Removal of Lead Ions from Wastewater by using a Local Adsorbent from Charring Tea Wastes

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Abstract

Adsorption of lead ions from wastewater by native agricultural waste, precisely tea waste. After the activation and carbonization of tea waste, there was a substantial improvement in surface area and other physical characteristics which include density, bulk density, and porosity. FTIR analysis indicates that the functional groups in tea waste adsorbent are aromatic and carboxylic. It can be concluded that the tea waste could be a good sorbent for the removal of Lead ions from wastewater. Different dosages of the adsorbents were used in the batch studies. A random series of experiments indicated a removal degree efficiency of lead reaching (95 %) at 5 ppm optimum concentration, with adsorbents R² =97.75% for tea. Three models (Langmuir, Freundlich, and Temkin) have been used to show which is the best operation. It was found that tea waste has an adsorption capacity (qmax) equal to 2.7972 (mg/g). Equilibrium data fitted well with the Freundlich isotherm because Freundlich assumptions are more suitable to represent the relationship between adsorbent and adsorbate. Two Kinetic Models were applied (first order, and second order) for this study. The adsorption kinetics was investigated and the best fit was achieved by a first-order equation with R²= 95.91%.

Keywords: Tea waste, Adsorption, Kinetic models, Wastewater, Removal, Pb²⁺.

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1- Introduction

Water pollution represents a well-known threat to the world's environment in recent decades [1]. Water is essential to humans, plants, and animals. Water pollution, on the other hand, has become a significant problem in recent years as a result of releasing municipal, agricultural, and industrial pollutants in it [2]. Heavy metals are one of the most significant environmental because of their toxicity, reliability, accumulation, and movement through the food chain. Various industries release heavy metals into the water. Therefore, they are one of the main pollutants in water such as Cd, Zn, Ni, Cu, Pb...etc. accumulating in living tissues because heavy metals do not biodegrade [4]. As a result, the aquatic ecosystems and human health will be threatened [3]. Lead is a bluish-gray heavy metal, soft, and malleable [5]. Pb²⁺ is a highly toxic metal that has harmful effects on the body of humans, especially the liver, kidneys, central nervous system (CNS) [6], myeloid structure, and propagative functions [7].

There are several traditional methods for extracting dissolved heavy metals from wastewater including ion exchange, adsorption, chemical precipitation, chelation, electrolytic recovery, solvent extraction, and liquid membrane separation. Effluent treatment technologies are being developed, however many of them are either ineffective or costly, especially for low-concentration metal spills. The capacity of adsorption to eliminate both organic and inorganic pollutants at a trace level makes it the best method among these methods. As a consequence, research into the efficacy of using agricultural wastes for this purpose has progressed. The existence of functional groups that may bind metals to improve the removal of lead ions from wastewater by batch experiments sets agricultural wastes. They are also readily available, inexpensive, environmentally friendly, and have a high capacity for heavy metal absorption [8].

The adsorption process is one of the most effective methods and best obtainable for removing these metals from the wastewater. This process is characterized by simple design, low cost, high effectiveness, and flexibility of usage [9]. The effluents containing heavy metal ions in solution, contribute to the substantial heavy metal contamination of the environment caused by many human industrial, agricultural, and petroleum operations [6,10]. Both organic and inorganic materials can be removed even at low concentrations. Although the availability of different carbonaceous materials to derive activated carbon (AC), agricultural wastes and by-products are considered a good materials source alternative to produce a low-cost adsorbent due to their cheap, available, and high carbon content [10]. The disposing solid wastes collected from the tea waste were obtained as an efficient low-cost adsorbent for removing heavy metals from the contaminated solution.
Waste tea can be a cheap sorbent because of the tannins’ metal-binding polyhydroxy polyphenol functional groups [8]. Natural materials have been improved through many studies, such as by thermal treatment, surface modification, and activation (physical or chemical) to prepare the activated carbon (AC) that leads to improve adsorption capacity of heavy metals [11]. FTIR analyses are carried out to determine the adsorption mechanism. The interaction between the adsorbent's surface and the adsorbed species determines the adsorption phenomenon. Chemical bonding, hydrogen bonding, hydrophobic forces, and van der Waals forces may all be involved in the interaction [12].

Adsorption isotherms explain the link between the quantity of solute adsorbed by a unit weight of solid adsorbent and the amount of solute left in solution when the system is at equilibrium. The Langmuir, Freundlich, and Temkin isotherms are often employed to characterize metal ion adsorption by diverse materials [12, 13].

The purpose of this study is to evaluate the viability of employing tea waste for the adsorptive removal of lead (II) from simulated wastewater. Weight, particle size, and initial lead (II) concentration have all been investigated as potential experimental influences. Many adsorbent models were tested in order to find one that would best fit the experimental data and provide a fitting description of the most likely adsorption process. Also, the isotherms and kinetics of adsorption were studied [15].

2- Materials and Methods

2.1. Adsorbents preparation

Tea wastes were collected from daily home tea waste and washed with water about 15 times to remove the color and debris from these products. The washed wastes had been dried naturally for 48 hours under the sunlight. The dried tea was ground and sieved to the size of 250 μm, 600 μm, and 1 mm obtained from by Abzar-E-Khnak, Tehran, Iran [7]. Fig. 1 shows the carbonized and activated samples produced using the furnace Model: 62700, Volts 220-240, AMPS 6.2, Watts 1488 Country of Manufacture: Japan at 200 °C for 1 hr. The adsorption capacity and efficiency were improved by increasing the adsorbent’s surface area by the carbonization and activation processes. The physical properties of tea waste's before and after activation are listed in Table 1. Different lead concentrations of 5, 10, 15, and 20 mg/L were made by dissolving various amounts of lead nitrate Pb(NO₃)₂ in purified water [15, 16]. Because nitrogen is a refrigerant gas that reduces the porosity size and reduces its value and results in shrinkage.

2.2. Batch Adsorption Experiments

The contribution of this research was carried out using various weights of adsorbents of 0.5, 1, 1.5, 2, 2.5, 3, 3.5, and 4 g produced from tea char. A lead solution holding the requisite concentration (20 mg/L) was prepared from lead nitrate ions, and its experimental measurement was carried out. The solution pH was 7 and all experiments are conducted at room temperature conditions. Parameters such as weight, particle size, and concentration of the solution. Batch adsorption experiments were performed by mechanically shaking 250 ml of lead solution in a flask for 12 hours at 100 rpm in a shaker. Eq. 1 was used to determine the quantity of metal ion adsorbed into biosorbent:

$$q_e = \frac{(C_0 - C_e) \cdot v}{w}$$

(1)
where \( q_e \) is the quantity of metal ion adsorbed, \( C_0 \) is the initial concentration of metal ions, \( C_e \) is the equilibrium metal ion concentration, \( w \) is the weight of sorbent, and \( V \) is the volume of metal ion solution [18] (Fig. 2). Absorbed concentrations are determined by Atomic absorption spectrophotometer.

The functional groups containing tea wastes were identified using Fourier Transform Infrared Spectroscopy (FTIR). Adsorbent functional groups influence adsorption behavior and also govern the adsorption process [19].

2.4. Analysis

The Market Investigation and Customer Safety Center, University of Baghdad, was using a flame Atomic absorption spectrophotometer ((AAS) model AA-7000 of Japanese origin from Shimadzu Corporation for measuring the concentration of dissolved Pb\(^{2+}\) ions under consideration).

3- Results and Discussion

3.1. FTIR Analysis

Fig. 3 and Fig. 4 shows the FTIR spectra of tea waste before and after activation. Several chemical functional groups have been found as possible adsorption sites the tea waste. When compared to unloaded Pb (II), the spectra pattern of loaded Pb (II) indicated changes in peak absorption, demonstrating the activity of adsorption sites [20].
The principal functional groups are the carboxylic (−OH) allocated with a wave number ranging from 2922.59-3443.48 cm⁻¹, as well as a functional group linked to the aromatic carboxylic groups (H-C-OH−) that appeared at 3626-3443.48 cm⁻¹. After being exposed to the pollutant, a sharp peak was revealed from the test confirming the success of the previously mentioned groups in adsorbing Pb²⁺ as the transmittance % decreased quickly with a smaller peak of the wave number appeared at 1633.41-1011.48 cm⁻¹ [19].

3.2. Effect of sorbed weight

Fig. 5 shows the relationship between the sorbent weight of tea waste (0.5, 1, 1.5, 2, 2.5, 3, 3.5, and 4 g) and the removal efficiency (R%) of Pb²⁺. The extracted tea revealed a remarkable Pb (II) ion removal efficiency at about 95.52%. This results in a removal efficiency of (90.38%) to (95.52%). The affinity of metal ions for active groups on the substrate accounts for the variation in heavy metal sorption capacity on the sorbent materials [21]. Fig. 5 shows the best removal efficiency was at a weight of 3 g fixed.

3.3. Effect of Particle size

The surface area of the adsorbent is an important adsorption property. Adsorbent sites are more reactive to metal ion interaction when the adsorbent has a large surface area. The smaller the particle size, the higher the surface area per unit weight of adsorbent with a higher proportion of metal removal is expected [12, 15]. The effect of using sieves (250 µm, 600 µm, and 1 mm) on the removal efficiency was studied at a solution pH of 7, initial concentration of 20 ppm, and at room temperature. The removal efficiency starts from (95.87 to 98.86) %, Fig. 6 shows the effect of the particle size on the removal efficiency. Fig. 6 shows the particle size of 250 µm of tea waste performed better than smaller the sorbent material.

3.4. Effect of initial concentration

The impact of various concentrations on removing Pb²⁺ from aqueous solutions was investigated at varying initial concentrations of 5, 10, 15, and 20 mg/L. The removal efficiency started from 85.91 to 95.90% and was obtained at pH of 7, a particle size of 250 µm, and at room temperature [22]. Fig. 7 shows the effect of different initial concentrations on removal efficiency.

4. Adsorption Isotherm Models

Adsorption isotherm research is necessary for supplying crucial data for designing the sorption process. They describe the expanse of adsorbate adsorbed on the adsorbent surface at constant temperature [13]. Most wastewater treatment applications are described using relationships known as isotherms such as Langmuir, Freundlich, and Temkin isotherm models [23].

4.1. Langmuir isotherm

Monolayer adsorption is compatible with the Langmuir adsorption model. It is predicated on the idea that a flooded monolayer of solute particles on adsorbent superficial correlates to maximal adsorption [24]. The Langmuir isotherm equation is:
\[ q_e = \frac{(q_{\text{max}} b C_e)}{(1 + b C_e)} \]  

(2)

$q_e$ (mg/g) indicates how much solute is absorbed per weight of adsorbent at equilibrium.

$C_e$ (mg/l) is the equilibrium concentration of the solvent in the substance solution, $q_{\text{max}}$ is the maximum adsorption capability. The linear plot of specific sorption ($1/q_e$) against the equilibrium concentration ($C_e$), and $b$ is the adsorption-free energy constant. Fig. 8 shows the Langmuir isotherm model.

The linearization form of the previous equation:

\[ q_e = \frac{B_1}{1/C_e} + B_1 \ln C_e \]  

(5)

Where $B_1 = R/T/b$; $R$ is the common gas constant (8.314 J/mol.K) and $T$ is the absolute temperature (K), $(K_T)$ (L/mg) is the stability binding constant conforming to the determined required energy and constant $B_1$ (KJ/mole) is related to temperature of adsorption. The experimental data for the batch experiment were fitted to the Langmuir, Freundlich, and Temkin isotherms, and it was observed that the Freundlich isotherm provided the best match based on the $R^2$ value, which was equal to (0.9775). Fig. 8 to Fig. 10 show data fitting to the Langmuir, Freundlich, and Temkin models which agreed to the results in [27].

4.2. Freundlich isotherm

For many years, the Freundlich equation was widely used. According to the Freundlich model, the porous material has an energetically heterogeneous surface, which causes adsorption capacity to depend on adsorption temperature. Fig. 9 shows the Freundlich isotherm model. The Freundlich model's linear equation is as follows:

\[ \ln q_e = \ln K + \frac{1}{n} \ln C_e \]  

(3)

Because Freundlich equation is an empirical equation, it can be used to describe data. Where $K$ indicates the Freundlich constant associated with maximum adsorption capacity and $n$ indicates the adsorption density or binding strength [25]. The heterogeneity coefficient is $1/n$. For a diverse range of concentrations, the Freundlich equation typically applies perfectly well to the experimental results [26, 14].

4.3. Temkin isotherm

Temkin isotherm reflects adsorbing species of adsorbent interaction. The following assumptions are made by this model [12]. Up to the maximal binding energy, the distribution of binding energies is uniform. Due to the interaction between the adsorbent and adsorbate, the heat of adsorption of all molecules in the layer reduces linearly through increasing analysis. The Temkin isotherm model is shown in Fig. 10. The isotherm equation is defined as:

\[ q_e = \frac{B_1}{1/C_e} \ln(K_T C) \]  

(4)

When applied to the systems under study, the three isotherm models suggest that both monolayer adsorption (where just a small fraction of the surface sites are adsorbing sites for the lead ions) and heterogeneous surface conditions are present under the experimental circumstances. The Freundlich model is applied to extremely heterogeneous surfaces with adsorbate molecules interacting in the plane of the surface, while the Langmuir model assumes that maximal adsorption corresponds to a saturated monolayer of solute molecules on the adsorbent surface [28]. Pb(II) adsorption on these surfaces is thus complex, involving multiple mechanisms. Langmuir, Freundlich and Temkin isotherms constants and the corresponding coefficients are shown in Table 2.
The maximum adsorption capacity of lead onto tea waste was calculated as 2.7972 (mg/g) using the Langmuir isotherm. According to the figures above, employing linearized models of the Freundlich isotherm model yields a straight line as shown in Fig. 8 which indicates a good fit of the data with the Freundlich isotherm for Pb\(^{2+}\) [13]. The researcher study the production of low-cost adsorbent from tea waste for the removal of zinc from an aqueous solution using batch and continuous experiments to investigate the behavior of the produced adsorbent. The data fitted well with Freundlich isotherm and it was found that the \(q_{\text{max}}\) equal to 4.55 (mg/g) and the removal efficiency of 96.8% by tea waste adsorbent.

5- Kinetic Models

5.1. Pseudo-First order Kinetic model

Lagergren’s model of pseudo-first order is given by Eq. 6:

\[
\frac{dq}{dt} = k_1 (q_{eq} - q_t)
\]  

This equation is the incorporation of the law rate for a pseudo-first-order response. Where \(q_{eq}\) represents the total weight of contaminant adsorbed at equilibrium (mg/g); \(q_t\) represents the total weight of contaminant that adsorbed at time \(t\) (mg/g), \(k_1\) is the rate constant of the pseudo-first sorption (1/min) [13]. At the circumstances \((t = 0), (qt = 0)\) and \((t = t), (q = qt)\), integration of Eq. 6 gives Eq. 7:

\[
\log(q_{eq} - q_t) = \log(q_{eq}) - \left(\frac{k_1 t}{2.303}\right)
\]  

The equilibrium adsorption capacity \(q_{eq}\) must be known to fit this equation for the experimental data shown in Table 3 and Fig. 11 [14].

5.2 Pseudo–second–order kinetic equation

Ho proposed a pseudo-second-order velocity law in 1995, demonstrating the absence of dependence on the concentration of the adsorption component and the velocity depending on the ability to adsorb in the solid phase [15]. Ho’s pseudo-second-order degree rule displays how the sorption capability of sorbate relies on the interval [16]. It is formulated as given by Eq. 8:

\[
\frac{dq}{dt} = k_2 (q_{eq} - q)^2
\]  

At the circumstances \((t = 0), (qt = 0)\) and \((t = t), (q = qt)\), integration of Eq. 8 gives Eq. 9:

\[
\frac{t}{q_t} = \frac{1}{k_2 q_{eq}^2} + \frac{t}{q_{eq}}
\]  

\(k_2\) is the rate constant of the pseudo-second-order (g/mg minute). The results are shown in Table 3 and Fig. 12.

Fig. 11 and Fig. 12 below show pseudo-first-order and pseudo second order kinetics for Pb(II) adsorption by waste tea. Experimental condition of initial concentration = 20ppm, pH = 7 particle size = 600µm, and room temperature.

Abdul-Hameed, 2006 and yan et al., 2022, these researchers studied the adsorption processes of heavy metals by low cost adsorbent and used the kinetic study and achieved the fitting by pseudo-first-order model. From the application of kinetics models, the conclusion
had been achieved that pseudo-first order was the most fitting model for experimental data. The adsorption capacity of tea waste was equal to 2.6649 (mg/g), this value was close to the experimental values of $q_{eq}$ which were 3.5093 (mg/g).

### Table 3. Pseudo-First Order and Pseudo-Second Order Kinetic Model Parameters for Adsorption of Pb(II) onto Tea Wastes

<table>
<thead>
<tr>
<th>Adsorbent type</th>
<th>Pseudo-first-order kinetic model</th>
<th>Pseudo-second-order kinetic model</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tea</td>
<td>$K_1$ (1/min)</td>
<td>$K_2$ (g/mg min)</td>
</tr>
<tr>
<td></td>
<td>$q_{cal}$ (mg/g)</td>
<td>$q_{cal}$ (mg/g)</td>
</tr>
<tr>
<td></td>
<td>$R^2$</td>
<td>$R^2$</td>
</tr>
<tr>
<td>Tea</td>
<td>0.0253</td>
<td>1.0599</td>
</tr>
<tr>
<td></td>
<td>0.9581</td>
<td>2.1240</td>
</tr>
<tr>
<td></td>
<td>0.6716</td>
<td></td>
</tr>
</tbody>
</table>

Fig. 11. Adsorption’s Pseudo-First Order for Lead Ion onto Produced Adsorbents

Fig. 12. Adsorption’s Pseudo-Second-Order for Lead Ion onto the Produced Adsorbent

### 6- Results and Discussions

Tea debris worked well as an adsorbent to remove Pb from wastewater. Over an initial period, the adsorption rate was high and subsequently steadily decreased. The experimental results and the Freundlich equation had a good agreement so, Pb obeys well Freundlich isotherm with a correlation coefficient of $R^2 = 0.9591\%$ and $R^2 = 0.6716$ of the Pseudo-first model and second order model, respectively. Renewal isn’t necessary and the metal-rich biomass can be prepared by carbonization in many regions of the world where tea trash is inexpensive or costless.

### 7- Conclusion

The effectiveness of adsorption technology in the removal of Pb (II) from synthetic water was investigated utilizing batch experimental setups. According on the findings, we may infer the following. The biomaterial sorbent was excellent in removing lead ions from wastewater from industrial settings. Using the biomaterial at lower quantities is possible since the equilibrium metal adsorption was reduced when Pb (II) ions were present from the outset. The Freundlich model performed very well in describing the experimental data. In this investigation, the bio-adsorbent tea trash had an effective weight of 3 g which removed 95% of Pb (II) from the water by adsorption. In almost 1.5 hours, the metal attained adsorption equilibrium. The adsorption process behaved according to first-order kinetics. Methods based on this principle may be utilized to purge wastewater of harmful metals effectively. The FTIR transmittance spectra of metal-loaded biomass from charred tea trash showed that aromatic and carboxylic functional groups are responsible for the adsorption of Pb(II) metal [33].

### Nomenclature

- AC: Activated carbon.
- $C_e$: Concentration of Pb$^{+2}$ residual in solution at stability (mg/L).
- $C_o$: Initial concentration (mg/L).
- $K_1$: Pseudo first order degree constant (1/min).
- $K_2$: Pseudo second order total constant (g/mg min).
- $q_e$: The amount of Pb$^{+2}$ concentration at equilibrium adsorption (mg/g).
- $T$: Time (min).
- $V$: Volume (ml).
- $W$: Weight (mg).

### References


إزالة الرصاص من المحلول المائي باستخدام مادة ماصة محلية من مخلفات الشاي كمادة ممتزة

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الخلاصة

امتزاز أيونات الرصاص من مياه الصرف الصحي من خلال النفايات الزراعية المحلية، وعلى وجه التحديد نفايات الشاي. بعد تشبيط وكربنة مخلفات الشاي، حدث تحسن كبير في مساحة السطح والخصائص الفيزيائية الأخرى التي تشمل الكثافة والكتافة الظاهرية والمسامية بعد أن تخضع هذه البقايا لعملية الكرننة والتشييط لتحويلها إلى مواد ماصة.

تم إجراء دراسات متساوية التوازن ودراسات حركية. تم استخدام جرعات مختلفة من الممتزات في الدراسات. تم استخدام ثلاثة موديلات للتوازن (Temkin و Freundlich و Langmuir) لإظهار أفضل عملية. وجد أن مخلفات الشاي لها قدرة امتصاص maximum (qmax) تساوي 72.79 (mg/g).

تم تطبيق نموذجين حركيين (من الدرجة الأولى والثانية) لهذه المادة الممتزة. تتوافق بيانات التوازن جيدا مع متساوي الحرارة Freundlich لأن افتراضات Freundlich للمتساويات، أشارت سلسلة عندما نظرية إلى كفاءة درجة إزالة الرصاص التي تصل إلى (95%) عند .

التركيز الأعلى 5 جزء في المليون، مع الممتزات 97.75 = R² من مخلفات الشاي عند تم دراسة حركيات الامتزاز وتم تحقيق أفضل ملاءمة باستخدام معادلة من الدرجة الأولى مع = R² 1.9159%). يشير تحليل FTIR إلى أن المجموعات الوظيفية في مواد امتصاص نفايات الشاي هي عطرية وكربوكسيلية. يمكن الاستنتاج أن مخلفات الشاي يمكن أن تكون مادة ماصة جيدة لإزالة أيونات الرصاص من مياه الصرف الصحي.

الكلمات الدالة: مخلفات الشاي، الامتزاز، النماذج الحركية، مياه الصرف الصحي، الإزالة، Pb²⁺.