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Heavy metals removal from drinking water by nanocomposite tannin resin- TiO_2

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Abstract
The aim of study was to determination the kinetics adsorption of heavy metals from water samples obtained after sand filtration stage in AL-Wihda station of drinking water production in Baghdad by using three types of synthesized nanocomposite resins of tannin loaded with TiO_2NPs in order to select the best formula. The photocatalytic degradation and photochemical characteristics of TiO_2NPs on different organic and inorganic pollutants in water types were exploited. form *Acacia nilotica* leaves powder and synthesized the tannin resin (TR). Three types of nancomposites of tannin resin (TR) loaded with TiO_2NPs (TR-TiO_2-1, TR-TiO_2-2, and TR-TiO_2-3) synthesized by adding the TiO_2NPs before the formalin (TR-TiO_2-1) and after formalin addition (TR-TiO_2-2) and chemical green synthesis of TiO_2NPs from $TiCl_4$ by TR solution (TR-TiO_2-3). The results showed that the nanocomposite TR-TiO_2 -2 was the most efficient in removing the heavy metals pollutants from water samples compared to the Iraqi and Word Health Organization (WHO) standareds. Four metals (Mn, Cr, Cd and Hg) were selected for monitoring their removal from water samples after treating with TR-TiO_2 -2 composite. The remaining concemtration of Mn was 0.03 mg/L after 10 min of treatment; Cr, 0.006 mg/L after 50 min; Cd and Hg were not detected in water samples before and after treatments. Study of the adsorption kinetics of heavy metals for both equilibrium and the relationship of mass adsorption with time was showed that the maximum adsorption at the fixed times for each mineral especially the Mn and Cr, where the equilibrium state of the maximum concentrations of the adsorbed material was obtained on the nanocomposite

TR-TiO_2-2. The results showed that the Cr and Mn adsorption equilibrium were subjected to the pseudo-second order equation.

Keywords: Adsorption kinetics; Heavy metals; Nanocomposites; Tannin resin; TiO_2NPs.

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Introduction

Water contamination represents a major problem threatened by several countries. The obtainability of fresh and harmless drinking water has too been a previous anxiety by many developing countries. There has continued an increasing request of fresh and unpolluted water due to the depletion of greatest water capitals by the development in population, overall deficiencies and pollutants from many industrial wastes. Further than five million people erupt your last every year from water connected diseases and more than about 2.3 billion harm from diseases related to the up taking of dirty water[1]. Most of Iraq's water comes from its two main rivers, the Tigris and the Euphrates, which are heavily polluted by household waste and litter, further contaminating the water supply. The worldwide population remains to increase, primary to a rise in actions that need great volumes of water. Greatest of these applies principal to great levels of contamination and opening the restrictions of sustainability about water resource usage[2]. The nanotechnology applied in many field include medicine, energy, nanodevices, water purification ,environment and bio technology[3].

The TiO_2 fabricate in nanoparticles, additional properties will be developed such as still safe, blocking of ultraviolet and defense, antimicrobial agent, photocatalytic activity, self-cleaning, available, and cheap. The photocatalytic degradation trait of TiO_2NPs on different structures of organic and inorganic pollutants in water types are used[4, 5]. Tannins are natural biomass extracted from natural resources comprising multiple adjacent hydroxyl groups and showing exact affinity to metal ions in aqueous solution and be able to use as alternate, active, and effectual adsorbents for the capture and recovery of mineral ions. It is used as bioadsorbents in wastewater treatment since 1994[6]. The machines of biosorption are usually based on physicochemical connections among adsorbents and the functional sets existing on the biomass surface[7]. Tannin resin has been used as a nanocarrier associated with nanocompounds in various composite structures for the purpose of adsorption of minerals like Cr, Pb, Hg and C[8]. The determination of sorption dynamics, it requires for sight of double significant physico-chemical limits for example kinetics and equilibrium of adsorption. Kinetics labeling the solute adsorption degree, which controls the reaction time. The equilibrium is the determining spreading of the solute among solid-liquid parts and determining efficiency and ability of the solute or adsorbent for adsorption. Several kinetic models presently in application to focusing on the machinery of adsorption development are very simple and extensively used is pseudo-first order and pseudo-second order equation of Lagergren[9]. The aim of study was to determination the kinetics adsorption of heavy metals from water samples obtained after sand filtration stage in AL-Wihda station of drinking water production in Baghdad, using three types of synthesized nanocomposite resins of tannin loaded with TiO_2NPs in order to select the best formula.

Materials and methods

The substances used in this study are, leaves of *Acacia nilotica*; Sodium hydroxide (NaOH), 0.5%; TiO_2NPs, 50 nm; $TiCl_4$, 5 mM; Formalin, 37%; HNO_3, 1M; dH_2O. All compounds were purchased from local companies.

Production the nanocompsites of tannin resin (TR) loaded with TiO_2 NPs (TR-TiO_2)

The method of Nakano *et al*., (2001)[10] was used in extraction of tannin form *Acacia nilotica* leaves powder and synthesized the tannin resin (TR). Three types of nanocompsites tannin resin loaded with TiO_2 (TR-TiO_2-1, TR-TiO_2-2 and TR-TiO_2-3) were prepared during the preparation of TR. The modification of method including the addition of TiO_2NPs and $TiCl_4$ (5 mM). TR-TiO_2-1 was prepared by adding 80 ml (5 mM) of TiO_2NPs before the addition of formalin (37%). TR-TiO_2-2 nanocomposite was prepared by adding formalin after adding TR-TiO_2-2 at the same concentrations. TR-TiO_2-3 was prepared by adding $TiCl_4$ (5 mM) solution before adding the formalin in order to green synthesis of TiO_2NPs by tannin.

Solubility of nanocompsites RT-TiO_2 NPs: Five grams from each nanocomposite (TR-TiO_2-1, 2 and 3) was added to beakers containing 25 ml deionized water and tap water separately. Dissolving ability was monitored for one hour**.**

Water samples: Water samples were collected from Al-Wihda station for drinking water production in Al-Masbah area, Al-Karrada Al-Sharqiya, Rusafa side, Baghdad, during the period from 1/12/2020 until the end of work.

Determination of HM: Heavy metals dtermination were conducted in the AL-Qadisiyaha water project, Municipality of Baghdad. Four heavy metals (Mn, Cr, Cd and Hg) were measured in the water samples. The Mn, Cd, Hg and Cr were determined using atomic absorption spectroscopy. All analysis were performed according to[10].

Field experiments: It was conducted in the AL-Qadisiyaha water project, Municipality of Baghdad. Treatments were performed on the three nanocompostes with the same steps, volumes and weights. The treatments included adding 4 liters of water samples taken after the sand filtration stage to resistive screw plastic containers with 4 liter capacity containing 30 gm of the nanocomposite for each type and in all containers (A, B and C) as shows in fig.1. The contents were mixed vigorously for 5 minutes and then lift. Treated water samples were collected every 10 minutes for an hour. The samples were subjected to heavy metal tests. The control treatment included untreated water from the same source.

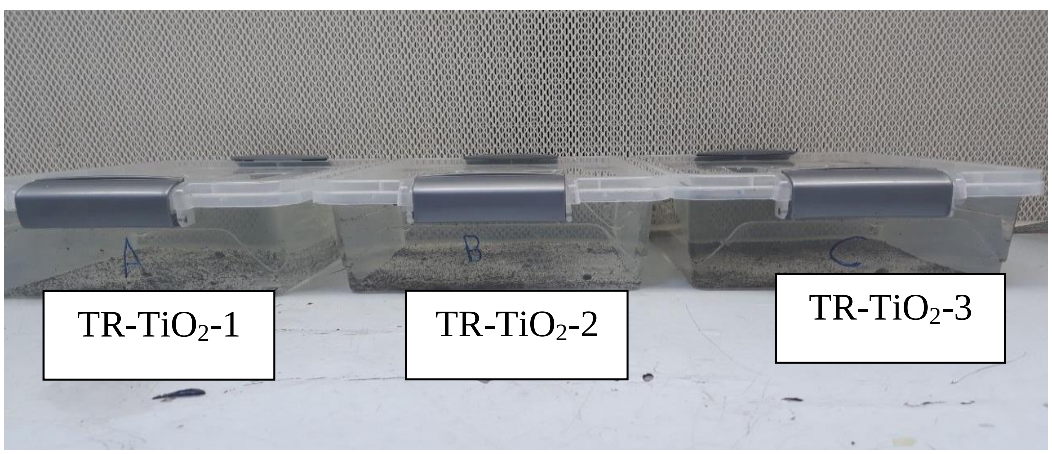

Figure 1: Treatment water samples with three nanocomposites (TR-TiO_2-1, TR-TiO_2-2 and TR-TiO_2-3).

Adsorption kinetics

From the initial and final concentrations, the percentage removal can be calculated by the use of the following formula[11]:

$$\textbf{Heavy metal removing}\ \% = \frac{C_0 - C_f}{C_o}\ \text{X}\ 100\%$$

Where C_0 is the initial concentration of ions in mg/L and C_f is the final concentration of ions in mg/L. The results obtained in batch mode were used to calculate the equilibrium metal uptake capacity. The amounts of pollutants uptake by TR-TiO_2 nanocomposite at the equilibrium (q_e) were calculated by the following mass-balance relationship[12]:

$$q_e = \frac{V(C_O - C_F)}{W}$$

Where q_e is the equilibrium uptake capacity in mg/g, V is the sample volume in liters, C_0 is the initial metal ion concentration in mg/L, C_F the equilibrium metal ion concentration in mg/L, and W is the dry weight of adsorbent in grams.

Pseudo-first order equation of Lagergren[13]:

$$\log(q_e - q_t) = log\ q_e - k_{ad}t/2.303$$

Where, q_e is the mass of metal adsorbed at equilibrium (mg/g); q_t, Is mass of metal adsorbed at time t (mg/g) and $k_{ad}t$ is the first order reaction constant (L/min).

The pseudo-first order kinetics reflects the rate of job of adsorption places is comparative to the amount of unoccupied places. A plot of log $(q_e - q_t)$ verses t designates the request of the first order kinetic model. On the other hand, equilibrium capacity might be stated by pseudo-second order equation as follows:

$$\frac{t}{q_t} = \frac{1}{K_{2,ad}q_e^2} + \frac{t}{q_e}$$

Where, K_2, ad is the second order reaction rate equilibrium constant (g/mg.min). A plot of t/qt versus to give a linear relationship for the applicability of the second order kinetic

Results and discussion

Preparation of nanocomposite tannin resin loaded with nano titanium oxide

Fig. 2 shows the preparation of three nanocomposites TR-TiO_2-1, 2 and 3.

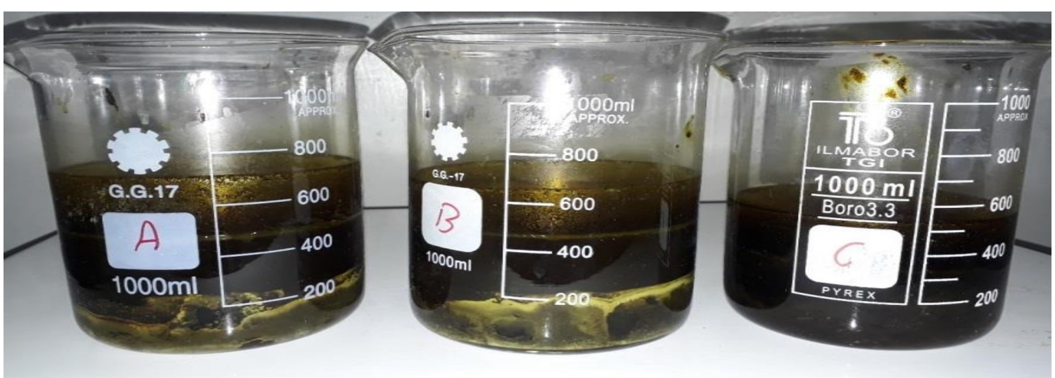

Figure 2: Preparation of the three nanocomposites TR-TiO_2 (1, 2 and 3). A, refers to nanocomposite TR-TiO_2-1; B, refers to nanocomposite TR-TiO_2-2; C, refers to nanocomposite TR-TiO_2-3.

The aim of preparing these three nanocomposites was included the choosing of the most efficient nanostructure in the adsorption of heavy metals and the stability of the nanocomposites. The method used in preparation the tannin resin was used for preparation of three nanocomposites tannin resin loaded with titanium oxide (TR-TiO_2)[14]. Modification of method was included the use of titanium oxide nanoparticles as a ready source of nanoparticles or the use of the titanium tetrachloride ($TiCl_4$) solution as a source for the green synthesis of the TiO_2NPs during the preparation of tannin resin nanoparticles. The difference between the preparation methods also included the addition of the formalin as polymerization catalyst before and after the addition of the titanium oxide sources.

Solubility in water: The results of the tests showed that the nanocomposite TR-TiO_2 -2 did not dissolve in tap water and deionized water, while the dissolution was very weak for the TR-TiO_2 -1 in deionized water and did not dissolve in tap water. The third mixture TR-TiO_2 -3 showed poor solubility in tap water and moderate solubility in deionized water. It was illustrated that the tannin resin extracted from *Acacia nilotica* by this method was insoluble in water, and thus the possibility of using it in the water[15].

Treatment water samples with TR-TiO_2 nanocomposites products Experiments for treating water samples taken after the sand filtration stage were carried out using the treatment method mentioned above for all the three products of nanocomposites. Samples were taken from each container every 10 min for a full one hour after adding water samples to the nanocomposites in the containers. These times were approved based on what was mentioned[16]. The results of the analysis for samples of treated water with the three mixtures were compared with the results of the analysis of drinking water produced by Al-Wihda station after the chlorination stage. The percentage of heavy metals removal was adopted between the control treatment and reaching the equilibrium state for the removed heavy metals.

The results of heavy metals analyzes of water samples treated with the three nanocomposites and at the time from the beginning of the treatment up to 60 min showed that the TR-TiO_2 -2 nanocomplosite is completely better in treating these heavy metals compared to other mixtures and the control treatment as a reference. Table (1) shows the results of the analysis of the water samples treated with TR-TiO_2 -2 nanocomplosite.

Table 1: Analysis of treated water with nanocomposite TR-TiO_2 -2

Parameter	Unit	Control treatment	Time /min						Water quality of Al-Wihda station after chlorination	Iraqi Stand.	WHO Stand.	Removing (%)
			10	20	30	40	50	60				
Manganese	mg/L	0.04	0.03	0.03	0.03	0.03	0.03	0.03	0.02	0.2	0.2	25
Mercury	mg/L	0	0	0	0	0	0	0	0	0.001	0.001	-
Chromium	mg/L	0.015	0.010	0.010	0.009	0.007	0.006	0.006	0.01	0.05	0.05	60
Cadmium	mg/L	0	0	0	0	0	0	0	0	0.003	0.003	-

It is evident from the results in table (1) that the Mn removal rate did not exceed 25% after 10 minutes, as the adsorption isotherm, which was reached after 10 min, and the value did not change after a full hour. The Mn concentration is close to the concentration in the drinking water produced at the station although there is a later stage of chlorination. The nanocomposite TR-TiO_2-2 was distinguished by its ability to remove an important part of this metal. The Hg and Cd in treated water samples with nanocomposite TR-TiO_2 -2 scored zero concentration for time from 10 to 60, respectively. While the mercury and cadmium for the control treatment was zero. The Hg and Cd for Al-Wihda station after chlorination stage was recorded zero, and for Iraqi Standard and WHO is 0.001 and 0.003 mg/L respectively. The adsorption isotherm equilibrium was reached the balance during the first 10 min of the

reaction and the value did not change after a full of hour. The past study was showed to the complete adsorption of all Hg within 10 minutes with stabilization by using TR[17] . The characterization results will show the differences in the composition of these mixtures. The Cr of treated water sample with nanocomposite TR-TiO_2-2 scored 0.010, 0.010, 0.009, 0.007, 0.006 and 0.006 mg/L for time from 10 to 60 min, respectively, While the Cr

for the control treatment was 0.015 mg/L. The Cr for Al-Wihda station after chlorination stage was recorded 0.01 mg/L, and for Iraqi Standard and WHO is 0.05 mg/L. The stability of removing the Cr is proven at 50 min after adding the mixture, and this mixture is more efficient in removing the Cr compared to its counterpart in drinking water produced from the Al-Wihda plant. The removing percentage was 60% compared to the control treatment.

Adsorption equilibrium kinetics

The chromium element was selected to study the absorption kinetics by using the three nanocomposites, due to its health importance and risks. The results of the water analysis showed that it was free of hazardous minerals such as Cr and Cd, with low concentrations of Cr and Mn that are among the allowable environmental concentrations in the water samples. Based on the results of tables (1), the second mixture (TR-TiO_2-2) was the best in adsorption of Cr and within the first 50 minutes of treatment. Tables (2) and figs. (3, 4, 5 and 6) show the concentrations of Cr (mg/gm) adsorbed by the nanocomposite TR-TiO_2-2 during the exposure of the water sample for a period of 60 minutes at interval time of 10 min. The results of applying the first and second pseudo order equations shows the adsorption of Cr on the nanocomposite TR-TiO_2-2 were subjected to pseudo-second order by obtaining a linear curve from the relationship between Log qe-qt and t/ qt versus time. As mentioned by author [18], the pseudo-second-order kinetic model has become among the most common ways to fit rate data for adsorption of metal ions from aqueous solution (water sample) onto nanopolymer, So the adsorption kinetics of nanopolymer resin according to the results is expected to mainly depend on diffusion-limited processes, as affected by heterogeneous distributions of pore sizes on nanoplymer resin and continual partitioning of metals ions between a dissolved state and a fixed state of adsorption.

Table 2: Concentrations of Cr adsorption in water sample by the nanocomposite TR-TiO_2-2

Time (min)	Remaining Cr conc. in water sample (mg /L)	Adsorbent Conc. of Cr (mg / gm)	qe-qt [(1)] (mg/gm)	Log qe-qt	t/ qt
٠	0.015	0	0.009	-	-
١٠	0.010	0.005	٠.004	-3.2	3.5
٢٠	0.010	0.005	٠.004	-3.2	6.9
٣٠	0.009	0.006	٠.003	-2.09	15.6
٤٠	0.007	0.008	٠.001	-2	20.2
٥٠	0.006	0.009	٠	-1.9	26.5
٦٠	0.006	0.009	٠	-1.9	31.8

(1):q_e is the mass of metal adsorbed at equilibrium (mg/g), q_t is mass of metal adsorbed at time t (mg/g)

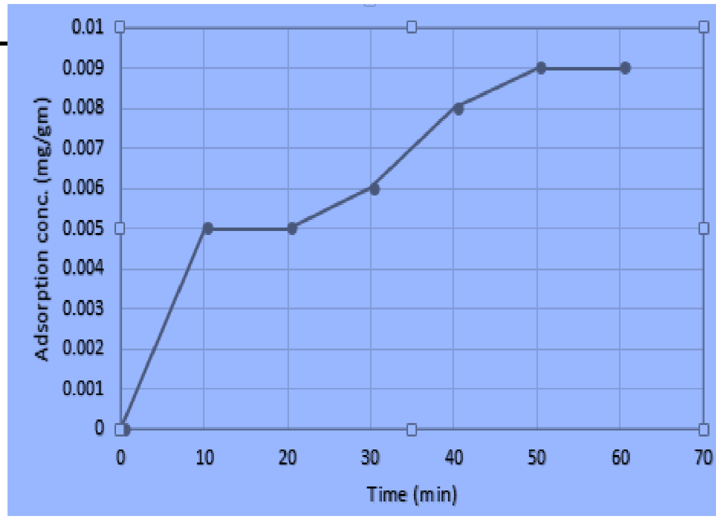

Figure 3: Effect of contact time on the adsorption of chromium by nanocomposite TR-TiO_2-2.

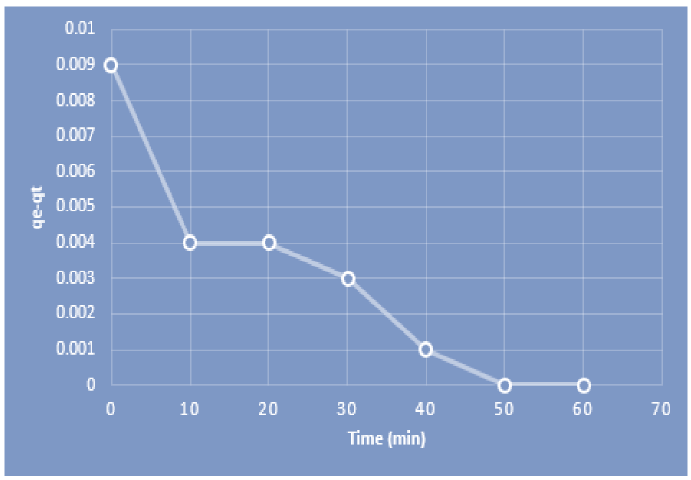

Figure 4: The mass of chromium adsorbed at equilibrium with time for nanocomposite TR-TiO_2-٢.

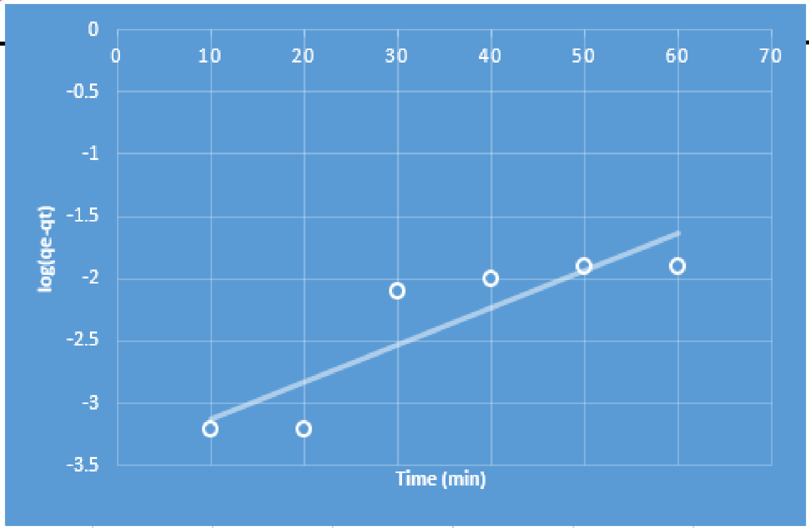

Figure 5: Pseudo-first order reaction for chromium onto nanocomposite TR-TiO_2-2.

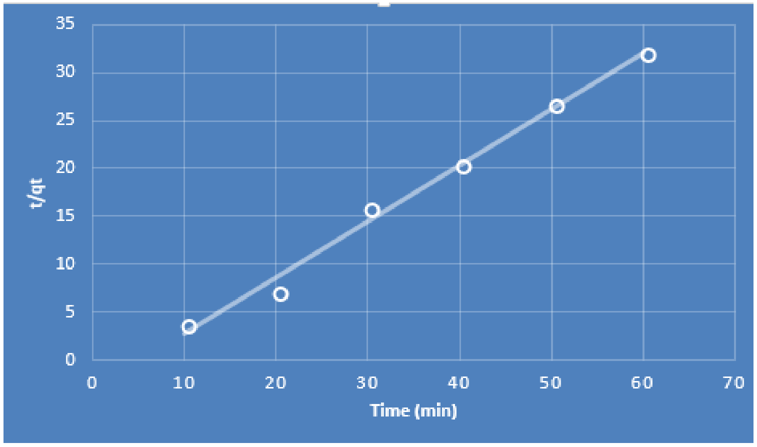

Figure 6: Pseudo-second order reaction for chromium onto nanocomposite TR-TiO_2-2.

Conclusion

In the current study, three types of nanocomposite (TR-TiO2-1, TR-TiO2-2, and TR-TiO2-3) were synthesized from tannin resin loaded with TiO2NPs for removing the pollution level of heavy metals in water samples taken after the sand filtration stage in one line of drinking water production from Tigris river in Al-Wihda station at Baghdad city and compared with the drinking water produced by Al-Wihda station. Tannin resin was extracted from Acacia nilotica leaves powder. There was a difference in the texture and colors of the three mixtures and their solubility in water. As the second mixture was distinguished by its insoluble in deionized water and the clear solubility of the third mixture. The nanocomposite TR-TiO2 -2 formula gave the best results in decreasing the most pollutants during a full hr compared with the others two nanocomposites.

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Author's Declaration

- We hereby confirm that all the Figures and Tables in the manuscript are original and have been created by us.
- We have obtained ethical clearance for our study from the local ethical committee at [Al-Nahrain University/College of Biotechnology]. This approval underscores our commitment to ethical research practices and the well-being of our participants.
- Ethical Clearance: The project was approved by the local ethical committee at [Al-Nahrain University/College of Biotechnology], ensuring adherence to ethical standards and the protection of participants' rights and welfare.
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Author's Contribution Statement

[First Author]: Conducted all the experiments, data analysis, drafted the initial manuscript.

[Second Author]: Contributed to the conception and design of the study, data rearrangement and drafted the initial manuscript.

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