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EICHHORNIA CRASSIPES AS AN EFFECTIVE EXTRACTOR OF METHYLENE BLUE DYE IN NATURAL SURFACE WATER OR INDUSTRIAL WASTE EFFLUENTS

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ABSTRACT

The removal of residual dyes released from many industrial projects as effluents is of great concern on environment (e.g., Textile and Dye Industry…) especially if the dye is sustainable and lasts long time till it is biologically or photochemically degraded by time. The dye chosen in this investigation is Methylene blue [MB] (C.I 52015). Eichhornia Crassipes (EC) known as [Water Hyacinth(WH)] plants has proved to be very effective extractor of such analytes in aqueous water at normal pH,s of such surface water or at broad range of pH,s. Methylene blue has proved to be photochemically degradable(≈20%) as well as its uptake by the plant(≈80%). The solid phase of the plant (dry parts as roots or leafs) has proved to be quite efficient in removing such dyes. Results have been elucidated impressing illustrations.

Key words:- Eichhornia Crassipes(EC) ;Water hyacinth (WH) plants; Methylene Blue (MB); dye effluents; industrial wastes; dye photochemistry.

1. INTRODUCTION

Eichhornia crassipes(C.F.P. Mart) Solms-Laub. (Water Hyacinth) belongs to the family pontederiaceae, order Liliiflor (Monocotyledonous). WH or EC were used to identify this plant, but for simplicity the abbreviation WH will be used only through the whole text. It is a perennial, surface free-floating, mat-forming aquatic plant of wide distribution in the tropics and subtropics **(Zahran & Willis, 2003)** reported it as one of the neotropical or intemperate .The WH propagates both by seed germination and by vegetative means where by mature plants produce rosettes of leaves and fibrous roots at each node of the growing stem. A single plant can produce approximately 65,000 offspring during a single season. Due to this phenomenal growth rate, 1 acre (0.40 ha) of plants can conceivably produce approximately 240 kg of dry weight per day in subtropical climates which far exceeds the yield of most productive agricultural crops. The plant WH consists of roots, rhizomes, and stolons, leaves, inflorescence, flowers and fruit clusters (Fig.1).Observed flowering in U.S.A. from mid-July to November. [(5)]Noted flowering in Egypt from May to September. The pH range suitable for growth of WH is very wide **(El-Sayed, 2003; Grandi, 1981; Gopal, 1987; Woleverton, & Mc Donald, 1978; Araujo RS,1979 and Tianhua, et al., 1990)** provided that all nutrient requirements are available WH has the distinction of being called A ' Demon " Bengal terror ' Blue devil,, 'Curse of Bengal, ' Million dollar weed and a ' Cinderella of the plant world .WH was first introduced to Egypt during the rule of Khedive Tewfik between 1879 – 1892as an ornamental plant. It was cultivated in ponds of public gardens and thirty years later it had spread to many water bodies in the Nile Delta. After the construction of the Aswan High Dam, the WH problem increased considerably and it is now hard to find a canal, a stream, or a drainage system free of this weed.

The major disadvantages related to WH may be summarized as follows:-

1- Series problems in irrigation canals and open drainage systems.

2- The rate of water loss through evapotranspiration of WH was found to be 1.3 to 6 times more than evaporation from open water surface **(Tag El-Seed, 1972)**. Transpiration of WH has been reported to cause a great loss of water from the water bodies where plants grow. Calculated that the water loss in evapotranspiration through WH exceeded 2-3 times the loss from open water. It is claimed that the total water loss due to WH in the Nile and tributaries in the Sudan Republic represents one tenth of the average of the normal yield of the Nile. In the present investigation, we proved a contrary view to this claim of wide acceptance all over the previous investigators.

3- The excessive spread of WH makes navigation impossible.

4- The large accumulation of decomposing vegetation creates an odoriferous nuisance that depressing the value of waterfront properties. Fishing is affected because of the competitive advantage to low quality fish species in weed–infested water. In many cases, fish populations become exterminated when oxygen levels are depleted through respiration and decomposition of senescing vegetation.

5- WH vegetation provides a favorable habitat for mosquitos which are vectors of diseases such as malaria, encephalitis and filariasis.

There are three ways of management of WH: Mechanical manual control, chemical control, and biological control. The mechanical or manual removal of WH from the water is relatively expensive. Manual control, however, cannot cope with extensive vegetation and is hazardous in areas where the bilharzias disease occurs. Mechanically removed plants may form nuclei for future reinfestations if the plants are deposited nearby the water. At the present time, the Egyptian government is trying to control the WH invasion, mainly by mechanical collection and dumping. This method is expensive and presents a solid waste problem to get rid of the WH dumps. Much research has been conducted in efforts to create a use for dumped WH. This includes research on biogas generation **(Ganesh, et al., 2005)**., fish feed **(El-Sayed, 2003)**, and animal feed **(Grandi, 1981).** These attempts have not yet been successful in utilizing WH on an industrial scale. In most cases, the chemical control does not give lasting protection and consequently does not solve the long-term problems. It should be emphasized that chemical means of control in water should be limited as much as possible.

Ironically, the WH is also one of the most promising candidates for solving many serious problems in areas of food supply, energy requirements and water pollution control. Boyd and others have shown that vascular aquatic plants such as the WH are a possible food source for animals and humans in studies examining the amino acid, protein, caloric, and mineral nutrient content of these plants. The conversion of plant material to usable products such as compost and methane gas through anaerobic fermentation is a promising approach to the problems of depleted energy sources. The plant contains eight vitamins **(Gopal, 1987)** with amounts (mg\kg dry weight) as follows: Vitamin A 2.41, Thiamine HCl (B) 5.91, Riboflavin (B) 30.7, Pyroxidine HCL (B) 15.2, Vitamin B 0.013, Chemical Niacin 79.4, Pantothenic acid 55.6, and Vitamin E 2.06., Riboflavin (0.24 ppm and oxalic acid (0.35 mg\g on a wet weight basis).Besides the macro-elements, WH absorbs a number of micro (trace) elements, some in fairly large quantities e.g. aluminium, boron, cadmium, copper, iron lead, manganese, molybdenum, zinc **(Gopal, 1987)** .Most of the heavy metals, e.g. copper, zinc, iron, and manganese accumulate largely in the roots, very small amounts being found in the leaves **(Woleverton & Mc Donald, 1978).**

WH remove nutrients and heavy metals of obvious toxicity from sewage and sludge ponds. This indicate that WH could play a prominent role against environmental pollution **(Araujo RS & Senner, 1979)** and hazardous elements. Recently, utilization of WH in the removal of color from wastewater of textile dyeing processes was studied **(Tianhua, et al., 1990)**.The purpose of this study is to examine the ability if WH to remove dyes and dye products from industrial effluents as well as domestic waste water disposed to natural waters (like Nile water which is the main source of drinking water).

2. MATERIALS

A)-Bio-Sorbent: The plant is used either in:

(I) Living WH

Samples of WH were collected from fresh water Nile River. The samples were thoroughly washed with tap water to remove dirt and put in plastic tank containing tap water.

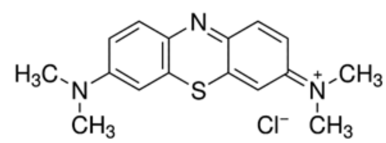
(II) Non-Living WH

After collection of fresh WH, the root ,the aerial parts (stem plus leaves) the whole plant was washed with tap water then with distilled water and then divided into two parts tops and roots and then kept on a filter paper to reduce the water content . The biomass was sun dried for 24h and then oven dried at 60^{o} C for 2h. After that it was grinded to powder form in a ball mill. The biomass was then passed through 52-mesh size screen for its application as a biomass collector of different pollutants applied in this investigation, e.g., dyes and metal ions…etc.

(Dry form which is further subdivided into aerial parts and the second part including its roots.)

B)- Dyestuffs: The dye chosen for this study is Methylene blue (C.I. 52015) which is photochemically degraded during investigations. The dye was used without further purification. Solution of 2 liter for the corresponding dye was prepared in proper concentrations. Some of its specifications are cited in the following table; table (1):

Table (1): Specifications of methylene Blue dye.

Common name	**Methylene Blue**
Molecular formula	$C_{16}H_{18}N_3ClS$
Molar mass	**319.9 g/mol**
Melting point	**100-110 °C**
structural formula	
C.I.	**52015**
λmax	**664 nm**
A 0.001 M solution	**0.32 gm in 1 L.**

C)- Equipment

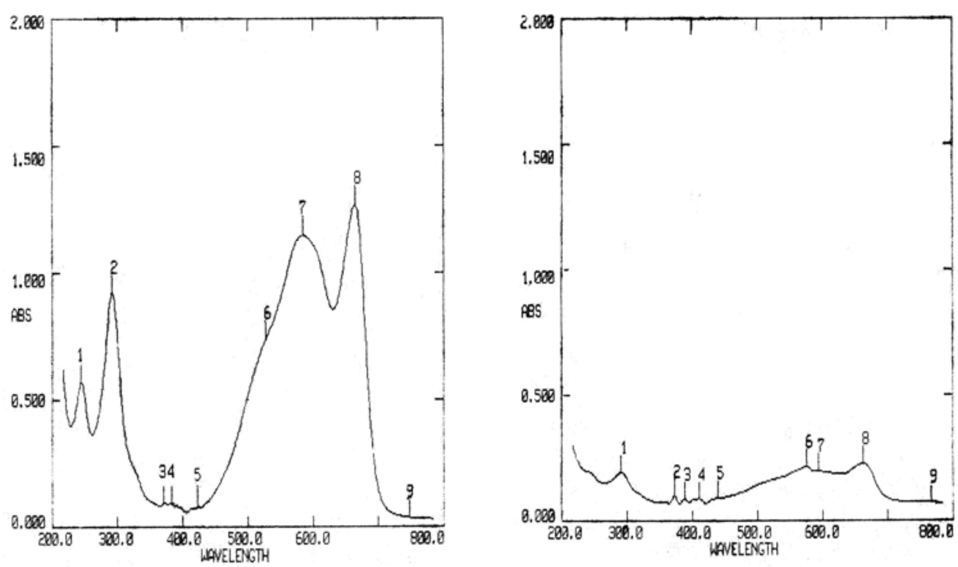
i) Water distillation apparatus: The corning mega pure 6 liter automatic water still is a compact unit, which designed to provide 6 liter per hour of ultra-high purity distilled water.
ii) Spectrophotometer: Unicam UV2-100 UV-visible spectrophotometer.
iii) pH-meter: Ion analyzer digital model 501 (Orion, U.S.A). The electrode is immersed in dilute acidic solution. The calibration of instrument is applied using different buffers near the area of measurements.
iv) Plant vegetation: The experiments were conducted in 2 liter Pyrex glass beakers. The plant is immersed in the dye solution while the second containing the same concentration of the dye free of the plant.
v) Shaker; shaking time for about 2 hrs was found quite reasonable for complete equilibration using dry plant in the corresponding batch experiments. The type of shaker used is: Heidolph Promax 2020 - Germany. RPM = 20 – 400.

3. RESULTS AND DISCUSSION

I – Living Plant

The experiments conducted on MB as a degradable dye were performed on two similar measuring flasks of this dye which has been kept either in dark or subjected to sun or diffused light. The absorbance was proved to decrease tremendously in light comparatively to the same dye kept in dark

The effect of WH plant on extraction of Methylene Blue has been studied at different concentrations of MB ([MB] $=1.5x10^{-4}$/ $1x10^{-4}$ / $0.5x1^{-4}$ M) and at different intervals. The plant shows a remarkable activity in extracting the MB dye from its solution. The degradation of the color increases with time till the solution becomes almost clear after several days. The effect of light on the degradation of the dye is shown in fig.2.

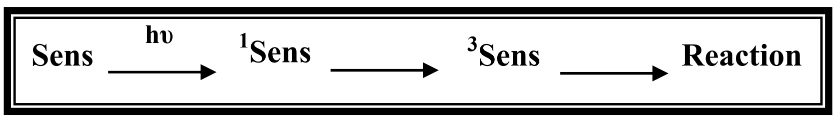


(a)Initial [MB] $_o$ **(b) After 8 day's**

Fig.2, The absorption spectrum of a fresh solution (a) of methylene blue (MB) and (b) for it after 8 days exposed to sunlight. It is quite clear the great difference in absorption spectrum, which proves the significant changes in MB due to photochemical interactions.

It becomes clear that light has a tremendous effect on the decay of MB color in solution.

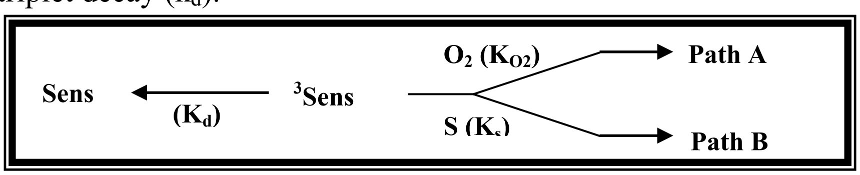
On the addition of EDTA solution in excess to the dye, the decay of color becomes of a slower rate this may be due to the formation of EDTA-complexes of higher stability than those which may be formed from MB with such ions. The sensitizing ability can be discussed conveniently in terms of the Jablonski diagram, which indicates the electronic states realizable by optical excitation. The two most important excited states from the viewpoint of sensitized chemical reactions are the first excited singlet state (S_1) and the lowest triplet state (T_1), which have quite different properties It was also stated that Photosensitized oxidation proceeded mainly through the formation of triplet sensitizer which was characterized by much longer life time than the excited singlet. The most effective sensitizers are, therefore, those that give a long-lived triplet state in high
quantum yield:



In an aerobic photo-oxidations (i.e., in presence of oxygen) there are two types of reactions in which the sensitizer triplet reacts:

a / with oxygen ; b / with substrate.

The path wayis controlled by several factors concerning the relative values of oxygen and substrate concentrations, the rates of reaction of sensitizer triplet with substrate (k_s) and with oxygen (K_{O2}), and the rate of triplet decay (k_d).



In oxygen - or air - saturated solutions, oxygen concentration is in the range of 10^{-2} to 10^{-3} M [10]. Since k_{O2} is invariably close to 10^{9} M^{-1} sec^{-1} [11], path A will predominate unless the product ks [S] is of the order of 10^{6} to 10^{7} sec^{-1}(Accordingly, even traces of oxygen will inhibit path B if k_s or S is small.

The interaction with oxygen (i.e. quenching of the triplet sensitizer) represented in Fig.4 produces singlet oxygen, which is the reactive species in this type of Oxidation. Some photo-oxidations apparently proceed via a singlet oxygen mechanism but others do not. Oxygen has two metastable singlets. With spectroscopic symmetry notations $^1\Sigma^+_g$ (37 kcal) and $^1\Delta_g$ (22 kcal). The $^1\Delta_g$ state is long-lived and survives at least 10^8 collisions with methanol in the vapour phase, whereas the $^1\Sigma^+_g$ state survives no more than 10 collisions under the same conditions.

Table (2): Electronic configurations of oxygen molecule**.**

State	Occupancy of highest orbitals		Energy
$^1\Sigma^+_g$	↑	↓	37 Kcal
$^1\Delta_g$	↑↓	—	22 Kcal
$^3\Sigma^-_g$	↑	↑	Ground state

Table (3): The absorbance of MB and MB +Fe at different concentrations.

Concn		$2x10^{-5}$	$1x10^{-5}$	$5x10^{-6}$	$3.3x10^{-6}$	$2.5x10^{-6}$
A	[MB]	2.234	1.310	0.719	0.471	0.347
	[MB+Fe]	2.281	1.330	0.732	0.484	0.358

We may say that the absorbance of MB in presence or absence of Fe^{3+} ions is almost the same at the specified concentration range. The last three results are almost completely obedient to Beer's law. The concentrations of the dye chosen during experiments falls within this range. The dye solution with metal ion was prepared as follows:-
4 ml of Fe^{+3} from stock $Fe_2 (SO_4)_3$ 0.01 M + 200 ml of MB from stock 0.001 M. Then complete to 2000 ml by dist water, the concentration of M.B is 1 x 10^{-4} & [Fe^{+3}] as ferric sulfate is $2x10^{-5}$ M. For Spector Chemical analysis, the solution should be diluted 20 times to obey Beer's law where the initial concentration measured is $5x10^{-6}$ M (A= 0.732).

Table(4): Effec of time on absorbance,degradation and the rate of evapouration in the presence and absence of the plant as well as Fe.

(Room temperature=23 ^{o}C and water is 20 ^{o}C)

It is clear that the total degradation of the dye is attained within almost several days (4-5 days) in the presence of the plant. While the instantaneous effect of the light never exceeds ≈ 30%.

It is very interesting from this table that the rate of evaporation due to the presence of the plant is the difference between the volum**es** of water evaporated from the beaker containing plant minus the blank (free from plant). This is almost equal to ≈ 28%.

A very simple observation has been found that the temperature of ambient water beneath the plant mat is lower than the water directly exposed to sunlight with an average of ≈ 7 ^{o}C. This will decrease the rate of water vaporization and should be subtracted from the higher rate of vaporization due to the plant itself. Nobody else in any similar investigation has mentioned such effect. In our study, we performed several experiments of very simple nature by measuring the temperature of the ambient water in Nile River in a naked area from the plant and another area covered completely with the plant (see next table).

Table (5) .Temperature of River Nile Stream at noon and at afternoon

Temperature / Time	Temp under the plant	Temp of Nile river	Temp of air
At noon(hr: 12.5)	19 ^{o}C	26 ^{o}C	29 ^{o}C
Afternoon (hr: 3)	21 ^{o}C	28 ^{o}C	32 ^{o}C

It is quite clear that during the daytime where the sun is bright and the climate is hot near the noon and after noon time, a difference of at least 7 ^{o}C equivalent to a difference in standard vapor pressures at 26 and 19 ^{o}C, respectively. At noon time, $\Delta p = 25.21 - 16.48 = 8.73$ mm Hg/ $cm^2 \equiv$ 118.73 cm^3 H_2O/ cm^2. If we consider that the relative humidity in average is 40% of standard vapor pressures, then the final value in this case would be 47.92 cm3 H_2O/ cm^2 . While afternoon time the difference = 28.35 – 18.65 = 9.70 mm Hg /cm^2 ≡131.92 cm^3 H_2O/ cm^2 . In a similar way this corresponds to 52.77 cm^3 H_2O/ cm^2 . Thus curtail in the rate of evaporated water is very impressive and of course it is in favor of our stand point to WH not against it as it is previously considered in all manuscripts dealing with WH **(Zahran & Willis, 2003)**.

This great curtail in V.P. H_2O would be considered as a strong proof against the opinion that WH is a great evaporator of H_2O from the river Nile and its streams. I wonder if we make a comparison between other plants, e.g. Rice and Maize where leaves are widely spread and of lager areas and distributed in open atmosphere of a soil land. The comparison would be in favor of W.H.

Another important fact, the plant WH constitutes a blanket on H_2O streams through the strong adhesion and penetration of the roots that an adult person can walk on H_2O surface through the plant without drainage. This means that the plant prevent direct evaporation from water covered by the plant and the evaporation of H_2O will be restricted to the perspiration process.

This simple facts have never been mentioned before in this way in any previous study.

Table (6): Effect of time on % of rate of evaporation of each of M.B. and M.B. + Fe

Time /day		1st day	2nd day	3rd day	4th day	5th day	Mean/5days
M.B	%Rate of evap.	25%	30%	31%	30%	28%	28%
M.B+Fe	%Rate of evap.	22%	50%	30%	15%	18%	27%

(II) Dry plant

Another series of batch experiments using the dry form for extracting MB where the concentration of MB is 1 x 10^{-5} M and the amount of dry plant is 0.1 g. The batch experiment was held as follow: 0.1 gm of dry green leaves (Aerial part or roots) + 20 ml MB concentration ($1x10^{-5}$). Then shaking for 2h till complete equilibration. The initial concentration of MB was held constant as $1x10^{-5}$ M (A = 1.301) during the batch experiments. The extraction of Dyes has proved to be very effective in extracting the selected dye as it is clear from the next table.

It has been observed that the solid stationary phase of the dry plant in the case of aerial part is divided into two layers one floating on water while the rest is settled in bottom, but in case of root phase it is settled at once in the form of one layer. For the same amount of solid stationary phases, it was found that the aerial part extracts more than the corresponding root.

3.1. PH effect:

The effect of pH in the case of living plant in this study is superficial , since our study is completely confined to river Nile whose pH is almost neutral to very slightly basic(>7 - < 8.5).

The effect of hydrogen ion concentration on the extraction of MB by the aerial part of the dried plant has been examined. An aliquot of the aqueous working solution of the dye's(25 ml) shacked for 2hr with 0.1 gm of aerial part at various pH's .It is interesting that the rate of dye recovery is almost constant over a wide range of pH,s (2 up to 9) as it is clear from the next table. This means that the dry plant is an efficient extractor allover a broad range of pH,s.

Table (7): Effect of pH on extraction%

pH	1.94	2.63	4.27	6.44	8.81	11.23
Extraction %	85	90	91	87	85	82

3.2. The shaking time effect:

Aliquots (20 cm^3) of $1x10^{-5}$M MB (A=1.30) was introduced to closely tight flasks where it is equipped with 0.1 g of the aerial part at the optimum pH tested before. Different shaking times were tested for the extraction of M.B as it follow:-

Table (8): Effect of shaking times on the extraction % of M.B

Shaking time	30 min	60 min	90 min	120 min	150 min
Extraction %	81.9	83	86	91	91.1

It is clear that 2hrs is quite sufficient for complete equilibration.

3.2. Different sorbents effect:

(Initial concentration in bottle is $1x10^{-5}$ M; A = 1.301).

A comparative study between different extractors among which WH has proved the excellent nature of it's among many other solid stationary phases. The plant after dryness has been divided into two main parts: the upper part which comprises the leaves, flowers and inflorescence was called (aerial part) while the second is the (roots). Other well known solid state stationary phases (e.g., Silica gel or alumina) as well as bio sorbent (Corchorus olitorus) were tested in this investigation.

Table (9):Relation between stationary phase and extraction%

Stationary phase	Extraction %
Aerial part	91
Roots	81
Whole Plant	83
Cellulose	75
Foam	69
Marbila	85
Corchorus olitorus(dry Molokhia)	81
Silica gel (70-150mish size)100-200µm woelm pharma (Germany)	97
Neutral alumina Activity grade I	63
Aluminium oxide (acidic)	43
Aluminium oxide (Basic)	81

The equilibration studies performed were done at the optimum Conditions of shaking time of 2h and the pH of a solution of MB in distilled water. The pH of distilled water is mildly acidic = 5.6 while it equals 4.8 for the studied initial concentration $1x10^{-5}$M MB.

The extraction of MB in different kinds of water (20 cm^3 dist water –tap water – river Nile – sea – underground water) adjusted to the optimum pH, shaking time with 0.1 gm of biosrbent WH was found almost invariably constant as it is clear from the following table.

Table (10): Effect of water source on extractability

Different water	Dist water	Tap water	River Nile	Water Sea	Under ground
%	91	88	87	85	89

Hundred articles dealing with WH plant and partially to its solid stationary powder were proved very fruitful in extracting many pollutants in different forms either as metal ions and it's radioactive isotopes, waste water, fertilizers, organic compounds, dyes…….. Etc. This means that it is well applied for the removal of very hazardous pollutants in our environment. This fact should be considered strongly on evaluating all the criterions concerning WH. This outstanding characters of the plant and its dry form may be understood on investigating the surface area of the plant and its cellular structure especially in the aerial part. The surface areas were determined by the dye sorption method for the roots and aerial parts of the plant. An earlier standard BET surface area measurement of the root material indicated a surface area of $150 m^2/g$ although it was not certain that equilibrium had been reached in the system. The next two Figures show scanning electron micrographs of *WH* roots and stems, respectively. From observing such micrographs it is apparent that these parts of the plant have an extremely porous structure which must account in large part for their very large surface areas **(Schneider, et al., 1995)**

3.3.Surface areas of *WH* individual parts

Biomass	*WH*, roots	*WH*, aerial part	*WH*, whole plant
Specific surface area (m2/gm)	243	223	231

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الملخص العربى

اثبت ورد النيل انـه مستخلص فعـال لصبغة ازرق المثيلين (C.I 52015) من المياه الملوثـة بـه سواء استخدم كنبـات حـى ام بعد تجفيف الجذور او الاوراق كما تم اضـافة احدى المميزات الى نبات ورد النيل موثقة بالحسابات العلمية على انه يحمى سطح النيل والقنوات من اشعة الشمس المباشرة وبالتالى تقل عملية التبخر واثبتنا ان درجة حرارة المياه تحت سطح النبات اقل بحوالى سبع درجات مئوية عن المياه المحيطة.