Modified FIA-CL system for the on-line analysis of Pb(II) in aqueous solution, following treatment with chemically modified tomato peel as a biosorbent

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Abstract: Low waste generation represents a comprehensive orientation in analytical chemistry. It also forms a goal of flow injection analysis (FIA). The current research aims at modifying the injection part of the lucigenin-H2O2-OH- Pb(II) chemiluminescence detection system with flow injection analysis (FIA-CL) for an online Pb(II) analysis. The modified system was employed to determine the Pb(II)concentration. This was followed by treatment with crude tomato peels as an absorbent as tomato peels were treated with NaOH, carbonized tomato peels with HCl, and carbonized tomato peels with H2SO4. Under optimum experimental conditions, a calibration graph, represented by peak height (mV), was constructed based on plotting the chemiluminescence (CL) intensity, against (µg.ml-1) Pb(II) concentration, 10–90 µg.ml-1 range, 0.9913 correlation coefficient. Langmuir and Freundlich, used as isotherm models to verify the equilibrium results. The adsorption of Pb(II) on crude tomato peels and treated tomato peel was followed by the Langmuir model due to the high correlation coefficient (R²).

1. Introduction

Lead is a trace heavy metal of considerable importance in the environmental protection sector because of its high toxicity[1]. Pb(II) is commonly present in the environment, not only from natural sources but also from industrial activities[2]. Pb(II) in water systems has a significant impact on the quality of life; even small levels of Pb(II) can cause adverse effects in the environment. The typical concentration of Pb(II) in natural water is between 0.002–0.010 mg / L[3]. Given that contamination with Pb(II) creates a major environmental and public health risk[4], it is important to determine Pb(II) rapidly and accurately and to find a suitable adsorbent for removing Pb(II) from water.

There are a variety of physical-chemical methods for removing wastewater elements. Adsorption is an efficient and economic method to remove metals and metalloids as it shows high efficiency and flexibility in the operation. Cost, efficiency, and ease of operation[5] represent the main factors that determine food waste adsorbents' favorable competition.

The most abundant waste from the canning industry is the tomato peels. The constituents of tomato peel, namely pectin, carotene, and phenolic compounds[6] have –NH2, –OH, and –COOH as functional groups that strongly adsorb various pollutants, especially cationic pollutants[7]. So in this study, it was chosen as bio adsorbed.

The choice of the analytical method for determining the concentration of Pb(II) in solutions will depend on the availability of the instruments; the sensitivity (detection limit) of the physical state of the matrix and the cost[8].

Various FIA methods have thus far been documented to quantify trace amounts of Pb (II) in different environmental samples. Most of these methods employ online pre-concentrated steps, before effecting Appropriate detection methods such as flame atomic absorption spectrometry (FAAS)[9-11], spectrophotometry detection[1,12-15], hydride generation (HG), atomic fluorescence spectrometry (AFS)[16], inductively coupled plasma-mass spectrometry (ICP-MS)[17], and the indirect potentiometric method[18].

Compared to the methods reported, the FIA has outstanding analytical merits represented by its high sensitivity, wide linear range, rapid detection, ease of operation, and low-cost equipment[19]. FIA modification is particularly characterized by limited sample dispersion, sample throughput, and reduced waste generation.

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Low waste generation is both a holistic orientation in analytical chemistry and forms a goal in FIA. Waste minimization including laboratory-on-valve and binary sampling form the basis for the most common approach[20].

The current research deals with the modification of the injection part of the lucigenin-H2O2-OH-Pb(II) system[21] for an online Pb(II) analysis to generate low waste. The injection part was placed behind the pump. Injecting both the reagents and samples into the system formed a decisive step in the FIA system as it plays a paramount role in the introduction of repeatable quantities of the sample into the carrier stream without changing the chemiluminescence signal.

For this study, the effect of various tomato peel treatments on the efficacy of taking out Pb(II) from aqueous solutions, tomato peel treated with hydrochloric acid, sulphuric acid, sodium hydroxide, and crude tomato peel was accounted for. To determine the Pb (II) concentration, the modified system was used, following treatment with tomato peels as an absorbent.

2. Material and Methods

2.1. Reagents

All used reagents were analytical grade, and distilled water (DW) was used to prepare all the solutions. Hydrogen peroxide (H2O2, Scharlau), Lucigenin (10,10-dimethyl-9,9-biacridinium nitrate, Surechem Ltd.), lead nitrate (Pb(NO3)2; East Analia Chemicals), hydrochloric acid (HCl), 2-propanol, Sulfuric acid (H2SO4), potassium hydroxide (KOH), and sodium hydroxide (NaOH) were purchased from the BDH Laboratory Supplies.

2.2. Preparation of adsorbent

2.2.1. Crude Tomato peels.

The experiments were performed using tomato peel as an absorbent. Tomato peels were collected from a local supermarket (Duhok Kurdistan region, Iraq). The outer shell was separated from tomato kernels and washed with DW several times. Then, the tomato peels were dried, ground using a domestic mixer, and sieved to the finest possible scale. The peels were re-washed with DW and dried for 24 h in an oven at 80°C for decolorization. The sample was dried stored without any chemical or physical treatment in sealed bottles for further use as crude adsorbent [22,23].

2.2.2. Tomato peels treated with NaOH.

To cleaving ester bonds and generating more hydroxyl groups, a given amount of the crude adsorbent was saponified with 0.5 M of NaOH and the excess base was washed away by means of deionized water. This was followed by sonicating the washed tomato peels in 2-propanol to extract the leachable organics. Then, deionized water was used to wash the resulting adsorbent which was in the oven at 80°C for 24 hours., and finally put in sealed bottles[24].

2.2.3. Carbonized tomato peels with HCl treatment.

The other portion of the crude adsorbent was soaked for 24 hours at room temperature in 0.5 M HCl, and rinsed with water to take out excess acid. The sorbent was left in an oven for three hours to dry at approximately 100 °C and then moved to a furnace at 750 °C for two hours. The charred product was placed in an airtight bottle for further usage[25].

2.2.4. Carbonized tomato peels with H2SO4 treatment.

To get carbonized tomato peels (CTPs), the last portion of the crude adsorbent was placed in a furnace at 400 °C for two hours. CTPs were treated at room temperature with 0.5 M H2SO4. Acidified CTPs were washed with DW, and dried at 120 °C, then stored for subsequent use [26,27].

2.3. Apparatus

The concentration of Pb(II) in experimental and control samples was analyzed using an FIA-CL method (see figure 1). The FIA system consisted of an 8-channel peristaltic pump (Watson-Marlow 205U), and a variable velocity regulator up to (10) ml/min for flow delivery. Also, 0.8 mm internal diameter (i.d) silicone rubber pump tubes were used to transport solutions. To modify the injection aspect, using a homemade tri-way glass valve, both lucigenin, Pb(II), and KOH was inserted into the flowing carrier stream.
The injection part comprised of a syringe, a known loop for the pre-injection retention of reagents, a valve for adjusting the hydraulic direction of the loading carrier current, and eight homemade three-way glass valves which were linked through a 0.8 mm inner diameter silicon rubber tube (see Fig. 1). The three primary steps included the manual injection process:

**Step 1 (loading):** To redirect the carrier flow from the pump to a line well away from the injection valve, the valves (v1 and v2) were rotated. An exact sample volume of the reagents from the vial was collected using a syringe. The reagents were then injected into the loops (L1, L2, and L3) via the injection portion of the port, as shown in figure 1A.

**Step 2 (injection):** On the immediate loading of the sample and the reagents, v1 and v2 were placed back into the role of 'injecting.' The rotor channels were moved, and various ports were linked to the stator. Now, the pump could drive the carrier flux through L1, L2, and L3. This resulted to the first step of the reagents on a mixing coil, after this, to the glass spiral flow cell, as shown in figure 1B.

**Step 3:** Immediately after the injection was done, the valve was reset to the 'load' position to prepare the loop-filling for the next injection.

In front of the detector, the glass spiral flow cell was positioned in the mixing position within the spectrophotometer (models 7310 and 7315) whose light source was obstructed. The spectrophotometer was attached to the computer to obtain a CL signal.

![Figure 1](image.png)

**Figure 1:** The FIA-CL schematic diagram used for evaluating Pb(II).
1A: Loading location of the device
1B: The device is in place to be injected.

### 2.4 General procedure

Following treatment with tomato peels, the FIA-CL manifold was used to assess the Pb(II) in the supernatant (See figure 1). This was followed by injecting the solutions having initial concentrations, namely, 0.15 ml of 10 µg/ml Pb(II), 0.1 ml of 1 x 10^{-3} mol.L^{-1} lucigenin, and 0.15 ml of 0.45 mol.L^{-1} KOH into the H2O as a carrier stream at a flow rate of 5.0 ml/min, and then combining them with a solution of 0.3 mol. L^{-1} H2O2 at the flow cell entrance before the detector. Finally, there were also emission light detections and a measurement of the signal's peak height as a CL signal.

### 3. Results and discussion

In an attempt to bring about a sensible sampling rate, low detection limits, and reproducible measurements, both chemical and physical parameters were optimised following preliminary
experiments. The selection of the range under study was made based on the influence practiced by the variable CL signal.

3.1. Chemical optimisations

3.1.1. H$_2$O$_2$ concentration effect

As figure 1 illustrates, the FIA-CL system was used to study the effects of different H$_2$O$_2$ concentrations (1.0x10$^{-2}$– 4.5x10$^{-2}$ mol. L$^{-1}$) on CL-intensity whose variation was expressed as peak height in emitted light (mV) vs H$_2$O$_2$ concentration (mol.L$^{-1}$) (See figure 2).

3.1.2 KOH concentration effect

KOH concentration effect on CL intensity has been tested using 5.0x10$^{-2}$– 6.5x10$^{-2}$ mol. L$^{-1}$. The maximum signal for CL gave the optimal concentration of 0.1 mol. L$^{-1}$ of KOH was, as demonstrated by figure 3.
3.1.3. The effect of lucigenin concentration.
An investigation was conducted into the impact that concentration of lucigenin had on the intensity of CL within the concentration of $1.0 \times 10^{-4} - 9.0 \times 10^{-4}$ mol L$^{-1}$. Figure 4 demonstrates the results.

3.2. Physical optimisations
3.2.1. The effect of reagent and sample volumes
Optimised reactant concentrations were used to study the effects of various injected reagent and samples volumes (0.025-0.2 ml) were tested, while other physical variables were kept constant (see figure 5).

3.2.2. The effect of the delayed reaction coil.
The effect that the duration of the delayed reaction coil had over a range of 0–60 cm was examined on the strength of CL (consider figure 6).

3.2.3. The effect of flow-rate.
Optimised reactant concentrations were used to study the effects of flow-rates from 1–8 ml/min, as figure 7 demonstrates:

![Figure 6: The effect of the delay reaction coil on the intensity of CL of 10 µg. ml$^{-1}$ Pb(II)](image)

![Figure 7: The effect of Flow-Rate on the intensity of CL of 10 µg. ml$^{-1}$ Pb (II)](image)

3.4. The Calibration graph
By using the FIA-CL system (Figure 1) under optimum experimental conditions (Table 1), access could be made to the calibration graphs of the proportional CL intensity vs the concentration of Pb(II). The calibration graph was constructed by CL intensity plotting. It was represented by the peak height for emitted light against Pb (II) concentration (see figure 8).

Table (1): Optimal physical and chemical conditions for the determination of Pb (II)

| Parameters          | Optimum value |
|---------------------|---------------|
| KOH Conc.           | 0.1 mol L$^{-1}$ |
| H$_2$O$_2$ Conc.    | 2.5$\times$10$^{-2}$ mol L$^{-1}$ |
| lucigenin Conc.     | 5.0$\times$10$^{-4}$ mol L$^{-1}$ |
| volume of lucigenin | 0.1 ml |
| Pb and KOH          | 0.15 ml |
| Volume of mixing coil | 10 cm |
| Flow - rate         | 6 ml / min |

Linear ranges, limits of detection, calibration equation, and correlation coefficient for Pb (II) represented the statistical treatments of the calibration results, as shown in Table 2.
Table (2): The analytical data for Pb (II) determination

| Ion     | Linear range (µg. ml⁻¹) | Correlation coefficient | Linear regression equation | Detection limit (µg. ml⁻¹) |
|---------|--------------------------|-------------------------|----------------------------|---------------------------|
| Pb (II) | 10 - 90                  | 0.9962                  | Y = 246.42 x + 4325.3      | 0.0407                    |

Determining the accuracy and precision of the present method required to evaluate five replicates for three different concentrations of standard Pb (II) solutions. Table 3 shows accuracy as the relative error (E %) and method precision as the relative standard deviation of the same solutions:

Table (3): The present method’s accuracy and precision

| Ion   | Conc. of Pb(II) (µg.ml⁻¹) | Mean* (mV) | E** (%) | SD*** (%) | RSD**** (%) |
|-------|---------------------------|------------|---------|-----------|-------------|
|       | added                     | found      |         |           |             |
| Pb(II)| 10                        | 10.4       | 6700    | 0.4       | 2.92        | 0.146       |
|       | 50                        | 51.75      | 17000   | 3.5       | 3.35        | 0.027       |
|       | 90                        | 92.42      | 27135   | 2.7       | 3.49        | 0.016       |

*Mean of five repeate(E %)**Relative error(SD)***Standard deviation(RSD)****Relative standard deviation.

3.5. Applications
The determination of the efficacy of tomato peels as a biosorbent for the removal of Pb(II) from aqueous solution was achieved by the application of the FIA-CL method, as shown in Fig. 1. A set of adsorbents, namely crude peels, peels treated with NaOH, carbonized peels with HCl treatment, and carbonized peels with H₂SO₄ treatment were used in the experiments.

3.5.1. Adsorption experimental procedure
Batch conditions were manipulated to primarily evaluate the uptake of Pb(II) by tomato peel. Also, investigating initial metal ion concentrations, effects of adsorbent dosage, and contact time on the adsorption of metal ions from an aqueous solution required carrying out batch experiments using a series of 100-ml conical flasks. This was followed by the addition of sorbents in known quantities to the solution containing 10 µg. mL⁻¹ Pb (II). A magnetic stirrer was used to gently stir the mixture at room temperature and pH 7. A Whatman filter paper no. 541 was used to filter the suspensions, while an FIA-CL system was used to analyse the concentrations of metal ions in the filtrate.
The calibration curve of Pb (II) standard solutions determined the concentration of the analyte. To calculate the percentage of the removal of Pb (II) \(25\), the following equation was used:

\[
\% \text{ Removal} = \left(\frac{C_1 - C_2}{C_1}\right) \times 100 \quad \ldots(1)
\]

where \(C_1\) and \(C_2\) respectively represent the initial concentration of Pb ions in the solution (\(\mu g . \, ml^{-1}\)) at a given time \(t\).

Calculating the adsorption capacity at equilibrium \([16]\) was as follows:

\[
Q_e = \frac{(C_1 - C_2) \times V}{M} \quad \ldots(2)
\]

where \(Q_e\) (mg/gm) is the adsorption capacity at equilibrium, \(C_1\) and \(C_2\) are the initial and equilibrium concentrations of the Pb(II) in a solution respectively, \(V\) is volume, and \(M\) is the weight of the adsorbent.

3.6 Adsorption studies

3.6.1. The adsorbent dosage effect.

Varying the mass of the adsorbent that ranged 0.05 to 0.3 g and had a constant initial Pb(II) concentration of 10 \(\mu g\cdot ml^{-1}\) at room temperature and pH 7 formed the basis for studying the effect of adsorbent dosage on Pb(II) removal efficiency. The same procedure of shaking, filtration, and the temperature was applied to all solutions. Figure 9 shows the relationship between the amounts and the percentage (R %) of the adsorbent dosage removed. The optimum values for the four types of adsorbent, 0.3 g/100 ml in crude tomato peels, and tomato peels treated with NaOH, 0.2 g/100 ml in carbonized tomato peels with H\(_2\)SO\(_4\) treatment, and 0.15 g/100 ml in carbonized tomato peels with HCl treatment. These values were selected for subsequent experiments.

3.6.2. The influence of the contact time.

Altering contact time, and keeping other parameters constant formed the basis for determining the effect of contact time on Pb(II) ions’ adsorption and the adsorbed amounts of Pb(II). In the current experiment, optimised values for the four types of adsorbents were used as fixing points for the adsorbent dosage, with 10 \(\mu g . \, ml^{-1}\) initial Pb(II) ions’ concentration at room temperature and pH 7. Equilibrium time stands as the name for the time needed to arrive at this status of equilibrium. Under these particular conditions, the adsorbent’s optimum adsorption capability was expressed at equilibrium time by the adsorbed volume of metal ions. As shown in figure 10, the adsorption efficiency versus the equilibrium time for the four types of adsorbent, 20 min for crude tomato peels, 30 min for tomato peels treated with NaOH, 60 min for carbonized tomato peels with H\(_2\)SO\(_4\)
treatment, and in carbonized tomato peels with HCl treatment. For subsequent experiments, those values were chosen.

3.6.3. The effect of the initial concentration of Pb (II).

In the current experiment, and for the four types of adsorbents, all the parameters were fixed at optimised values. The only exception was the initial Pb (II) concentration which varied from 10–90 µg ml⁻¹. Figure 11 shows the effect of initial Pb(II) concentration on adsorption efficiency:

![Figure 11: The effect of varying concentration of Pb(II)](image)

There was a decrease in the removal percentage of metal ions decreased against an increase in the concentration of metal ions. This was since the available sites for adsorption got fewer as all adsorption sites became saturated.

3.7. Adsorption isotherms

The distribution of metal ions between the aqueous solution and the solid phase, (the adsorbent) was displayed by the adsorption isotherms. Distribution of the metal ions will be defined in several mathematical relationships, [28,29] viz. the standard isotherm models of Langmuir and Freundlich. The isotherm model of Langmuir [30] is defined by the following equation:

\[
\frac{1}{Q_e} = \left(\frac{1}{K_L Q_m}\right) \frac{1}{C_e} + \frac{1}{Q_m} \quad \ldots \ldots (3)
\]

Where \( Q_e \) is the amount of Pb(II) adsorbed per gram of the adsorbent at equilibrium (mg/g), and \( C_e \) is the concentration of the adsorbent in solution (µg.ml⁻¹) at equilibrium. \( Q_m \) is the maximum mono-layer capacity of the adsorbent (mg/g), and \( K_L \) is the adsorption equilibrium constant (L. mg⁻¹).

Langmuir isotherm is expressed by a plot of \( 1/q_e \) vs. \( 1/C_e \), and the linear relationship of statistical significance as demonstrated by the values of \( R^2 \) that are close to one unit indicates the application of the Langmuir isotherm model to the removal of Pb(II) from solutions using adsorbents made from tomato peel as shown in figure 12. The values of \( Q_m \) and \( K_L \) were calculated for the linear expression of the Langmuir isotherm of slopes and intersection as shown in Table 4.

Table (4): Langmuir Isotherm constants for Pb(II) adsorption to differently treated tomato peels

| Adsorbed type                                      | \( Q_0 \) (mg/g) | \( K_L \) (L/mg) | \( R_L \) (10-90) µg.ml⁻¹ | \( R^2 \)   |
|---------------------------------------------------|------------------|------------------|--------------------------|------------|
| Crude tomato peel                                 | 81.30            | 0.129            | 0.4367-0.0793            | 0.9944     |
| Tomato peel powder treated with NaOH              | 54.05            | 0.078            | 0.5618-0.1247            | 0.9813     |
| Carbonized tomato peels treated with HCl          | 19.57            | 0.154            | 0.3937-0.0673            | 0.9917     |
| Carbonized tomato peels treated with H₂SO₄        | 69.93            | 0.021            | 0.8264-0.3460            | 0.9934     |
Since the quantitative formation of a monolayer adsorbate on the outer surface of an adsorbent is generally indicated by the Langmuir adsorption isotherm, the latter’s outstanding feature can be expressed to a Parameter of dimensionless equilibrium ($R_L$) known as the separation factor ($R_L$, and also named as equilibrium parameter) that is defined by the following equation:

$$R_L = \frac{1}{1+K_L C_0} \quad \ldots \ldots (4)$$

Where $C_0$ (µg. ml$^{-1}$) is the initial concentration of adsorbate and $K_L$ (L/mg) is the Langmuir constant in terms of the adsorption energy. The meaning of $R_L$ indicated to a different form that isotherms, i.e. linear ($R_L = 1$), favorable (0 < $R_L < 1$), unfavorable ($R_L > 1$), or irreversible ($R_L = 0$).

The calculated $R_L$ has taken from the experimental data of the current research (see table 4) ranged from 0.4367 to 0.0793 for Pb(II) that was adsorbed by crude tomato peel powder, 0.5618 to 0.1247 for Pb(II) adsorbed by tomato peel powder treated with NaOH, 0.3937 to 0.0673 for Pb(II) adsorbed by carbonized tomato peels with HCl treatment, and 0.8264 to 0.3460 for Pb(II) adsorbed by carbonized tomato peels with H$_2$SO$_4$ treatment for metal ion concentrations ranging from 10–90 µg.ml$^{-1}$. It is noticeable that the favorable adsorption of Pb(II) was on adsorbents made from tomato peels.

The Freundlich adsorption isotherm assumed the initial occupation of the strongest binding site on the adsorbent, while there was a decrease in the affinity of binding as site occupation increased. As such, the Freundlich model is based on heterogeneous surfaces [32].

The expression of Freundlich isotherm [20] is based on plotting $\log q_e$ vs $\log C_e$, and as outlined by the equation:

$$\log Q_e = \log K_f + \frac{1}{n} \log C_e \quad \ldots \ldots (5)$$

where $Q_e$ is the amount of Pb(II) adsorbed per gram of the adsorbent at equilibrium (mg/g), and $C_e$ is the equilibrium concentration of the adsorbent in solution (µg.ml$^{-1}$), $K_F$ is the constant indicating to the capacity of the adsorption (L.mg$^{-1}$) and $n$ is a constant indicating intensity of the adsorption.

The slope and the intercept correspond to $(1/n)$ and $K_F$, respectively. It was evident that a straight line was yielded by the plot of $\log Q_e$ and $\log C_e$ (see figure 13). Table 5 presents the results. This model’s favorable adsorption can be characterized by the fact that in case of value for $n$ exceeds unity, adsorption is favorable and it is a physical process [32]. In the present study, the (2.67-3.90) value of $n$ is more than 1for the four types of adsorbents; which indicates that the adsorption process is favorable. But the value of the correlation coefficient ($R^2$) is lower than the Langmuir isotherm value as shown in Tables 4 and 5.
The equilibrium of adsorption isotherms is the most important aspect of the adsorption isotherm design process. This is due to its indication of the manner of the distribution of metal ions between the surface of the adsorbent and a liquid phase (metal ion solution) at equilibrium, as a metal concentration function [33].

| Adsorbed type                                      | 1/n   | Freundlich Isotherm | k (mg/g) | R²  |
|---------------------------------------------------|-------|---------------------|----------|-----|
| Crude tomato peel                                 | 0.2566| 3.90                | 9.110    | 0.9895 |
| Tomato peel powder treated with NaOH              | 0.3739| 2.67                | 5.947    | 0.9691 |
| Carbonized tomato peels treated with HCl          | 0.2888| 3.46                | 4.607    | 0.9845 |
| Carbonized tomato peels treated with H₂SO₄        | 0.3313| 3.02                | 3.592    | 0.9915 |

4. Conclusion
An investigation of the equilibrium of adsorption isotherms was conducted using simple and cost-effective equipment. The resulting sorption data fit both the Langmuir and Freundlich isotherms. On this basis, it can be concluded that both modified tomato peels, namely base and acid, and crude tomato peels present the potential for use as a biosorbent for the removal of Pb(II) from an aqueous solution. Its application should thus be recommended for use in industrial wastewater management. Lower Kₘ values (< 1) obtained from all the adsorption processes outlined that tomato peels have a relatively high affinity to remove metal ions.

The current study has also come out with the finding that the sorption of metal ions, by using modified and unmodified tomato peels, was at an R² > 0.98 ratios. This outlines the Langmuir model which is well suited to the results. This model is what describes monolayer adsorption. It also indicates that the sorption of metal ions on both modified tomato peels (base, acid) and crude tomato peels represents a chemisorption mechanism. On using tomato peels, adsorption capacities of 69.93mg/g, 19.57 mg/g, 54.05 mg/g, and 81.30 mg/g were respectively recorded by Pb²⁺ ions.

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