

New Design Valve in Flow Injection System for the Determination of Pb(II) in Biological and Environmental Samples

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Abstract: A strategy to design an injection valve for a streamlined flow injection technique is described as speed and low-cost materials available in the environment for the determination of Pb(II) ion using the organic reagent 4-((4-methoxyphenyl)diazanyl)benzene-1,3-diol at a wavelength of 498 nm. The scope of the study is to find the optimal conditions, including the flow rate of the carrier, the dispersion coefficient, the length of the reaction coil, and the calibration drawing. The results showed that the optimum length of the reaction coil is 20 cm, and the optimum flow rate is 9.1 mL/min, which is equivalent to the pumping rate of 70 F/min. The range of linearity of the study was revealed by a calibration curve of 0.5–27 mg/L, slope = 1.507, correlation coefficient = 0.9995, the limit of quantitative (LOQ) = 0.088 mg/L, and limit of detection (LOD) = 0.026 mg/L. The system under study has a characteristic efficiency. The dispersion coefficient was calculated for concentrations of 10–15 mg/L Pb(II) ion. Furthermore, the accuracy of the flow injection technique in the estimation process was studied and compared with the Flame Atomic Absorption Spectroscopy (FAAS) technique.

Keywords: flow injection analysis; 4-((4-methoxy phenyl)diazanyl)benzene-1,3-diol reagent; lead ion; environmental samples; homemade valve

■ INTRODUCTION

The ancient Romans used lead (Pb) in the manufacture of water pipes, as it was a mixture of Pb soldered with tin. Pb ion (Pb(II)) is considered an important element because of its high level of contamination in different forms, including water, soil and vegetables, which directly affects human and animal health [1]. Pb is a flexible metal and has a bluish-white color that is resistant to corrosion 207.19 g/m² d and belongs to group IVA. The elements IVA are characterized by the external quantitative level that has a level of d¹⁰, and the s level is saturated. In addition, the two electrons are in the p level, and the change in the ionization energies of Pb to a gradual change of the elements of this group, as Pb turns into an amphoteric element [2]. The Pb(II) contains three non-radioactive and stable forms, which include Pb₂O₆, Pb₂O₇, and Pb₂O₈ [3]. Among its most important compounds, it contains three oxides: Pb₃O₄ and PbO (called red Pb), and PbO₂ [4]. Pb(II) is classified as a highly toxic heavy metal [5],

and one of its most important uses is to reduce nuclear radiation and is used as a radiation insulator in the form of thick Pb sheets because of its high density and corrosion resistance [6]. It is used in the manufacturing of colors, dyes and paints, where it is called white Pb and red Pb. It is used in painting bridges and steel buildings in order to prevent corrosion [7]. It has an important role in environmental pollution. Also, radiant nature is considered a hazardous element that is sometimes transmitted from plants to the consumer body of humans and animals through the food chain [8-9]. It is considered a toxic metal regardless of whether it is ingested or inhaled. It has a great effect on the nervous system, both in children and adults. When exposed to Pb for a long time, Pb causes a decrease in performance in some functions of the nervous system, and it is absorbed by the soft tissues so that Pb has no known function inside the body and its concentration is higher overall [10-11]. It has been evaluated in several ways, including ICP-AES (Inductively Coupled Plasma- Atomic

Emission Spectroscopy) [12], ETAAS (Electrothermal Atomic Absorption Spectrometry) [13], FIA (Flow Injection Analysis) [14], SWASV (Square Wave Anodic Stripping Voltammetry), and DPSV (Differential Pulse Stripping voltammetry) [15].

Azo compounds are among the important compounds that are used for the determination and extraction of elements from environmental and health pollutants. They are characterized by many properties, including their molecules that contain functional groups or atoms that have electronic doublets capable of linking with metal ions with coordination bonds to form coordination complexes. The most prominent of these reagents are azo derivatives. In the analytical aspects, azo derivatives were used in the spectroscopic and quantitative methods for estimation the metal ions present in very few concentrations in different analytical models. It has a large molecular weight, and the aromatic azo derivatives are more stable than the aliphatic azo compounds because of the resonance in them [16-17]. Azo heterogeneous dyes have been extensively studied in thermal, optical and medical applications such as antiviral, antifungal and antioxidant properties [18]. Azo compound 4-(methoxyphenyl)diazenylbenzene-1,3-diol (4-MDD) has a maximum wavelength of 387 nm and has high stability and behaves like a dual-clutch ligand. The FTIR study of the compound showed medium intensity bands at a frequency of 1473 cm^{-1} because of the absorption of the N=N bond. It was noted that a wide band appeared at a frequency of 3269 cm^{-1} , belonging to the hydroxyl group [19].

The technique of FIA is one of the most important analytical techniques in estimating the ions of elements in different models as it depends on the principle of chemical and physical treatments of the dispersed model area according to a continuous carrier current, and then a suitable reagent is used to detect the interaction, where the technique occupied an important and prominent position within the analytical techniques [20]. Since 1975 it has had a significant impact in many areas of application, including the pharmaceutical [21], agricultural [22], environmental [23], and life fields [24]. It has several advantages, including the transformation of

open-system interactions into a closed system. Inexpensive and small in volume with a very fast response, where the time is between 5–20 s and therefore, more than one model can be analyzed within 60 s. It can reduce the analysis time by replacing mechanical processes instead of manual processes such as separation and blending and is able to rate the modeling speed at an average rate of 120 samples per h. The volume of the injected sample is between 10–20 μL , and this does not require more than 0.5 μL of reagent solution at each analysis. Individual errors are minimal when compared with other techniques [25].

This study aims to use organic reagent for the determination of Pb(II) ion in different samples by FIA technique to estimate the Pb(II) ion, which is one of the most important pollutants in the environment and human health in different models, including water and soil in different places and life models. Then, knowing the accuracy and efficiency of the technique used to estimate the Pb(II) ions under study after finding the optimum conditions of complexity. Finally, we calculated the percentage of Pb(II) ion recovery under study in different models and compared the results with the FAAS technique.

■ EXPERIMENTAL SECTION

Materials

The materials used in this study were 4-MDD organic reagent, $\text{CH}_3\text{CH}_2\text{OH}$ with a purity of 96% GT. Becker, HCl 36.50–38.00% from BGG, Na_2HPO_4 99% from M&B, Na_2CO_3 99% from Merck, and PbCl_2 99% from BDH Azo. The chemicals and reagents used were of analytical grade, and the water used in the study was distilled water.

Instrumentation

The instrumentations used in this study were homemade valves Manual injection valve made of acrylic and plastic three-way dispenser Shimadzu UV-1700 spectrophotometer, the spectrophotometer was Labomed in Single beam G, USA connected to a Siemens (Germany) Kompensograph C1032 recorder to acquire data as a peak altitude, peristaltic pump Germany,

reaction coils with 0.5 mm radius, pH meter, Denver sensitive instrument, analytical balance, Teflon tubing load, and electronic digital caliper, China.

Procedure

Prepare stock solutions

Solution of Pb(II) ion 500 mg/L: A stock solution was prepared through dissolving 0.0671 g of PbCl_2 in 100 mL of distilled water and by using the law of dilution, the solutions were prepared less concentrated. **Solution of Na_2CO_3 500 mg/L:** A stock solution was prepared through dissolving 0.0883 g of Na_2CO_3 in 100 mL of distilled water, and by the law of dilution, the solutions were prepared less concentrated. **Preparation of the solutions of masking agents:** 100 mg/L of the solutions of the blocking agents, each containing potassium chloride and aqueous potassium sodium tartrate, were prepared with a weight of 0.01 g and each of them dissolved in a 25 mL volumetric flask and then transferred to a 100 mL volumetric flask filled to the mark after setting the pH to 9. **Reagent solution 1×10^{-3} mg/L:** A stock solution prepared by dissolving a 0.0244 g of 4-MDD in 100 mL of distilled water and by using the law of dilution, the solutions were prepared less concentrated.

Design valve for injection model

The most important thing in the FIA work is the injection valve which has been designed in the laboratory from cheap and eco-friendly materials that can be recycled to give more identical results where the valve contains four secondary valves for loading chemicals. Linked on the one hand to a peristaltic pump with 8 rollers to eliminate the pump speed pulsations of 70 r/min and connected on the one hand. On the other hand, the

reaction coil of 20 cm in a coiled manner is used to get rid of the dilution of the mixed materials and then connected to the injection cell that contains two input and output ports of the spectral cell, then the detector is connected to a cording device to give a record of the analytical signal by a record based on the height of the peak as in Fig. 1. We concluded that through our study, an innovative valve made of high-efficiency and cost-effective raw materials, and the injection and loading control process can be implemented by three-way sub-valves, which are fixed outside the chip.

RESULTS AND DISCUSSION

Absorption Spectrum Maximum for Complex Pb(II) and Compare It with λ_{max} of the Reagent

In a test tube 2 mL of a solution of Pb(II) ion was mixed in it at a concentration of 10 mg/L at pH = 9 and 2 mL of a reagent solution at a concentration of 1×10^{-4} M. Then a spectroscopic scan of the solution of the above-prepared compound was carried out in the region confined between 190–800 nm, where the λ_{max} values of the complex were determined in this region with the highest absorption value at 498 nm. Then, it was compared with the wavelength of the pre-equipped reagent of 387 nm, where we conclude the complex shift towards a longer wavelength and lower energy of 111 nm.

Flow Injection System

Chemical parameters

The effect of pH on the determination of the Pb(II) ion. Different media of pH levels 2–11 were prepared under the conditions of reagent volume 157.0 μL , Pb(II) ion volume 157.0 μL , metal ion concentration 15 mg/L,

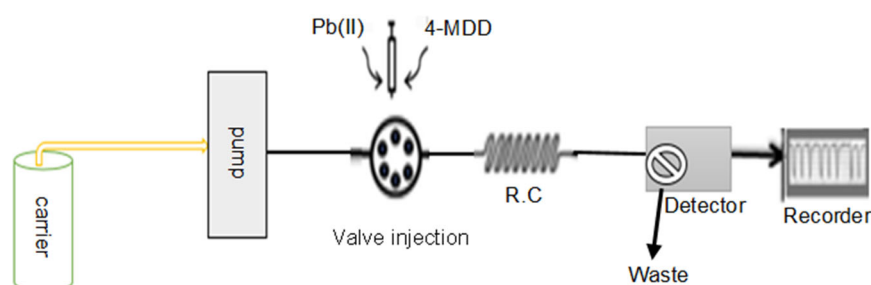


Fig 1. New design of FIA unit [4-MDD: 4-((4-methoxy phenyl)diazenyl)benzene-1,3-diol, R.C: Reaction coil, carrier: water]

reagent concentration = 1×10^{-4} M, reaction coil length = 15 cm, cell flow rate = 3.600 mL/min, optimal pH = 9. This is all shown in Fig. 2, gave the highest and best height, an ideal buffer solution was prepared tetrasodium ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$) and boric acid (H_3BO_3)] because our study in the flow injection technique depends on the pick height and not the absorbance.

Optimum reagent concentration. Different concentrations of the reagent were prepared, ranging from 1×10^{-6} to 1×10^{-4} molar, to study the effect of the concentration of the organic reagent and through the work, we can conclude that the optimal concentration was 8×10^{-5} M, which gave the highest pick, and therefore, it is the best pick. Then, it started to decline due to the increase in the dilution of the reagent and the experiment was conducted under the following conditions: reagent

volume 157.0 μL , Pb(II) ion volume 157.0 μL , metal ion concentration = 15 mg/L, pH = 9, and reaction coil length = 15 cm, cell flow rate is 3.600 mL/min. The results are shown in Fig. 3.

Physical parameters

Flow rate. After studying the optimal conditions for the chemical variables, the optimum flow velocity of the Pb(II) ion estimation process was studied in the conditions the reagent volume is 157.0 μL , and the Pb(II) ion volume is 157.0 μL , the metal ion concentration = 15 mg/L, pH = 9, reaction coil length = 15 cm, and reagent concentration 8×10^{-5} M, we obtained the highest, best height and uniform peak shape at 9.100 mL/min for mobile stage. The selection is due to the effect of increasing the dispersion, which leads to a complex concentration dilution, as shown in Fig. 4

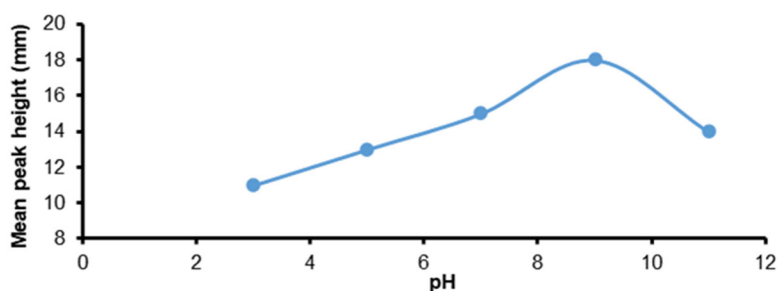


Fig 2. The effect of the pH on mean peak height

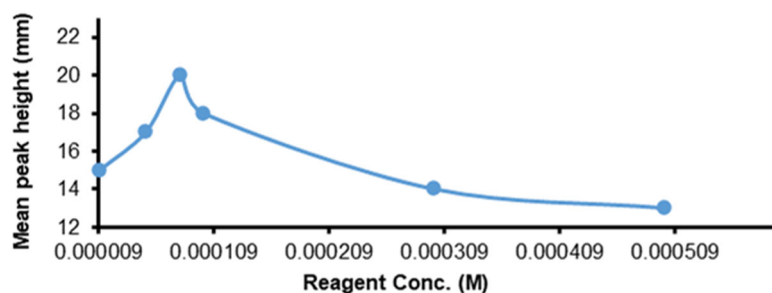


Fig 3. The effect of reagent concentration on mean peak height

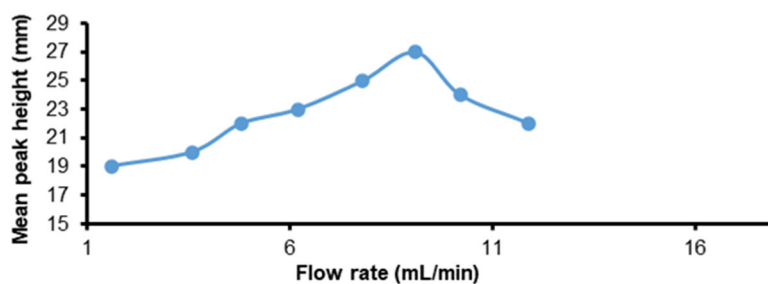


Fig 4. The effect of flow rate on mean peak height

selected because the response was sharp and dependable. Authors found that low flow rates cause double, distorted, and wide peaks, while fast flow rates decrease the response.

Reaction coil length effect. Different lengths of the reaction coil and a radius tube of 0.05 cm, which ranged between 15–35 cm, were used to know the effect of the length of the reaction coil in the estimation of the Pb(II) ion 157.0 μL , Pb(II) ion concentration = 15 mg/L, pH = 9, flow rate = 9.100 mL/min, and reagent concentration 8×10^{-5} M. At this length, we obtained a high sensitivity peak and then reduced the height to increase dispersion and attenuation [26] as shown in Fig. 5.

The effect of the volume of the organic reagent

Prepare a series of volumes for the organic reagent under study, 235.5–78.50 μL , junction length changes of 157.0 μL , Pb(II) ion concentration = 15 mg/L, flow rate = 9.100 mL/min, reagent concentration 8×10^{-5} M and

reaction coil length 157.0 μL . It turns out that the optimal volume of the detector is 117.8 μL corresponding to the best peak height equivalent to a tube with a length of 15 cm, as shown in Fig. 6. An increase in the volume of the detector leads to a decrease in the response and the appearance of the double peak because the excess volume of the detector is confined between two regions that form the product of this interaction [27].

The volume of the metal ion

Different volumes of Pb(II) metal ions were used in preparing the complex to find out the ideal metal ion volume for the estimation process. It was found that the best volume of metal ion, which gives the best sensitivity and the best peak height, is 117.8 μL , which is equivalent to a tube length of 15 cm and a radius of 0.05 cm, which gives the best peak height as shown in Fig. 7, and this

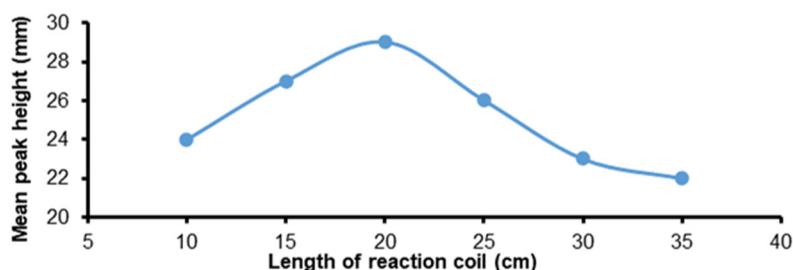


Fig 5. Effect of coil length effect on mean peak height

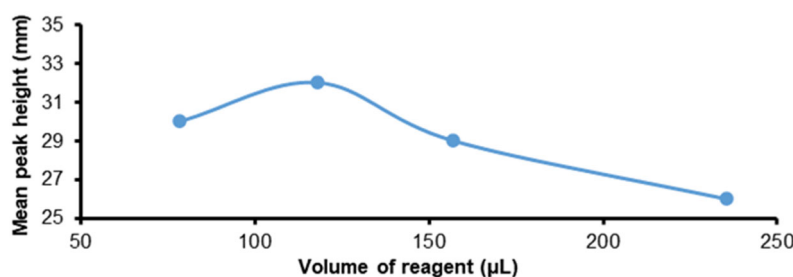


Fig 6. Effect of reagent volume on mean peak height

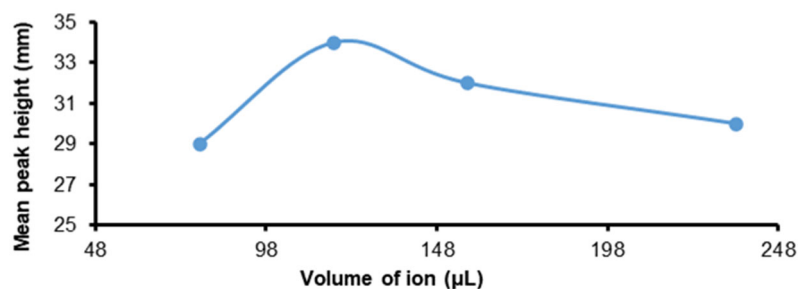


Fig 7. Effect of volume of the Pb(II) ions on mean peak height

experiment was conducted under the best conditions. The volume of the organic reagent is 117.8 μL , the concentration of the Pb(II) metal ion = 15 mg/L, pH = 9, the flow rate = 9.100 mL/min, the concentration of the reagent 8×10^{-5} M and the reaction coil length is 157.0 μL .

Dead volume study

The aim of this study is to clarify the fact that the complex is formed within the flow injection system, where two experiments were conducted. First, the reagent was injected into the first ring and in the second ring, H_2O was injected, instead of injecting the Pb(II) ion, as there was a response of 8.91 mm. In the second experiment H_2O was injected into the first ring instead of the reagent and in the ring second there is Pb(II) ion where we found that there is no response where the smaller the dead volume, means the results are better, then the Pb(II) ion and the reagent were injected for complex formation and measured the height of the peak where the result is as shown in the Table 1 and Fig. 8.

Calibration curve at optimum conditions

A calibration curve study after preparing the optimal conditions for the determination of the Pb(II) ion in different environmental and life models was used, after preparing a series of ion concentrations under study

between 0.05–30 mg/L, where we get the correlation coefficient = 0.9995, the limit of detection (LOD) = 0.026 mg/L, the limit of quantification (LOQ) = 0.088 mg/L, linearity = 0.5–27 mg/L as shown in Fig. 9. The method under study was validated as the calibration curve indicated the linearity of Beer's law.

Applications to different biological and environmental samples

The purpose of this experiment was to design an injection valve for the determination of Pb(II) ions in environmental and biological models. The prepared samples were taken and analyzed using the flow injection technique. Table 2 shows satisfactory results for different samples, including agricultural and non-agricultural soils in the district of Rifai Al-Fajr, Nahr Al-Fajr, celery, cauliflower, and cabbage 100.4–96.67%. It was a comparison of the technique under study with the FAAS flame atomic absorption technique.

Table 1. Study of dead volume

No.	Test type	The height of the peak (mm)
1	Pb(II) + H_2O	0.000
2	H_2O + reagent	8.910
3	Pb(II) + reagent	25.00

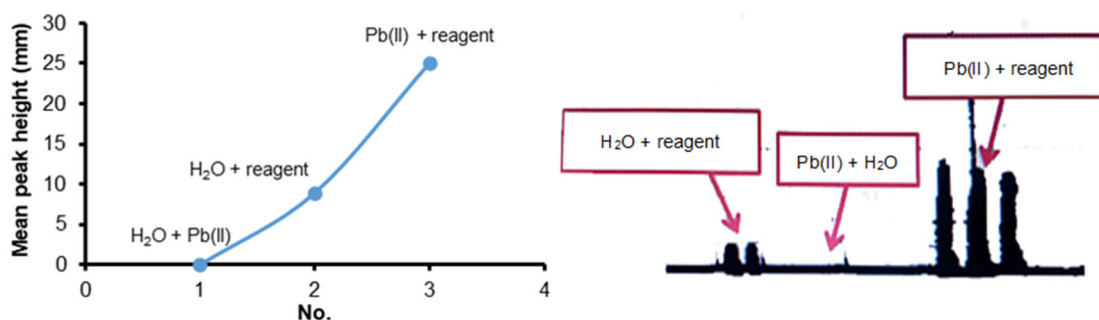


Fig 8. Study of the dead volume in FIA

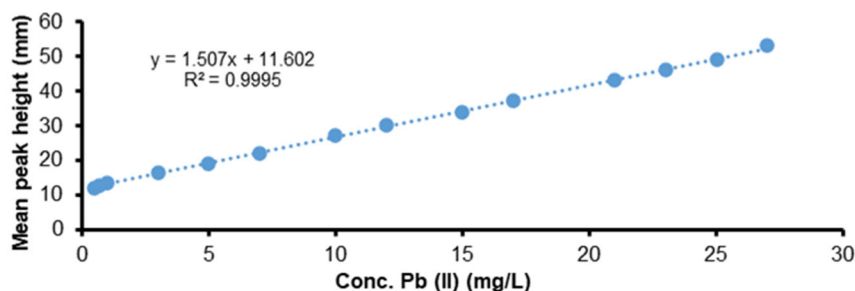


Fig 9. Calibration curve study at optimum conditions

Table 2. Determination of Pb(II) ion by FIA and FAAS technique in different samples

Sample	Value take (mg/L)	Value round mg/L FIA:FAAS	Er FIA: FAAS %	Rec FIA:FAAS %
Rifai River	0.700	0.701:0.703	0.1429:0.429	100.1:100.4
Soil agricultural land in Al-Fajr	6.000	6.025 :6.060	0.416:1.000	100.4:101.0
Soil non-agricultural land in Al-Fajr	6.000	6.015:6.018	0.250:0.300	100.3:100.3
Dirt close to the industrial neighborhood in Al-Fajr	6.000	6.130: 5.080	-3.330:2.166	96.67:102.2
Soil agricultural land in Rifai				
Soil non-agricultural land in Rifai	6.000	6.023:6.020	0.383:0.330	100.4:100.3
The dust of the wall of Al-Nibras gas station	6.000	6.008:5.700	0.133:-5.000	100.1:95.00
Water from the car wash station	6.000	6.010:6.007	0.160:0.110	100.2:100.1
Dirt from a car wash station	6.000	6.000:6.003	0.000:0.050	100.0:100.1
Fish	6.000	6.013:6.010	0.210:0.166	100.2:100.2
Celery	7.000	7.004:7.012	0.057:0.170	7.012:100.2
Cauliflower	7.000	7.014:7.010	0.200:0.143	100.2:100.1
Cabbage	7.000	7.014:7.000	0.000:0.200	100.0:100.2
Bean	7.000	7.025:7.007	0.357:0.100	100.4:100.1
	7.000	6.890:7.032	-1.570:0.457	98.43:100.5

■ CONCLUSION

Through this study, the investigated system was able to estimate the aforementioned (Pb(II)) ion using the organic azo reagent with high efficiency and accuracy using the confluent areas' flow injection technique. We can dispense with other classical methods of analysis because they are stressful and use expensive chemicals. Our system is simple and eco-friendly because it is possible to be manufactured in a laboratory-designed system from environmentally available and recycled materials. The flow injection system in the confluent regions showed higher sensitivity compared to the FAAS method.

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■ AUTHOR CONTRIBUTIONS

Thekayat Joodi Jassim conducted the experiment, Raisan Kadhim Taresh did the calculations, and Thekayat Joodi Jassim and Raisan Kadhim Taresh wrote and reviewed the manuscript. All authors approved the final version of this manuscript.

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