ENVIRONMENTAL MONITORING AND PHYCOREMIDATION OF POLLUTION IN IBRAHEMIA CANAL AND SOME DRAINAGES IN MINIA GOVERNORATE

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7. SUMMARY

The present study aimed to determine variability in phytoplankton distribution, abundance and community structure in relation to physico-chemical properties in various fresh water ecosystem (polluted and non-polluted sites at Minia-Egypt), and to study the effect of various concentrations of heavy metals (Cu^{2+} and Fe^{3+}) on the growth and some metabolites of some isolated algae (*Chlorella ellipsoidea* and *Scenedesmus subsicatus*). As well as, to assess the phycoremediation potential of *Chlorella ellipsoidea* and *Scenedesmus subsicatus* for Cu^{2+} and Fe^{3+} ions using the Langmuir, Freundlish, Temkin and Dubinin–Radushkevich isotherm constants.

This study showed the following results:

I- Distribution and diversity of microalgae:

1- Water samples from fourteen sites were collected seasonally from July 2017 to May 2018.

2- The physico-chemical analysis of water samples showed that, water temperature has been found to vary between 19 and 34^{o}C. The highest pH value was recorded during autumn at site 4 (Tuna drain) and the lowest was recorded during summer at site 11 (Al-Muheit drain). The electrical conductivity and total dissolved solids fluctuated within 247 µmho.cm^{-1} and

176.1 mg/L during summer at site 9 and 1145 µmho.cm^{-1}, and 816.4 mg/L during winter at site 10, respectively. The content of total alkalinity ranged between 107.5 mg/L at site 5 during summer and 385 mg/L at site 11 during winter. Nitrate- nitrogen showed the maximum content during winter at site 7, whereas the minimum content was recorded in summer at site 12. Phosphate-phosphorus was fluctuated within 0.05 mg/L at site 8 and 9 to 22.9 mg/L at site 11 during summer and winter, respectively. Content of chloride in the water samples ranged between 35.5 mg/L at site 5 in summer and 230.5 mg/L at site 10 in autumn and winter. On the other hand, the high content of sodium was recorded at site 3 in spring while, the lowest content was recorded at site 2 and 5 in summer. Potassium concentration was the highest in winter at site 11 (Al-Muheit Drain) and the lowest in summer at site 7 (Kab-kab Drain). Calcium content was seasonally ranged between 116 mg/L at site 7 and 31.9 mg/L at site 2 during summer and autumn, respectively. Whereas, the maximum value of magnesium was at site 10 and the minimum was recorded at site 9 in winter and summer, respectively. The highest value of dissolved oxygen was at site 10 in autumn and was not detected at site 11 in all seasons. The maximum value of biological oxygen demand was at site 10 in autumn, and was not detected at site 11 in all seasons. The content of ammonia was only detected at site 11 in summer, autumn, winter and spring. Sulfate-sulfur concentration ranged between 0.23 mg/L during winter at site 9 and 2.4 mg/L during summer at site 13 and 14. The turbidity was high at site 11 and the low value was recorded at site 14 in autumn and winter, respectively.

3- The maximum algal biomass (2803.5 µg/L) was recorded at site 12 in spring; and the minimum (26.7 µg/L) was recorded at site 9 and site 10 in winter.

4- In total, 178 algal species were identified, of which 93 species (20 genera) belong to Bacillariophyceae, 56 species (28 genera) belong to Chlorophyceae, 12 species (9 genera) belong to Cyanophyceae, 9 species (2 genera) belong to Euglenophyceae, 6 species (2 genera) belong to Charophyceae and 2 species (1 genus) belong to Dinophyceae.

5- Bacillariophyceae was the most dominant algal group (52.25%) during the four seasons, followed by Chlorophyceae (31.46%), Cyanophyceae (6.74%), Euglenophyceae (5.06%), Charophyceae (3.37%) and Dinophyceae (1.12%).

6- The highest number of microalgal species was 80 species recorded at site 3 in spring, while the lowest total number was recorded at site 1 (22 species) in summer.

7- The highest total algal count expressed as individuals was 50120 ind. $x10^3$ L^{-1} that recorded at site 13 during autumn, but the lowest one (2700 ind. $x10^3$ L^{-1}) was recorded at site 1 in summer.

8- *Oscillatoria limosa*, *Scenedesmus quadricauda*, *Cyclotella striata*, *Euglena proxima*, *Staurastrum chaetoceras* and *Peridinium lomnicki* were the most abundant species.

9- The diversity indices such as Margalef's Index (d'), Shannon-Wiener diversity (H', $\log_e$ based), Pielou's evenness (J'), Fisher's Index (α), Simpson Dominance index (D), Simpson's Diversity Index (1-D) and Berger-Parker index (d) were studied based on the abundance of algae

10- Margalef's index showed that phytoplankton diversity was highest (8.4) at site 3 in spring, while the least diversity (2.66) was recorded at site 1 in summer. The maximum value of Pielou's Evenness index (0.88) was estimated at site 10 in spring, whereas the minimum (0.45) was estimated at site 5 and site 9 in winter. The parametric index of diversity (Fisher's index) was recorded its highest value at site 10 (11.89) in spring, while it recorded its lowest value (3.28) at site 1 in summer. The Shannon-Wiener diversity index ranged between 1.85 at site 9 in autumn and 3.71 at site 10 in spring. On the other hand, Simpson's dominance index was ranged from 0.038 at site 10 in spring to 0.295 at site 9 in winter. The highest value of Simpson's index of diversity (0.96) was recorded at site 10 in spring, while the less value was 0.71 at site 9 in winter. The highest value of Berger-Parker index (0.51) was recorded at site 9 in winter and the lowest (0.07) was recorded at site 10 in spring.

11- PERMANOVA revealed that the spatial variation was the most important factor that induced the variation in assemblages of algae ($p=0.001$), followed by the season that able to show the difference between algal species.

12- Water temperature, total alkalinity, nitrate and phosphate were the highest abiotic variables correlated with variation in algal composition.

II- Effect of various concentrations of Cu^{2+} and Fe^{3+} ions on the growth and metabolites of *Chlorella ellipsoidea* and *Scenedesmus subsicatus*

a. Copper ions:

1- Chl. *a* of *Ch. ellipsoidea* and dry weight of *Ch. ellipsoidea* and *Sc. subsicatus* were decreased with increasing the concentrations of Cu^{2+} ions.

2- Soluble, insoluble and total carbohydrate contents of *Ch. ellipsoidea* were decreased by increasing the concentrations of copper.

3- The treatment of *Sc. subsicatus* by Cu^{2+} ions caused increment in all carbohydrate fractions.

4- The low concentration (0.1 mgl^{-1}) of copper ions leads to an increase in the insoluble and total proteins contents of *Ch. ellipsoidea*. However, a significant decrease in the insoluble and total proteins contents was observed by the treatment of *Sc. subsicatus* with different concentrations of copper.

5- The highest content of the free amino acids was recorded at 0.5 and 1 mgl^{-1} of copper in *Ch. ellipsoidea* and *Sc. subsicatus,* respectively.

6- The total lipid contents were decreased by the treatment of the tested algae with different concentrations of copper ions.

b. Ferric ions:

1- Treatment of *Ch. ellipsoidea* and *Sc. subsicatus* with different concentrations of ferric ions caused an increase in chlorophyll *a* content However, the dry weight of *Ch. ellipsoidea* and *Sc. subsicatus* were decreased with increasing the concentrations of ferric ions**.**

2- Treatment of *Ch. ellipsoidea* with various ferric ions concentrations caused a decrease in soluble, insoluble and total carbohydrates.

3- The high value of soluble, insoluble and total proteins was obtained at 2 mgl^{-1} of ferric ions by *Ch. ellipsoidea*. On the other side, the maximum content of insoluble and total proteins of *Sc. subsicatus* was recorded at 0.2 mgl^{-1} of ferric ions concentration.

4- The high value of free amino acid content was obtained by the control culture of *Ch. ellipsoidea* and it increased in *Sc. subsicatus* at 1 mgl^{-1} of ferric ions.

5- The total lipid contents were increased by the treatment of *Ch. ellipsoidea* with various concentrations of ferric ions with compared to control while, inverse trend was observed with *Sc. subsicatus*.

III- Phycoremediation and sorption isotherms of Cu^{2+} and Fe^{3+} ions by *Chlorella ellipsoidea* and *Scenedesmus subsicatus*

1- Results of metal uptake indicated that *Scenedesmus subsicatus* was an efficient biosorbent to remove Cu^{+2} and Fe^{3+} than *Chlorella ellipsoidea* from the culture media.

2- The maximum reduction for Cu^{2+} and Fe^{3+} by *Chlorella ellipsoidea* was recorded at 0.1 and 1 mgl^{-1} (68.66% and 65.79%), respectively; while in *Scenedesmus subsicatus* exhibited a maximum reduction at 0.1 mgl^{-1} (59.52%) for Cu^{2+} and Fe^{3+} (73.06%).

3- Estimation of the parameters of Langmuir, Freundlich, Temkin and Dubinin–Radushkevich models enabled us to compare the properties of metal binding of *Chlorella ellipsoidea* and *Scenedesmus subsicatus*.

4- Langmuir model data revealed that *Chlorella ellipsoidea* is more tolerant to the toxicity of Fe^{3+} than Cu^{2+}. While, the sensitivity of *Scenedesmus subsicatus* to Fe^{3+} is more than Cu^{2+}.

5- Dubinin–Radushkevich isotherm suggesting that the adsorption mechanism was physical in nature.

6- The data suggested that the Langmuir, Freundlich, Temkin and D-R models were well adapted to describe the *Ch. ellipsoidea* and *Sc. subsicatus* adsorption isotherm of Cu^{2+}. However, The Freundlich and

Temkin model does not fit well with the experimental data of sorption isotherm of Fe^{3+} for *Ch. ellipsoidea and Sc. subsicatus*, respectively.

7- FTIR analysis confirmed the changes in the functional groups and the properties of algal biosorbent surface as a result of heavy metal stress. FTIR reported the role of O–H (hydroxyl), N–H (amide), CHO (aldehyde), C=O (carbonyl), carboxyl (C-O-O), aromatics (C-C), aliphatic amines (C-N) and alkyl halides (C-Br) or (C-Cl) groups in chelating of metal ions.