Indian Journal of Chemical Technology
Vol. 24, January, 2017 pp. 82-87

Equilibrium, isotherms and thermodynamic studies of congo red adsorption onto *Ceratophyllum Demersum*

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Received 25 June 2015; accepted 11 March 2016

The adsorption of Congo red onto *Ceratophyllum demersum* (C. *demersum*) has been investigated. It is observed from the experiments that an adsorbent prepared from the *Ceratophyllum demersum* plant is effective for the removal of Congo red from aqueous solutions at room temperature. The adsorption of Congo red is found to be dependent on contact time, initial dye concentration and adsorbent dose. The results indicate that *Ceratophyllum demersum* has a strong capability of removing Congo red dye directly from contaminated water. Therefore, it can be concluded that *Ceratophyllum demersum* could be used for the removal of pollutants from aqueous solutions. The equilibrium adsorption data is analyzed using three common adsorption models: Freundlich, Langmuir and Temkin. The thermodynamic parameters ΔG°, ΔH°, and ΔS° are calculated for the adsorption of Congo red onto *Ceratophyllum demersum*. The Gibbs free energy change values show that the adsorption of Congo red onto *Ceratophyllum demersum* is spontaneous.

Keywords: Congo red, *Ceratophyllum demersum*, Adsorption, Isotherms, Thermodynamic

Water is one of the most stable and abundant complexes in nature that can be polluted by natural and human factors. Polluted water is harmful to human health and other organisms[1]. Industrial wastewater is considered one of the main pollutants of the environment[2]. Dyes are one of the most important industrial pollutants[3]. Synthetic dyes are difficult to biodegrade because these dyes have a complex structure and aromatic rings which make them more difficult to degrade[4,5]. Direct dyes are the most problematic due to their bright colour, acidity and water soluble reactive characteristics, with their high conjugated molecular structure, and they contain one or more anionic sulfate groups which aid the solubility of the dye molecule in water[6,7]. Many organic dyes are hazardous and may affect aquatic life and even the food chain. Additionally, the dyes' presence in natural water systems inhibits the diffusion of sunlight into the water, consequently reducing the photosynthetic processes of aquatic plants[8]. Therefore, it is very important to develop new systems that can be used for removing dyes from water[9]. Several successful treatment systems using physicochemical, chemical and biological technologies have been designed such as flocculation, coagulation, precipitation, adsorption, different types of oxidation process[10], electrochemical techniques, ozonization, sedimentation, reverse osmosis, fungal degradation, and photo degradation[11], for the removal of colored dye from wastewater.

Adsorption is an important technology and is considered more effective and less expensive than other technologies for the removal of dyes in industrial applications[12]. Many attempts have been made by researchers to synthesize low-cost adsorbents from widely available agricultural wastes such as sawdust[13], wheat straw[14], coir pith[15], sugar cane bagasse[16,17], and others. Some of these materials are chemically modified to improve their adsorption capacity[18,19]. The biosorption process is a type of adsorption which has been strongly recommended by researchers worldwide as an efficient and economically sustainable technology for the removal of synthetic dyes and organic compounds from industrial wastewater. It utilizes not only plant materials, but also a wide variety of micro-organisms in dead, pretreated, and immobilized (materials of biological origin) form as adsorbing agents. These materials are cheap to produce and carry a wide range of binding sites for dye molecules[20-22]. Recently, aquatic plants have been used in the removal of some polluted dyes from wastewater and industrial water such as *Salvinia herzogoi, Eichhornia crassipes, Myriophyllum spicatum* and *Ceratophyllum demersum*[23,24]. *Ceratophyllum demersum* is a completely submersed plant and is commonly seen in shallows, rivers, lakes, ditches, and quiet streams with moderate to high nutrient levels. It is a submerged, rootless, free floating perennial and is cosmopolitan in distribution, absorbing all the nutrients it requires from the surrounding water. If it is growing near the lake bottom, it will form modified leaves, which it uses to anchor to the sediment. However, it can float free in the water column and sometimes forms dense mats just below the surface[25]. In the Hilla River in Iraq, the *Ceratophyllum demersum* plant has been synthesized by a physiochemical activation method and by using dilute hydrochloric acid as an activator. The activity of *Ceratophyllum demersum* was tested by the adsorption of Congo red as a direct red dye from aqueous solutions.

Experimental Section

Direct red 28, or Congo red ($C_{32}H_{24}N_6O_6S_2.2Na$), the dye used as an adsorbate model in this study, was used as it was provided without any further purification being necessary. Distilled water was used to prepare all the solutions and reagents in this work. The molecular weight of Congo red is 696.67 g/mol. The structure of this dye is shown in (Fig. 1).

A *Ceratophyllum demersum* plant biomass was collected locally from the Hilla River in Iraq, and consisted of the floating part of the plant. The plant was washed with distilled water and dried in an oven at room temperature for seven days. The dry plant was immersed in dilute hydrochloric acid (3%) for 24 h, after which it was washed with distilled water and was allowed to dry in a hot-air oven at 80°C for three days. The plants were weighed for their dry weight and crushed into a fine powder; the *Ceratophyllum demersum* was then sieved and the particle size obtained was around 200 mesh, after which it was kept in a tightly closed plastic container and used as an adsorbent to remove Congo red dye in the adsorption experiments.

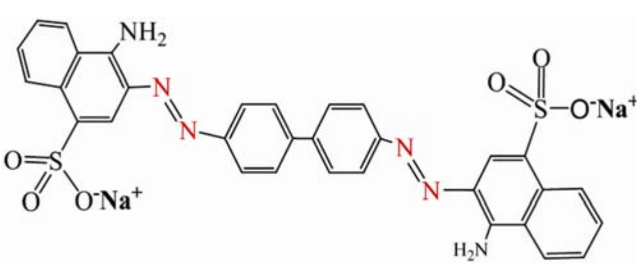

Fig. 1 — Chemical structure of Congo red dye.

Many adsorption studies were investigated in this study in order to determine the effects of different parameters that influence adsorption processes. In this context, all the adsorption tests were conducted in a magnetic stirrer at temperatures ranging from 283.15 to 308.15 K. The adsorption processes were performed using a concentration of the used dye, which was Congo red equal to 10 ppm. The adsorbent was loaded in different masses into 100 mL of aqueous solution of the dye; these masses were: 0.05, 0.10, 0.20, 0.30, and 0.40 g. Periodically 2 mL of the solution was withdrawn from the reaction mixture, centrifuged, and the absorbance was recorded at a wavelength of 498 nm. The absorbance was measured using a 1650 PC-UV-visible spectrometer Shimadzu. The efficiency for Congo red removal from the suspension (R %) was calculated using the following equation:

$$\text{Removal } \% = \frac{C_i - C_f}{C_i} \times 100 \qquad \text{... (1)}$$

where C_i is the initial concentration of the dye and C_f is the final concentration at the end of adsorption process. A specific amount of dye was adsorbed onto the adsorbent (q), which is referred to as (mg/g). Adsorption capacity at a given time (q_t) can be obtained as follows:

$$q_t = \frac{(C_i - C_t) \times v}{m} \qquad \text{... (2)}$$

where C_t represents the concentration of the dye as a function of time, (v) refers to the volume of the solution, and (m) is mass of the *C. demersum*.

Results and Discussion

The surface morphological changes of the *C.demersum* samples were investigated using a Scanning Electron Microscope (SEM).

The effect of contact time on the adsorption capacity of Congo red onto *C. demersum* is shown in (Fig. 2); when the initial Congo red concentration is increased from 10 to 50 ppm the amount of Congo red adsorbed onto *C. demersum*, at 60 min contact time, a *p*H value of 6, an adsorbent dose of 0.3g, and a constant temperature of 298.15 K, increased from 3 to 12 mg g^{-1} (Ref. 26). These results show that a rapid

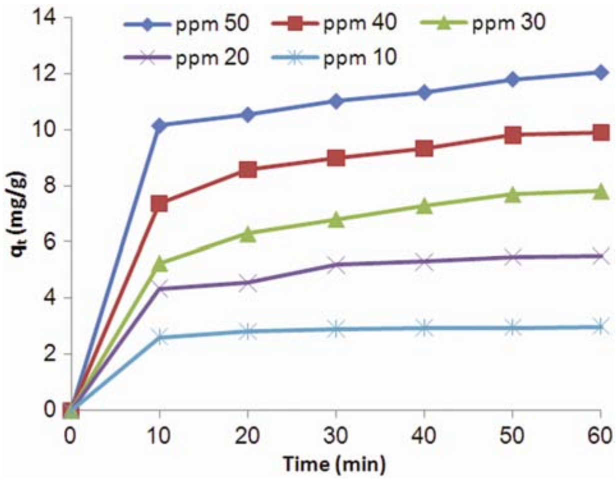

Fig. 2 — Effect of contact time on the adsorption of Congo red dye by *C. demersum*.

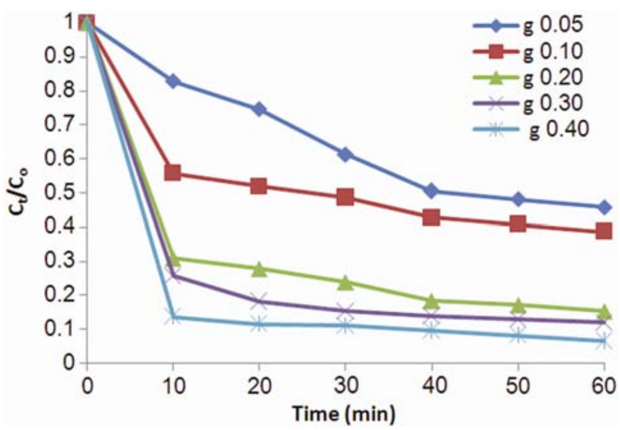

Fig. 3a — Effect of *C.demersum* dosage on Congo red adsorption.

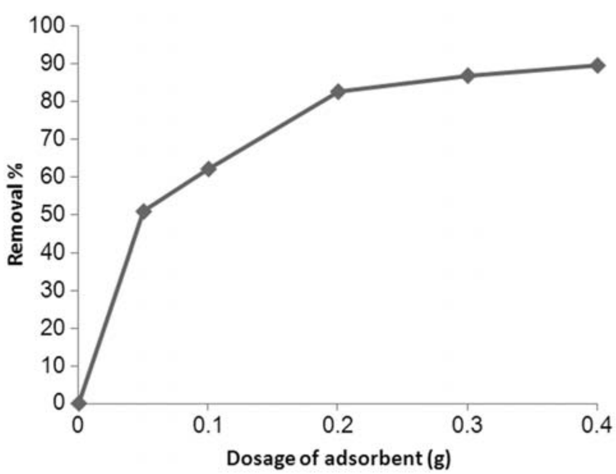

Fig. 3b — Effect of *C. demersum* dosage on the adsorption percentage of Congo red.

increase in the adsorbed amount of Congo red was achieved during the first 10 min. Similar results had been reported before for the removal of hazardous contaminants from wastewater[27].

The effect of the *C. demersum* dose was studied by varying the dose between 0.05 and 0.40 g. To determine the effect of the adsorbent dosage on the adsorption of Congo red, a series of adsorption experiments were carried out with different adsorbent masses at an initial dye concentration of 10 ppm. (Figs. 3a and 3b), show the effect of the adsorbent dose on the removal of Congo red. The percentage of Congo red adsorbed increased from 50.88 to 89.74% after 60min of adsorption time. This result was expected as the number of available adsorption sites goes up with increases in the adsorbent amount[28-30].

Different concentrations of Congo red of 10, 20, 30, 40, and 50 ppm were selected to study the effect of the initial concentration of dye on *C. demersum*. The amounts of dye adsorbed at a *p*H of 6, an adsorbent dosage of 0.3 g, and a constant temperature of 298.15 K are given in (Figs 4a and 4b). By increasing the initial concentration of Congo red from

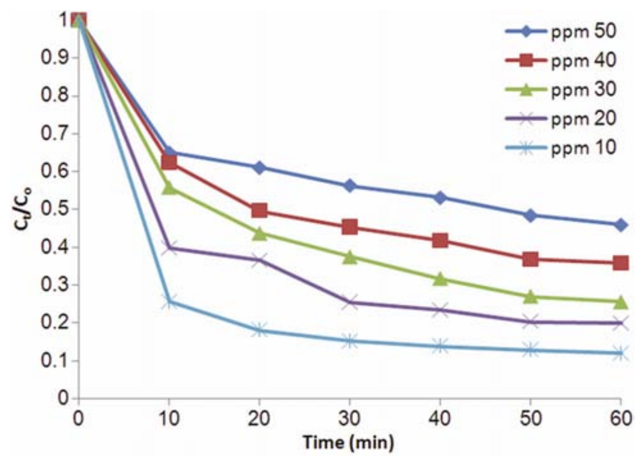

Fig. 4a — Change of (C_t/C_o) with adsorption time at different dye concentrations.

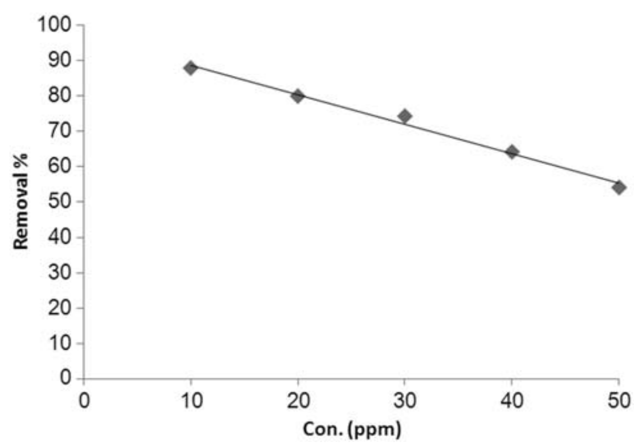

Fig. 4b — Effect of the initial concentration on the adsorption percentage of Congo red on *C. demersum*.

10 to 50 ppm, the removal of dye molecules decreases from 87.97 to 53.98% after 60min of adsorption time. These results agree with the adsorption of heavy metal ions onto carbon nanotubes[31].

The effect of temperature on the adsorption of Congo red in a water solution was investigated over a range of 283.15 to 308.15 K by *C. demersum*. (Figs 5a and 5b) show the influence of temperature on the adsorption of Congo red onto *C. demersum*. Observations showed that the equilibrium adsorption capacity of Congo red onto *C. demersum* was found to go up with an increase in temperature. This fact indicates that the mobility of the dye molecules increases with temperature; moreover, the viscosity of the dye solution reduces with a rise in temperature, and as a result it increases the rate of diffusion of the dye molecules. These results were in agreement with the effect of the solution's *p*H, ionic strength, and

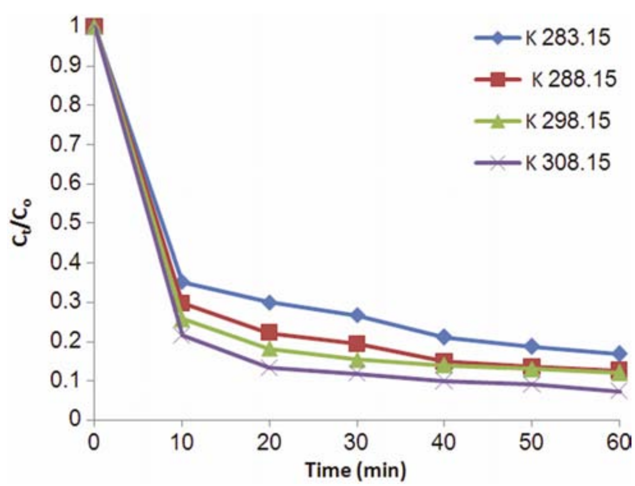

Fig. 5a — Change of (C_t/C_o) with adsorption time at different temperatures.

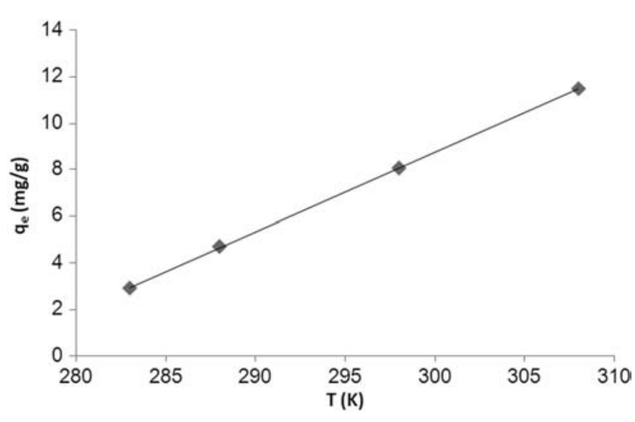

Fig. 5b — Effect of temperature on the adsorption amount of Congo red onto *C. demersum*.

temperature on the adsorption behavior of dyes on activated carbon[32].

In this study, adsorption isotherms were studied by applying Langmuir, Freundlich and Temkin isotherms for the adsorption of Congo red onto *C. demersum*. It is well known that the first model is based on the adsorption on homogeneous monolayer coverage. According to this model of adsorption, all adsorption sites are energetically equivalent. The Freundlich model is used to conduct a physisorption that occurs on heterogeneous surfaces. Both of these models are represented mathematically in the following equations[33-36]:

Langmuir $1/q_e = 1/q_m + 1/K_L q_m C_e$ … (3)

Freundlich $\log q_e = \log K_F + 1/n \log C_e$ … (4)

Temkin $q_e = B_1 \ln C_e + B_1 \ln K_T$ ... (5)

where, q_e (mg/g) is the concentration of the Congo red dye used in this study, q_m (mg/g) is the capacity of monolayer adsorption, K_L (L/mg) is the Langmuir adsorption constant related to the energy required for the adsorption, C_e (mg/L) is the concentration of Congo red dye required for equilibrium, and K_F and 1/n are the Freundlich adsorption isotherm constants. K_T and B_1 are the Temkin constants (K_T is the equilibrium binding constant (L/g) and B_1 is related to the heat of adsorption).

Generally, the Langmuir adsorption isotherm equation can be used to calculate the maximum adsorption capacity of the *C. demersum*. The conditions under which these were applied were a constant temperature of 298.15 K, a *p*H of 6, and the initial concentration of Congo red dye was 10 ppm. The amount of adsorbent used (*C. demersum*) ranged from 0.05 to 0. 40 g. The results of the isotherm constants and R^2 are shown in Table 1, and these results are plotted in Figs 6a, 6b, and 6c as 1/qe

Table 1 — Isotherm parameters for congo red adsorption onto *C.demersum.*

Isotherm	Parameters/ values		
Langmuir	$R^2 q_m k_L$		
	0.95616.83060.2144		
Freundlich	R^2	K_F	n
	0.79722.00902.5926		
Temkin	R^2	K_T	$B_{1.}$
	13 0.79724.34091.2412		

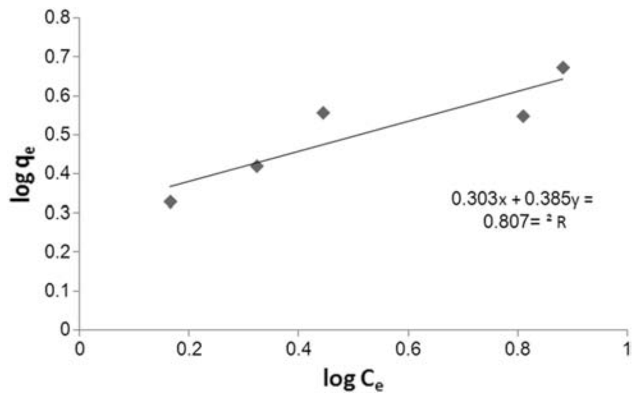

Fig. 6a — Freundlich isotherm for Congo red adsorption onto *C.demersum*.

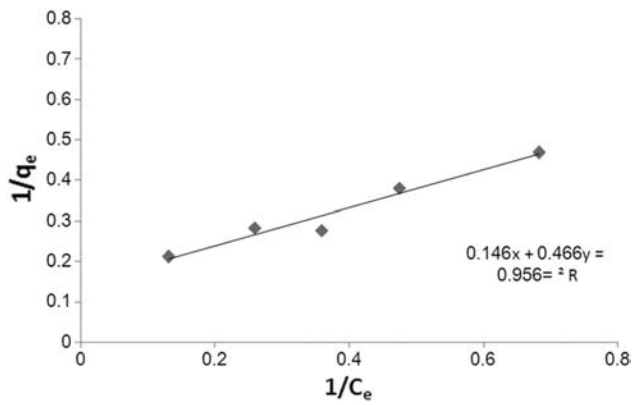

Fig. 6b — Langmuir isotherm for Congo red adsorption onto *C.demersum*.

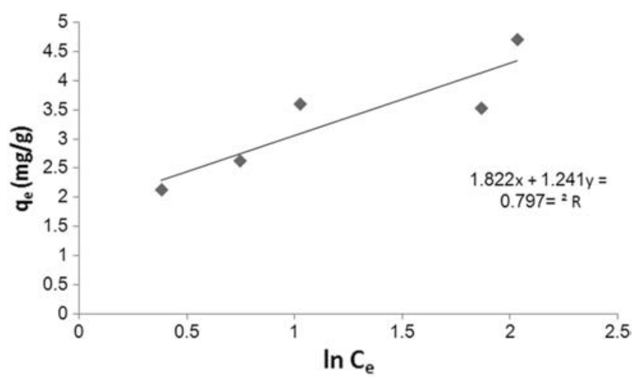

Fig. 6c — Temkin isotherm for Congo red adsorption onto *C.demersum*.

against 1/Ce. From a high value correlation coefficient it can be suggested that these results are in good agreement with the Langmuir isotherm. All the parameters of the adsorption isotherm were derived from the slope and the intercept; these results are summarized in Table 1.

The thermodynamic parameters, namely Gibbs free energy change (ΔG°), enthalpy change (ΔH°), and entropy change ΔS° for the adsorption processes were determined using the following equations[37-41]:

Table 2 — The thermodynamic parameters of the adsorption of Congo red onto *C. demersum*.

Temperature/K	ΔG°/ kJ mol^{-1}
283.15	-1.98
288.15	-3.99
298.15	-5.62
303.15	-7.59
ΔH°/ kJ mol^{-1}	57.91
ΔS°/ kJ mol^{-1}	0.21

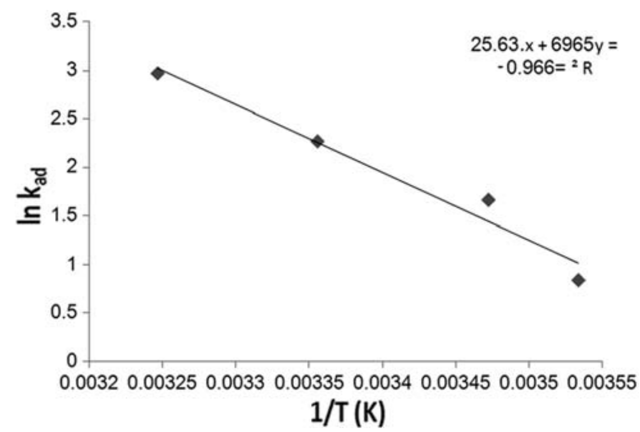

Fig. 7 — The plot of Ln K_{ad} versus 1/T for the estimation of thermodynamic parameters.

$$\Delta G^{\circ} = -RT ln K_{ad} \quad \ldots (6)$$

$$ln K_{ad} = -\frac{\Delta H^{\circ}}{RT} + \frac{\Delta S^{\circ}}{R} \quad \ldots (7)$$

where R is universal gas constant (8.314J mol^{-1}K^{-1}) and T is the absolute temperature in Kelvin. The thermodynamic parameters are summarized in Table 2.

The negative values of ΔG° indicate that the adsorption process was a spontaneous process. The decrease in ΔG° with the increase in temperature indicates a more efficient adsorption at higher temperatures[42]. The positive values of ΔH° confirm that the adsorption of Congo red onto *C. demersum* is endothermic in nature. Fig. 7, shows the Van't Hoff plot for the adsorption of Congo red onto *C. demersum*.

Conclusion

The data show that *C.demersum* can be used effectively for the removal of Congo red from an aqueous solution. 0.3 g is the optimum dosage of *C. demersum* to adsorb Congo red. The adsorption capacity of the Congo red onto *C. demersum* increases with an increase in the initial concentration of Congo red. The equilibrium adsorption capacity of Congo red increases with temperature. The adsorption of Congo red onto *C. demersum* is described using the Freundlich, Langmuir, and Temkin adsorption isotherm models. The equilibrium data fitted with the Langmuir isotherm. The adsorption of Congo red is found to be spontaneous at the temperatures under investigation. The positive value of ΔH° confirmed the adsorption process was endothermic. Therefore, it can be concluded that *C. demersum* can be used for the removal of pollutants from aqueous solutions.

Acknowledgement

Authors are gratefully acknowledge the financial support that was provided by Babylon University, College of Science, IRAQ for funding this work.

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