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Evaluation of the efficiency of biological and chemical treatment of agricultural wastewater

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Abstract: The study included the analysis and measurement of some physical and chemical pollutants in the agricultural wastewater with the aim of treating it and reusing it in the agricultural field. The study dealt with the application of the phytoremediation system to treat the agricultural wastewater. The purpose of the study was to use the *Ceratophyllum demersum* L. and *Lemna minor* L. plants to treat the agricultural wastewater and the possibility of using them for irrigation or other uses. The duration of the study is in September, October and November of 2023 AD. Some pollutants were analyzed and measured, such as turbidity, dissolved oxygen (DO), electrical conductivity (EC), total hardness (TH), sodium (Na), and phosphate (PO4). The results of the study showed a clear difference in the physical and chemical factors of water quality, as the two treatment T3 and T4 were given the best results compared to the rest of the treatments in the percentage of removal through treatment with C. *demersum* and L.*minor* plants.

Keywords: : phytoremediation; *Ceratophyllum demersum* L.; *Lemna minor* L.; agricultural wastewater ; Aluminum sulphate.

1. Introduction

The use of agricultural wastewater for the purposes of irrigating agricultural crops is one of the issues proposed to solve the water scarcity crisis that agricultural lands in Iraq suffer from, as the problem of water scarcity due to lack of rain and climate change, especially in recent times, has led to finding solutions and available alternatives to address the water shortage in particular. Used in the field of irrigation. The water of rivers and streams in Iraq has standard acceptable specifications when used for irrigation purposes. Therefore, research studies focused on determining the specifications of groundwater and agricultural wastewater due to their variation from one region to another, and the difference in their degree of suitability for irrigation purposes [1]. Agricultural wastewater is considered one of the types of sources resulting from human activity. It is a complex environment that changes depending on natural and human activities resulting from domestic, industrial, craftsmanship, and agricultural use (fertilizers and pesticides) and its discharge into the aquatic environment [2]. Traditional treatments for polluted water require pumping and treatment operations, as well as the establishment of many units to remove various pollutants. These treatments are expensive and uneconomical and require installation, maintenance, and manpower. As a result, researchers searched for environmentally friendly alternatives that are low in cost and effort and have little harm to the environment [3]. Recent research has shown that aquatic plants have the potential to remove organic and inorganic pollutants. Whereas Phytoremediation technology is a branch of bioremediation in which plants are used to treat polluted water, as these plants have the ability to accumulate a specific or wide range of pollutants and reduce or eliminate them [4].

The C. *demersum*, is a member of the cotyledon and dicotyledon seed plant family. It is a member of the *Ceratophyllaceae* family. It is a submersible, floating aquatic plant. It does not have roots at the bottom of the water stream. It is also considered a dark green perennial plant. The leaves are densely clustered at the end of the plant's branches to give with an appearance resembling a cat's tail, the C.*demersum* grows in shallow, muddy places and quiet flat surfaces. and is an important element in supplying Aquatic environment with oxygen, in addition to being an effective filter in removing many pollutants such as heavy metals and others, the C.*demersum* plant reproduces by cutting or division and seed [5].

Regarding the L.*minor*, it is a member of the *Arecidae* class, a subclass of the *Lemnaceae* family, it is regarded as one of the tiniest aquatic plants that float freely and don't attach themselves to the ground. They do not have true roots or leaves, and their body consists of leaflets. A green plate whose dimensions do not exceed several millimeters, and its upper surface differs from its lower surface, from which stems stem in the form of unbranched hairs. This plant adapts to different environments [6].

2. Materials and Methods

2.1 Collection of samples: September of 2023 saw the collection of samples in the city of Dujail for the Al-Ishaqi River's water as well as the agricultural wastewater. samples of the L. *minor* and C. *demersum* plant were both obtained by hand. (the same place where the samples were collected). Randomly Because of the lack of bias towards a specific region over another, as well as to cover the study area more broadly, taking into account that the plants are close in age. The plants were washed with distilled water several times to get rid of the materials stuck in it. The samples were placed in plastic tubs prepared for this purpose. Insect eggs and unwanted organisms such as snails were treated with a snail (*Anentome helena*), which is capable of killing these organisms for a period of about two weeks [7], and after that, in order to cultivate them in ponds, they were moved to the treatment system. Regarding Aluminum sulfate Al2(SO4)3 that was acquired at the neighborhood market.

2.2 Description of the treatment system: The treatment system for the L.*minor* and the C. *demersum* plant included basins made of wood and lined with polyethylene bags to prevent water leakage, rectangular in shape, with a length of 80 cm, a width of 40 cm, and a height of 40 cm. The bottom of the tanks was covered with two layers of supportive medium, the first layer. It was gravel, 7 cm high, and the second layer was agricultural sand (zamij), 7 cm high. These supporting media (gravel, agricultural sand) are good media for the growth of aquatic plants [8]. After that, both the L.*minor* and the C.*demersum* plant were planted at a rate of 1000 grams of fresh weight for each tank, and 100 liters of agricultural wastewater were added to the treatment basins, and physical and chemical tests were conducted for them. The experiment lasted (15) weeks, and the shortage of agricultural wastewater was compensated for with distilled water [9].

2.3 Experiment design: (5) treatments were adopted, as in Table (1) below, with three (replicates) readings for each of the agricultural wastewater with the C.*demersum* plant, the agricultural wastewater with the L.*minor* plant, and the agricultural wastewater with aluminum sulfate.

Table 1: Overview of Treatment Methods Applied to Agricultural Wastewater

No.	Sample	treatment
1		
	T 0	Ishaqi River water (control) by conducting chemical, physical tests
2	T 1	Puncturing water before treatment by conducting chemical, physical tests
3	T 2	Treatment with aluminum sulfate $Al_{12}(SO_4)_3$ of agricultural wastewater (T1) using a test jar to choose the optimal concentration of aluminum sulfate.
4	T 3	C. demersum treatment of agricultural wastewater (T1).
5	T 4	Treatment with L. minor for agricultural wastewater (T1).

2.4 Measuring the physical and chemical properties of agricultural wastewater:

2.4.1 Turbidity (NTU): The turbidity of the water was measured using a turbidity meter (HANNA) LP2000 made by Portugal, which measures turbidity in NTU according to the method [10]. The sample was shaken well until the sample was mixed. After that, the cell designated for measurement was filled to the marked mark. Care was taken to not leave finger marks by wiping the cell with a piece of cloth

2.4.2 Dissolved Oxygen (DO): Dissolved oxygen was measured according to the method described in [11] using a device (Oxygen meter EZ D.O) made by Taiwan, device is calibrated for each reading by calibrating it with the amount of oxygen in the atmospheric air. The device's reading is 20.9%, which is the amount of oxygen in the atmospheric air, and then The reading is converted to mg/L and the dissolved oxygen in the water is measured.

2.4.3 Electrical Conductivity (EC): The electrical conductivity of the samples was measured using a Digital Conductivity device, model WTW, manufactured by the German company HANNA. The device was zeroed each time using distilled water, and the results were expressed in units of µs/cm, according to the method [12].

2.4.4 Total Hardness (TH): It was conducted according to the method [13] in estimating total hardness by using the EDTA method, where 50 ml of sample water was taken and 0.5 ml of buffer solution ($NH_3CL + NH_3OH$) was added to it, then some drops of indicator (Eriochrome black T) were added to it, so that it turned color. The violet is then washed with a solution of Na_2EDTA at a concentration of (0.05 N) until the color turns blue, and the total amount of hardness is calculated according to the following equation (1):

$$\mathbf{TH} = \frac{\text{CaCO3 equivalent weight x 1000 x standard x volume of EDTA used in deburring}}{\text{Sample volume}} \quad \mathbf{(1)}$$

2.4.5 Sodium Ion (Na^+): The sodium ion of the filtered sample was measured using a flame photometer, English model JENWAY pfp7, and after preparing standard solutions and measuring the absorbance of the sample and drawing the standard curve, the sodium concentration was found, and the result was expressed in units of mg/L.

2.4.6 phosphate (PO_4): The method [13] was adopted to estimate phosphorus, and it was measured with a Spectrophotometer device from JENWAY at a wavelength of 885 nm, and the results were expressed in mg/L.

2.4.7 Calculating the removal efficiency: Using the [14] approach, the physical and chemical characteristics were measured during the experiment time and the elimination % was determined using the aforementioned equation. The result was expressed as a percentage. as in the following equation (2):

$$\textbf{Removal efficiency \%} = \frac{initial\ concentration\left(\frac{l}{mg}\right) - final\ \ concentration\ \left(\frac{l}{mg}\right)}{initial\ concentration\left(\frac{l}{mg}\right)} \mathbf{100} \qquad \textbf{(2)}$$

2.4.8 Statistical analysis: The results were analyzed statistically by applying the statistical program SAS (statistical analysis system) and using the analysis of variance (ANOVA) test, where the arithmetic means were compared by choosing a multinomial Duncan with a probability level of $P \leq 0.05$ [15] and [16].

3. Results and discussion

3.1 Physical and chemical properties

3.1.1 Turbidity (NTU): It is noted from Figure (1) that there are differences in the turbidity values, and there were significant differences at a significant level ($P \leq 0.05$) between the treated and untreated treatments and the control, as the highest value of turbidity was recorded in the agricultural wastewater, which was in the treatment with the agricultural wastewater T1 before treatment, with a value of NTU. 48, followed by T2, which is treated with aluminum sulfate. It recorded 10.33 NTU, with a removal rate of 78.48% of the agricultural wastewater, this decrease is attributed to the fact that aluminum sulfate is a safe natural chemical and plays a major role in precipitating plankton and purifying water [17]. As for the T3 and T4 plant treatments, represented by treatment with the *C. demersal* and *Luminor* plants, the lowest value was given, which is 9.67 NTU and 16.33 NTU, with a removal efficiency of 79.85% and 65.98%, respectively. The noticeable decrease in the turbidity value in phytoremediation may be due to the adhesion and deposition of suspended materials on aquatic plants, especially the *C. demersal* plant. As mentioned, [18], water turbidity is caused by suspended and colloidal particles such as clay and silt, as well as organic and inorganic materials broken down into fine particles, in addition to microscopic organisms such as protozoa, for which plants provide an ideal filter.

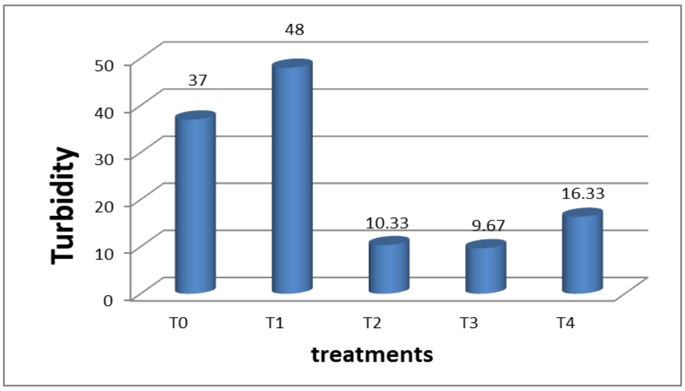

Fig. 1 Effect of treatments on the turbidity value (NTU).

3.1.2 Dissolved Oxygen (DO): The results of the statistical analysis of dissolved oxygen values showed that there were significant differences at a significant level ($P \leq 0.05$) between the treatments and through the results shown in Figure (2) for the treatment system with the control T0, which was given 5.3 mg/L, and the treatment with agricultural wastewater T1 before treatment was given a value 2.3 mg/L was the lowest value, while the plant treatment compliant with T3 and T4 recorded the highest value, reaching 7.6 mg/L and 6.76 mg/L, respectively. The increase in dissolved oxygen values recorded by T3 and T4 is a result of aquatic plants performing the process of photosynthesis, that is, consuming dissolved carbon dioxide gas and excreting dissolved oxygen gas during this process [19]. As for T2, which is treatment with aluminum sulfate, it did not show any significant difference at a significant level ($P \leq 0.05$) in the treatment system.

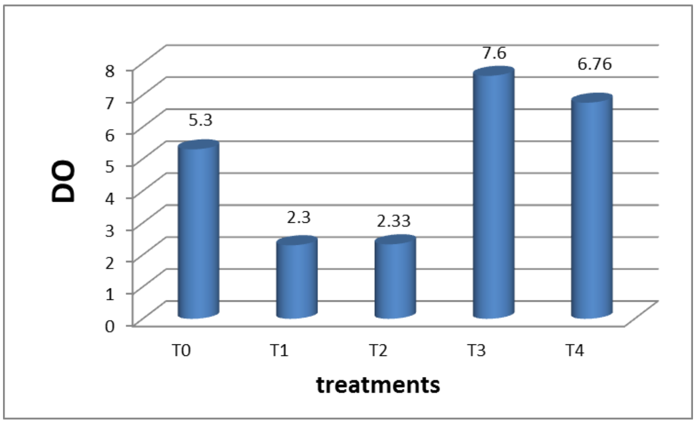

Fig. 2 Effect of parameters on the dissolved oxygen value (mg/L).

3.1.3 Electrical Conductivity (EC): Figure (3) indicates that the plant treatment represented by both the *C. demersum* T3 and the *L.minor* T4 gave efficiency in reducing electrical conductivity compared to the treatment with tap water T1 before treatment. The results showed a significant difference at a significant level ($P \leq 0.05$). It was recorded the electrical conductivity of the agricultural wastewater T1 is 2160 μs/cm before treatment. Treatment T3 was the highest in reducing electrical conductivity, as it gave a value of 1311.33 μs/cm, with a removal rate of 39.29%, followed by treatment T4, which gave 1511.67 μs/cm, with a removal efficiency of 30.02%, compared with control T0, which had a value of 460 μs/cm. This decrease in the value of electrical conductivity is due to the existence of a direct relationship between the TDS (Total dissolved substances) and the value of conductivity EC in the water [20]. As for T2, which is treatment with aluminum sulfate, it did not show any significant difference at a significant level ($P \leq 0.05$) In the agricultural wastewater treatment system.

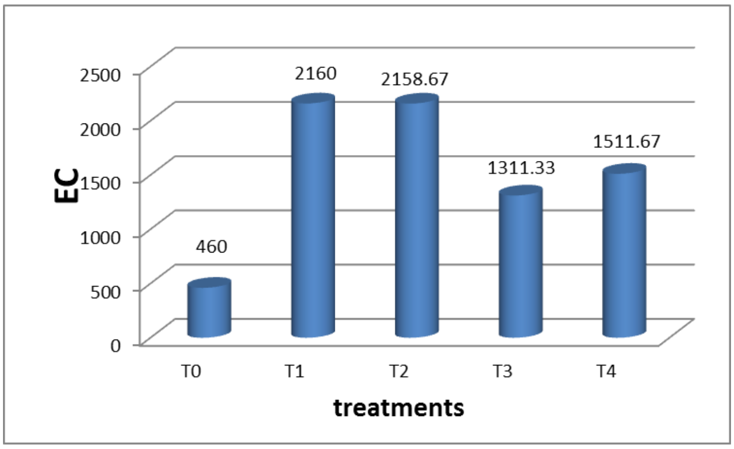

Fig. 3 Effect of treatments on the value of electrical conductivity (µs/cm).

3.1.4 Total Hardness (TH): The treatment results showed in Figure (4) that the total hardness value differed significantly, and there were significant differences at a significant level ($P \leq 0.05$) between the treated and untreated treatments and the control, as its highest value was recorded in the T1 agricultural waste water before treatment with a value of It reached 540 mg/L, while both treatment T4 and T3 recorded a noticeable and significant decrease, reaching 311.33 mg/L, with a removal rate of 42.35%, and 244 mg/L, with a removal rate of 54.81%, respectively, which differed from the control treatment T0, which recorded 125 mg/L. This decrease in total hardness is its dependence on the concentration of a group of ions, including calcium, magnesium, potassium, chloride, and sulfate ions, and the plant absorbs some of these ions to carry out metabolic processes. The magnesium ion represents one of the nutritional elements, an effective element for photosynthesis enzymes, and the basic component of chlorophyll molecules, but within its composition. A few [21], As for T2, which is treatment with aluminum sulfate, it did not show any significant difference at a significant level ($P \leq 0.05$) in the treatment system.

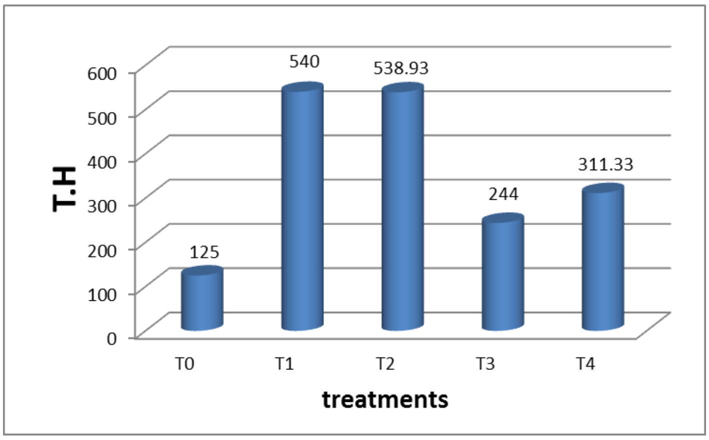

Fig. 4 Effect of treatments on the total hardness value (mg/L).

3.1.5 Sodium Ion (Na^+): The results of the treatment are shown in Figure (5) that the plant treatment was effective in reducing the value of the sodium ion compared to the control agricultural wastewater, as significant differences appeared and also showed a significant difference at a significant level of ($P \leq 0.05$). T1 before treatment gave a value of 287 mg/L, while it gave the lowest concentration of sodium ion after plant treatment with treatment T4 and T3, which amounted to 228 mg/L and 203.67 mg/L, with a removal rate of 20.56% and 29.03%, respectively, compared to the control T0, which reached a value of 20.4 mg/L. The sodium ion is one of the most important problems for irrigation water. This decrease in the value of the sodium ion in the water treated with aquatic plants may be attributed to the fact that the sodium ion tends to accumulate in plant tissues during the treatment period. As for T2, which is treated with aluminum sulfate, it did not show any significant difference at a significant level of ($P \leq 0.05$) In agricultural wastewater treatment.

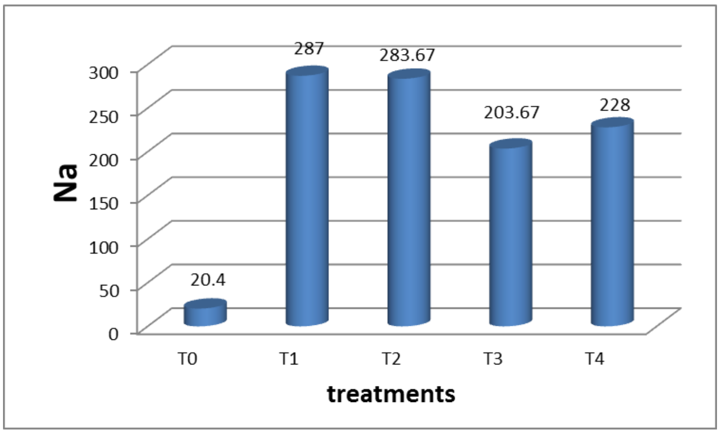

Fig. 5 Effect of treatments on sodium ions (mg/L).

3.1.6 phosphate (PO_4): The treatment results in Figure (6) indicate that there are significant differences and also showed a significant difference at a significant level of ($P \leq 0.05$) as the plant treatment achieved efficiency in removing phosphate compared to the control treatment of the agricultural wastewater, where T1 before treatment gave the highest value of 2.1 mg/L. Followed by treatment T3, which gave 0.48 mg/L with a removal rate of 77.14%, and then while treatment T4 gave a value of 0.33 mg/L and a removal rate of 84.29, while control river water T0 gave the lowest concentration of phosphate, reaching 0.3 mg/L. The reason for the decrease in phosphate concentration in plant treatment is that phosphate is considered the main component in building energy in the form of adenosine triphosphate (ATP), which in turn serves as a building block for nucleic acids, as well as in building nucleotides...etc., especially during growth. Active for plants and their maturity. Phosphate is essential for energy transfer, especially in the process of photosynthesis and respiration [22]. As for T2, which is treatment with aluminum sulfate, it did not show any significant difference at a significant level of ($P \leq 0.05$) in the treatment of agricultural wastewater.

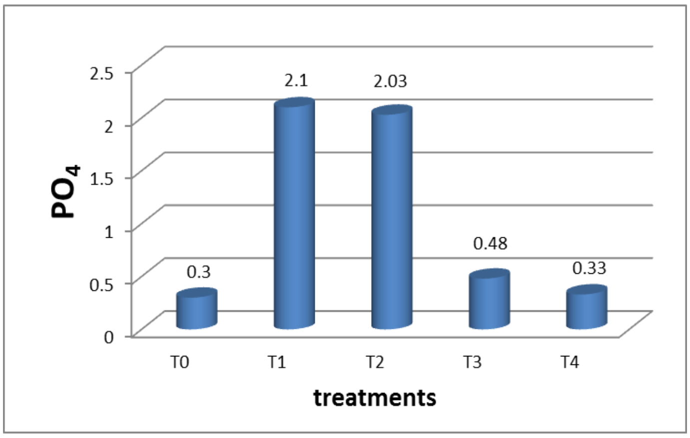

Fig. 6 Effect of treatments on the phosphate value (mg/L).

4. Conclusions

Low level of pollution for all chemical and physical characteristics in the treated agricultural wastewater, as the plant treatment represented by the C. *demersum* plant and the L. *minor* plant recorded a high efficiency in reducing it. The C. *demersum* and L. *minor* plants are also considered among the plants capable of filtering and purifying polluted water, in addition to being suitable for irrigation after treatment, especially in terms of total dissolved solids (TDS) concentrations and in terms of electrical conductivity (EC), and they were among the Iraqi and Food and Agriculture Organization specifications.

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