption. It was observed that, the efficacy of the removal of Pb(II) ions decreased from 97.9 to 81.2 percent by increasing temperature from 25 to 55 °C. It might be due breakdown of the adsorptive forces between the metal ions and the binding groups present on the surface of the adsorbent, indicating exothermic nature of process.

In order to elucidate the Pb(II) adsorption process on tea wastes, particularly the potential rate-controlling step, the metal adsorption data were analyzed using the pseudo-first-order and pseudo-second-order models, which are described below.

The pseudo-first-order kinetic model was suggested by Lagergren [24] for the adsorption of solid/liquid systems and its formula is:

$$\mathrm{In}(q_e - q_t) = \mathrm{In}(q_e) - \frac{k_1 t}{2.303} \quad (3)$$

Where $q_t$ and $q_e$ (mg $g^{-1}$) denote the amount of metal adsorbed at time t (min) and at the equilibrium time, respectively, and $k_1$ (1/min) is the rate constant of the pseudo-first-order adsorption. $k_1$ is calculated from a plot of $\ln(q_e _ q_t)$ against t.

The linear form of the pseudo-second-order kinetic model [24] can be expressed as:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (4)$$

Where $k_2$ (g $mg^{-1}$ $min^{-1}$) is the rate constant of the pseudo-second-order adsorption, obtained from linear plots of $t/q_t$ against t.

The correlation coefficient ($R^2$) for pseudo-second-order model was higher than pseudo-first-order model (Figure 7) and the experimental data fitted better to pseudo-second-order model than pseudo-first-order model (Table 2). The results indicated that chemical adsorption might be the rate-limiting step.

Adsorption isotherm shows the distribution of adsorbate molecules among the liquid and solid phases at equilibrium conditions. The empirical equation is fundamental in describing the interactive behavior of solutes and adsorbent to design economic and efficient adsorption systems. In this study Langmuir and Freundlich models were used to correlate the experimental data.

The Langmuir model is applied in cases where monolayer adsorption occurs on homogeneous surfaces. The linear form of Langmuir model [25] is described by the following equation:

$$\frac{c_e}{q_e} = \frac{c_e}{q_m} + \frac{1}{q_m b_1} \quad (5)$$

where $C_e$ ($mgL^{-1}$) is the equilibrium concentration of metal ions in solution, $q_e$ (mg $g^{-1}$) is the equilibrium capacity of metal ions on the adsorbent, $q_{max}$ (mg $g^{-1}$) is the maximum adsorption capacity of the adsorbent corresponding to complete monolayer coverage of the surface, and b (L $mg^{-1}$) is the Langmuir adsorption constant and is related to the free energy of adsorption. The constants $q_{max}$ and b can be calculated from the intercepts and the slopes of the linear plots of $C_e/q_e$ versus $C_e$.

The Freundlich adsorption model [26] assumes that adsorption takes place on heterogeneous surfaces. The linear form of the Freundlich equation is:

$$\mathrm{In}q_e = \frac{1}{n}\mathrm{In}c_e + \mathrm{In}k_f \quad (6)$$

Where $K_f$ and 1/n are characteristic constants representing the adsorption capacity and adsorption intensity of the system respectively. The values of $K_f$ and 1/n are obtained from linear plots of $\ln q_e$ versus $\ln C_e$.

Based on the higher values of correlation coefficient ($R^2$) for Langmuir model compared to the Freundlich model, adsorption data was better described by Langmuir model. This implies that the adsorption of Pb(II) on the surface of the tea wastes occurred by monolayer formation, which further indicates the homogeneity of the adsorbent surface.

## CONCLUSION

The present study shows that the waste tea leaves is an effective adsorbent for removal of Pb(II) ions from aqueous solutions. The rate of adsorption is relatively fast, and most of the adsorption takes place within 60 minutes. The percentage of adsorption is maximal at pH value of around 6 and decreases with acidic strength of the metal solution. The obtained maximum adsorption capacity for lead ion was 166.6 mg $g^{-1}$ and the process was exothermic in nature. The experimental data of adsorption kinetics fit to the pseudo-second-order model better than pseudo-first-order model and the adsorption behavior was more consistent with the Langmuir isotherm than Freundlich. Furthermore, as an agricultural byproduct, tea wastes are widely available and cheap, subsequently it shows great potential for future use for water decontamination from lead.

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