Water quality assessment of Qarun Lake and heavy metals decontamination from its drains using nanocomposites

M E Goher¹, W M A El-Rouby², S I El-Dek²*, S M El-Sayed¹ and S G Noaemy¹²

¹ Chemistry Lab., Fresh water and Lakes division, NIOF, National Institute of Oceanography and Fisheries, Egypt.
² Materials Science and Nanotechnology Department, Faculty of Postgraduate Studies for Advanced Sciences, (PSAS), Beni-Suef University, Beni-Suef, Egypt.

* Corresponding author: e-mail:didi5550000@gmail.com, samaa@psas.bsu.edu.eg (S.I.ELDek)

Abstract. Qarun Lake is one of the most important lakes in Egypt; it is the shrunken remnant of Moeris Lake. It is a closed ecosystem represented as a tank for discharged agricultural wastewater of El-Fayoum province. To assess the quality of the lake water for fishing and aquatic life utilization, Oregon water quality and metal pollution indices are computed. Based on the obtained results, water of the Qarun Lake is classified as very poor for the fishing utilization, where water quality index changed from 17.05 to 67.4 at the different stations. The metal indices; Pollution index (PI) and metal index (MI) showed that Qarun Lake water undergoes from a several grade of contamination for usage of aquatic life because of the enormous amount of wastes that discharging into the lake. Novel synthesized alginate nanocomposites (alginate, chitosan-alginate, and LDH-alginate and LDH-chitosan-alginate beads) were applied to remove heavy metal such as (Cd²⁺, Cu²⁺, Cr⁶⁺, Mn²⁺, Fe²⁺, Ni²⁺, Pb²⁺, and Zn²⁺) from different wastewater discharging into Qarun Lake. LDH-chitosan-alginate beads the exhibited the maximum removal efficiency that varied between 92.253 and 98.833 % for Cr⁶⁺ and Fe²⁺, respectively; in contrast, the alginate beads recorded the lowest one. The study indicated that the nanocomposite adsorbents, especially, LDH-chitosan-alginate beads are an effective substance for metal removal from different wastewater.

Keywords: Alginate nanocomposite beads; Heavy metal removal; Qarun Lake; Pollution index; Metal index; Water quality index.

1. Introduction

Water is an essential substance on which the life depends. Where there is water there is life. Only 0.3% of the freshwater on Earth is consisted of lakes, river systems and reservoirs that included the greatest available water source to satisfy life requirements in our daily lives [1]. On the other hand, Lakes are integrators and mirrors for the effects of climate change and human activity on watersheds, airsheds, and other landscape components. Qarun Lake is a closed ecosystem, receives annually about 400 million cubic meters of drainage water through 12 drains of which ‘El-Bats’ and ‘El-Wadi’ are the main drains that transfer most of the wastewater into the lake. The minor drains were recently attached with a huge channel; namely Dayer El-Birka Drain, which transport a lot of wastewater to the lake by pumping. The Egyptian company of salts and Minerals (EMISAL) was built on its coast to extract salts and minerals [2]. The water level in the lake depends on the balance between the inflow of drainage water coming from the cultivated land of Fayoum Province [3] and evaporation rate.
In recent years, the aquatic environment and related issues have been a main concern of the public because most of our ecological water systems are being continuously contaminated. The existence of harmful organic compounds in water supplies and in discharged wastewater is mainly because of the contribution of chemical industries, power plants, landfills, and agricultural sources. Surface runoff may also participate [4]. The result of the poorly water quality affected all living organisms health of an aquatic system [5].

As wastewater discharged without effective treatment into water bodies, hazardous severe effects to environment and ecosystem are increased [6] according to the elevation of heavy metal in waters and sediments causing the destruction of entire aquatic life [7]. Exposing fishes to the high level of trace elements in the polluted aquatic system make and force them to take up metals directly from the environment. This happened through their blood and so with contact with their organs and tissues and accumulated to different degrees [8].

In the past decades, wastewater was treated using traditional treatment methods. There are several treatment processes were available for remediation of industrial wastewater such as biological treatment, coagulation/flocculation, ozone treatment, oxidation, ion exchange, adsorption and photocatalytic degradation [9]. Nanomaterials have facilitated to be applicable in water wastewater treatment [10,11]. The recent advantage of its usage in wastewater remediation usually as it has a higher density of active sites per unit mass. This is because of their larger specific surface area as well as nanomaterials have a great surface free energy. Consequently, it enhanced surface reactivity. By utilizing the size-dependent effects advantage, the current wastewater treatment process could be greatly improved via entering nanomaterials into the system [11]. Abd el Moaty [12] synthesized Co–Fe LDH using the ball milling method that used as an adsorbent for the removal of Cd$^{2+}$ ions from aqueous solutions. That demonstrated 95% Cd$^{2+}$ removal at pH 9 and 6 hrs. which could be applied in wastewater treatment characterized by a high efficiency and low cost. Mahmoud [13] used Novel adsorbent Ti–Fe chitosan LDH intercalate with the nitrate ions that utilized in removing Cd$^{2+}$, PO$_4^{3-}$, and benzoquinone from wastewater in single and multiple solutions with agreeable results compared with the previous studies like Moaty [14]. Also, the fabricated LDH showed moderated antimicrobial potency with MIC values ranging from 62.5 to 700 μg/mL as antibacterial agents [13].

The main objective of the current study to evaluate the quality of Qarun Lake water due to the effect of drains wastewater discharging into the lake. In addition, to assess the efficiency of our synthesized nanocomposites for the removal of trace metals from the different wastewaters.

2. Materials and methods

2.1. Study area

Lake Qarun is a remnant of "the historic Lake Moreis" and was originally a fresh water lake. It is a general tank for agricultural wastewater of El Fayoum province. Its surface area is about 243 km$^2$ with an irregular shape of about 40 Km length and 6.7 Km maximum width, mean depth 4 m and a volume about 1 Billion m$^3$ and it lies in the arid zone, so it is considered as a tropical lake [15]. The lake is located between longitudes of 30° 24′ & 30° 49′ E and latitude of 29° 24′ & 29° 33′ N [16]; latitudes at 43-44 m below the sea level. The lake received its water from agriculture waste of El Fayoum province via El-Wadi and El-Bats drains as well as a group of the minor drains that are collected together in Dayer El Birka Drain, the pump station transfer the wastewater from Dayer El Birka Darin into Qarun Lake [17].

2.2. Samples Collection

Six stations were selected to cover the area under investigation beside three main drains; El-Bats, El-Pump station and El-Wadi drains (Figure 1 and Table 1)
Table 1: Details, longitude and latitude of the sampling locations at Qarun Lake.

| Code | Name                                      | Latitude (N)       | Longitude (E)       |
|------|-------------------------------------------|--------------------|---------------------|
| Q1   | In the far eastern side, in front of El-Bats Drain | 29° 30´ 55˝       | 30° 48´ 21˝         |
| Q2   | In the eastern side, in front of pump station outlet | 29° 29´ 35˝       | 30° 46´ 45˝         |
| Q3   | In the middle sector,                      | 29° 30´ 05˝       | 30° 43´ 05˝         |
| Q4   | In the middle sector, in front Emisal Company. | 29° 28´ 55˝       | 30° 41´ 17˝         |
| Q5   | In front of El-Wadi Drain.                 | 29° 28´ 15˝       | 30° 39´ 038˝        |
| Q6   | In the western sector,                     | 29° 26´ 06˝       | 30° 37´ 32˝         |

Figure 1. Map showing sample locations along Qarun Lake.

2.3. Methodology of water parameters evaluation

pH, Electrical conductivity (EC), and water temperature were measured in-situ using hydro-lab model Orion Research Ion Analyzer 399A, and transparency was estimated via the Secchi disk (diameter 30 cm). Water samples were kept in 2-L polyethylene bottles in an icebox to analyze later in the laboratory. The methods of water analyses were done according to APHA, [16]. Total heavy metals were determined after digestion by conc. HNO₃ using the GBC atomic absorption reader model Savant AA-AAS with GF 5000 graphite furnace.

2.4. Statistics

One-way ANOVA was examined through the Excel-Stat software to analyze the spatial and temporal variations; where p <0.05 and p <0.01 were taken for significance and highly significant levels, respectively. The correlations coefficients (r) between the measured parameters were calculated.

2.5. Oregon water quality index (OWQI).

The quality of Qarun lake water was evaluated according to The Oregon Water Quality Index. The OWQI was computed according to Cude [17] as in equation (1)

\[ WQI = \left( \frac{n}{\sum_{i=1}^{n} \frac{1}{S_i^2}} \right)^{1/2} \]  

(1)
Where, (WQI) defined as the water quality index result, (n) refer to the number of sub-indices and $S_i$ is the sub-index i. the details of calculation of sub-index for each parameter were shown in Cude data [18].

2.6. Metal quality indices

Two different quality indices are used to evaluate the metal contamination of Qarun lake water.

2.6.1. Pollution Index (PI)

It is based on individual metal calculations and categorized to five classes according to equation (2) [19]

$$P_I = \left( \frac{\left( \frac{C_i}{S_i} \right)_{max}^2 + \left( \frac{C_i}{S_i} \right)_{min}^2}{2} \right)^{1/2}$$

(2)

2.6.2. Metal Index (MI)

It is based on a total trend evaluation of the present status. Elevate concentration of metals as comparing to its respective MAC value, resulted in a worse impact on water quality. As, MI value more than unity is the warning limit [20]. According to Tamasi and Cini [21], the MI is calculated by the equation (3).

$$MI = \sum_{i=1}^{N} \frac{C_i}{(MAC)_i}$$

(3)

Where, $C_i$: is the concentration of each element and MAC: refer to maximum allowable concentration.

2.7. Metal removal with synthesized adsorbents nanocomposites

Four synthesized nanocomposites (alginate, chitosan-alginate, and Ni-AL-LDH-alginate and Ni-Al-LDH-chitosan alginate beads (that were discussed in details in El-Rouby et al., [22]), were assessed to remove the metals from the different wastes that discharge into Qarun Lake.

The treatment process was done for the wastewater by two ways, the first one was achieved to eliminate the metals from the raw wastewater at ambient temperature and normal pH (7.68, 754 and 7.85 for El-Bats, El-Wadi and pump station wastewater, respectively), using 2g/l prepared nanocomposite beads and 300 rpm agitation speed for 2 h.

In the second way, 10 times concentrated samples were treated with the synthesized nanocomposites. For the concentrated samples, mix well 2000 ml in a beaker on a hot plate, add 10 ml of conc. HNO$_3$ then slow boil, and evaporate, till the lowest volume possible 200 ml and adjust pH using 1N NaOH. The metal removal of the waste was processed at ambient temperature using 2g/l prepared nanocomposite beads and 300 rpm agitation speed for 2 h.

Generally, The concentration of studied metals (Cu$^{2+}$, Cr$^{6+}$, Cd$^{2+}$, Fe$^{2+}$, Ni$^{2+}$, Mn$^{2+}$, Pb$^{2+}$ and Zn$^{2+}$) was examined in the different wastewater before and after the removal process using atomic absorption spectroscopy (Savant AA AAS with GF 5000 Graphite Furnace).

3. Results and discussion

The standard deviations, mean values, and ranges of the obtained results are presented in tables 2 & 3.

3.1. Physical characteristics

Temperature is an important factor in the aquatic environment since it affects directly or indirectly not only on the survival and distribution of the aquatic species at different stage of life, but also on their development, growth rate, activity, reproduction and make it susceptibility to many diseases [23]. It ranged between the lowest value 15.40 °C during winter and the highest one 30.50 °C during summer with highly temporal significant difference ($p<0.01$). The variation in water temperature depends
mainly on the climatic conditions, sampling times, the number of sunshine hours and affected by specific characteristics of water environment such as turbidity, wind force, plant cover and humidity [24]. Temperature is positively correlated (n=24, P<0.05) with BOD (r=0.51), While it is negative correlated (n=24, P<0.01) with COD (r=-0.85).

Water transparency evaluates the depth of the photic zone and thus affects the lower limit of light penetration that influences the primary productivity of a lake. Plankton and suspended particles reduce transparency in natural waters. Transparency was fluctuated between 20 and 100 cm with spatial significant difference (p<0.01). Generally, Qarun Lake is characterized by water turbidity due to the deteriorating effect of El-Bats and El-Wadi drains [25]. The sites in front of the drains exhibited the lowest transparency values. On the other hand, the western part of the lake exhibited the highest values of transparency as confirmed by Fishar et al [26]. Transparency is a high negatively correlated (n=24, P<0.01) with TSS (r=-0.61), Fe²⁺ (r=-0.66), Mn²⁺ (r=-0.77), Ni²⁺ (r=-0.60), Cr⁶⁺ (r=-0.59), NH₄ (r=-0.81), NO₂ (r=-0.73) and NO₃ (r=-0.72), TP (r=-0.79) and PO₄ (r=-0.72).

Water electrical conductivity (EC) is the ability of water to conduct an electrical current, and the dissolved ions are the conductors [27]. Where the higher value of conductivity, the greater ions and higher dissolved solids. In Qarun Lake water, EC was fluctuated between 17.09 and 47.24 ms/cm with spatial significant difference (p<0.01). The stations that are facing the drains (El-Bats, pump station and El-Wadi drains) exhibited the lowest E.C values than other lake station. This may be related to the direct dilution effect of the drainage water. E.C is a high positively correlated (n=24, P<0.01) with TS (r=0.98), Salinity (r=0.98) as agreed with many authors [24]. While, it is negatively correlated with high significance (n=24, P<0.01) with TSS (r=-0.66) and NH₄ (r=-0.81).

Total solids denote to any substance either suspended (TSS) or dissolved (TDS) in water. It described the chemical contents of Lake water to evaluate edaphic relationships of aquatic environment that affected productivity within the aquatic system [23]. TS, TDS, and TSS in Qarun Lake varied in the range of (13.19-37.82)g/l, (13.22-37.84)g/l and (13.60-39.26) mg/l, respectively. TDS and TS show a spatial significant difference (p<0.01). The maximum salinity (TDS) and TS value have observed during summer due to temperature elevation and evaporation rate. TS and TDS are positively correlated (n=24, P<0.01) with pH (r=0.81) in addition to the most major ions, that is in agreement with Goher [24]. The corresponding values in the drains water fluctuated in the ranges (2.03-3.78) and (1.99-3.74) g/l, which are much lower than the lake water, while TSS showed a remarkable increase in the drains wastewater and ranged between (31.98-52.16) mg/l.

3.2. Chemical parameters

The pH measures the acidity or alkalinity of water. A level of pH is an important factor in the chemical and biological systems of natural waters [28], pH of Qarun Lake water lies in the alkaline side and it varied in the ranges of (7.97-8.95). The maximum pH~8.97 was recorded at station (3) during summer, while the minimum pH~7.67 was recorded at station (5) during autumn. ANOVA study show a high spatial significant difference (p<0.01). However, in the drainages water pH ranged between 7.16 and 8.02, pH is positively correlated (n=24, P<0.01) with E.C (r=0.8), anions like SO₄²⁻ (r=0.79) and cations like Na⁺ (r=0.80) and Mg²⁺ (r=0.79). While it is negatively correlated with heavy metals as Mn (r=-0.67), Ni (r=-0.73) and Cr (r=-0.69).

Dissolved oxygen (DO), Chemical Oxygen Demand (COD) and Biological Oxygen Demand (BOD) values varied in the ranges of (6.20-10.62), (18.78-30.12) and (4.10-8.66) mg/l. The lowest DO value was observed at station 5 in front El-Wadi drain, which may be related to the impact of the huge amount wastewater loaded with the organic matter. Moreover, the maximum COD and BOD values were recorded in summer, which may be attributed to the higher rate of decomposition of organic substance under the effect of the high temperature and bacterial activity, this finding is in a harmony with those obtained by both Abdel-Satar et al [2] and Goher [24]. COD showed a temporal significant difference (p<0.01). Nevertheless, DO and BOD values exhibited a spatial significant difference (p<0.05). The coefficient correlation data showed that COD is negatively correlated with temperature (r=-0.85, P<0.01), however, BOD is positively correlated (n=24, P<0.5) with temperature (r=0.51) and DO (r=0.48). DO is negatively correlated to most nutrient as ammonia NH₄ (r=-0.45, P<0.05) and
with metals as Cr (r= -0.45), Mn (r= -0.42) and Ni (r= -0.66, p<0.01) which indicate the role of high dissolved oxygen in the settling of metal into the sediment, these results are in agreement with Abdel-Satar et al [2]. On the other hand, DO, BOD and COD of drains water were in the ranges of (2.37 - 8.12) mg/l, (4.43 - 7.67) mg/l and (15.46 - 21.80) mg/l, respectively.

Table 2. Range and mean of Qarun Lake water parameters compared to guidelines of aquatic life protection.

| parameter | Range | Mean±SD | Aquatic live<sup>a</sup> |
|-----------|-------|---------|--------------------------|
| Temp. (ºC) | 15.3-31.7 | 21.58±5.47 | 8–28 |
| Transparency (cm) | 20-100 | 57.71±20.16 | |
| EC (ms/cm) | 17.09-47.24 | 36.37±8.43 | |
| TDS (g/l) | 13.19-37.82 | 29.59±7.26 | |
| TSS (mg/l) | 13.60-39.26 | 24.32±6.34 | 25 |
| TS (g/l) | 13.22-37.84 | 29.62±7.25 | |
| pH | 7.97-8.95 | 8.40±0.26 | 6.5–9 |
| DO (mg/l) | 6.20-10.62 | 8.32±1.10 | >5.5 |
| BOD (mg/l) | 4.10-8.66 | 6.55±2.02 | < 6 |
| COD (mg/l) | 18.78-30.12 | 24.10±3.29 | |
| CO3 (mg/l) | 9.12-16.21 | 12.66±2.39 | |
| HCO3 (mg/l) | 292.0-347.0 | 317.24±14.89 | |
| Cl (mg/l) | 4.65-13.31 | 10.73±2.54 | |
| SO4 (mg/l) | 3.42-9.88 | 7.87±1.88 | |
| Ca (mg/l) | 0.16-0.52 | 1.17±1.49 | |
| Mg (mg/l) | 0.47-1.35 | 1.07±0.26 | |
| Na (mg/l) | 3.78-10.93 | 8.68±2.11 | |
| K (mg/l) | 0.08-0.24 | 0.19±0.047 | |
| NO3-N (mg/l) | 0.03-1.06 | 0.30±0.36 | 2.93 |
| NO2-N (lg/l) | 0.00-288.90 | 60.55±84.12 | 60 |
| NH4-N (mg/l) | 0.05-2.15 | 0.55±0.59 | 1.37 |
| TN | 0.86-5.14 | 2.49±2.54 | |
| PO4-P (lg/l) | 1.10-78.42 | 26.08±22.36 | |
| TP (lg/l) | 32.77-232.0 | 91.97±59.77 | |
| SiO3 (mg/l) | 4.48-0.44 | 6.15±0.74 | |
| Fe (µg/l) | 111.91-481.24 | 205.34±95.81 | 300 |
| Mn (µg/l) | 11.00-40.85 | 20.51±6.93 | 50 |
| Zn (µg/l) | 13.60-38.36 | 27.30±6.39 | 50 |
| Cu (µg/l) | 4.09-10.32 | 7.00±1.78 | 4 |
| Ni (µg/l) | 3.59-12.65 | 7.90±2.70 | 25 |
| Cr (µg/l) | 7.06-17.06 | 10.43±2.62 | 10 |
| Cd (µg/l) | 0.43-1.49 | 0.99±0.28 | 1 |
| Pb (µg/l) | 11.87-36.41 | 20.28±5.56 | 7 |

<sup>a</sup> Canadian Council of Ministers of the Environment (CCME) [29].

3.2.1. Major Ions

Although the salinity value of Qarun Lake is similar to the salinity of sea water. But the ionic composition of Qarun Lake water differ completely from the composition of sea water, due to the different source of salts which discharging to the oceans and Qarun Lake [24]. This observation is based mainly on the chloride and sulphate levels. Sulphate in Qarun Lake water up to about 10 g/l, which is considerable higher than in sea water 2.65 g/l, on the other side, chloride in Qarun Lake water is lower than that in sea water, where it recorded about 14 and 19.35 g/l, in Qarun Lake and sea respectively.

In the current study, carbonate, bicarbonate, chloride and sulphate values were in the ranges of (9.12-16.21) mg/l, (292.0-347.0) mg/l, (4.65-13.31) g/l and (3.42-9.88) g/l with a highly spatial significant difference (p< 0.01). Generally, the increase of the anions concentrations in summer may be related to the evaporation effect, Also, the increase of carbonate levels during summer may be attributed to photosynthetic activity in addition to the elevation of water temperature that leads to decrease in solubility of carbon dioxide [30]. On the other hand, carbonate in the drains wastewater was
completely depleted, while bicarbonate, chloride, and sulphate were varied in the ranges of (352.0-422.0) mg/l, (0.46-1.20) g/l and (0.28-0.59) g/l, respectively.

**Table 3. Range and mean of wastewater parameters discharging into Qarun Lake during (2015).**

| Parameter (mg/l) | El-Wadi drain | Mean±SD | El- Bats Drain | Mean±SD | Pump station | Mean±SD |
|-----------------|----------------|---------|----------------|---------|--------------|---------|
| Temp. (°C)      | 15.40±30.50   | 21.68±2.59 | 15.60±29.40   | 21.23±6.04 | 15.60±30.50 | 21.73±6.52 |
| Transparency (cm)| 5.0±20.0      | 15.00±7.07 | 10.0±30.00    | 22.50±8.66 | 25.0±35.0   | 31.25±4.79  |
| EC (ms/cm)      | 3.17±4.91     | 3.99±0.73  | 2.78±5.28     | 3.76±1.11  | 2.54±3.33   | 3.01±0.33   |
| TDS (g/l)       | 2.26±3.40     | 2.79±0.47  | 1.99±3.74     | 2.61±0.79  | 2.25±3.39   | 2.78±0.47   |
| TSS (mg/l)      | 41.86±52.16   | 44.66±5.00 | 38.34±42.00   | 40.22±1.54 | 31.98±37.67 | 35.04±2.83  |
| TS (g/l)        | 2.30±3.44     | 2.83±0.47  | 2.03±3.78     | 2.65±0.79  | 2.28±3.43   | 2.81±0.48   |
| pH              | 7.16±7.91     | 7.64±0.35  | 7.38±7.97     | 7.66±0.25  | 7.67±8.02   | 7.87±0.145  |
| DO (mg/l)       | 2.37±7.81     | 5.26±2.38  | 2.59±6.67     | 4.58±1.74  | 6.08±12.72  | 7.02±0.84   |
| BOD (mg/l)      | 4.43±7.67     | 6.16±1.38  | 4.85±6.82     | 5.66±0.88  | 5.42±6.62   | 5.97±0.64   |
| COD (mg/l)      | 15.88±19.16   | 18.18±1.55 | 17.62±21.80   | 19.32±1.93 | 15.46±18.24 | 16.38±1.26  |
| NO3 (mg/l)      | 0.03±0.06     | 0.09±0.11  | 0.09±0.11     | 0.09±0.11  | 0.09±0.11   | 0.10±0.11   |
| P (µg/l)        | 3.24±4.21     | 3.97±1.43  | 3.79±2.86     | 4.60±1.82  | 4.43±2.67   | 5.07±1.23   |
| N (mg/l)        | 0.00±0.01     | 0.00±0.01  | 0.00±0.01     | 0.00±0.01  | 0.00±0.01   | 0.00±0.01   |
| K (µg/l)        | 0.00±0.01     | 0.00±0.01  | 0.00±0.01     | 0.00±0.01  | 0.00±0.01   | 0.00±0.01   |
| Mg (mg/l)       | 1.20±0.09     | 1.20±0.09  | 1.20±0.09     | 1.20±0.09  | 1.20±0.09   | 1.20±0.09   |
| Ca (µg/l)       | 0.00±0.01     | 0.00±0.01  | 0.00±0.01     | 0.00±0.01  | 0.00±0.01   | 0.00±0.01   |
| Na (µg/l)       | 0.00±0.01     | 0.00±0.01  | 0.00±0.01     | 0.00±0.01  | 0.00±0.01   | 0.00±0.01   |
| Zn (µg/l)       | 0.00±0.01     | 0.00±0.01  | 0.00±0.01     | 0.00±0.01  | 0.00±0.01   | 0.00±0.01   |
| Cu (µg/l)       | 0.00±0.01     | 0.00±0.01  | 0.00±0.01     | 0.00±0.01  | 0.00±0.01   | 0.00±0.01   |
| Ni (µg/l)       | 0.00±0.01     | 0.00±0.01  | 0.00±0.01     | 0.00±0.01  | 0.00±0.01   | 0.00±0.01   |
| Cr (µg/l)       | 0.00±0.01     | 0.00±0.01  | 0.00±0.01     | 0.00±0.01  | 0.00±0.01   | 0.00±0.01   |
| Cd (µg/l)       | 0.00±0.01     | 0.00±0.01  | 0.00±0.01     | 0.00±0.01  | 0.00±0.01   | 0.00±0.01   |
| Pb (µg/l)       | 0.00±0.01     | 0.00±0.01  | 0.00±0.01     | 0.00±0.01  | 0.00±0.01   | 0.00±0.01   |

The major cations; calcium, magnesium, sodium and potassium varied in the ranges of (0.16-0.52) mg/l, (0.47-1.35) mg/l, (3.78-10.93) g/l and (0.08-0.24) mg/l, respectively, with highly spatial significant difference (p<0.01). The results revealed that Ca²⁺, Mg²⁺, Na⁺ and K⁺ have the same distribution pattern of Cl⁻ and SO₄²⁻, where it increased westwards and decreased at the stations close to the discharging points of the drains. The corresponding values in the drains fluctuated between (0.03-0.09) mg/l, (0.04-0.08) mg/l, (0.46-0.58) g/l and (0.02-0.04) mg/l for Ca²⁺, Mg²⁺, Na⁺ and K⁺, respectively.

Carbonates is negatively correlated (n= 24, p< 0.05) with heavy metals as Fe²⁺ (r=-0.48), Cu²⁺ (r=-0.48) and Pb²⁺ (r=-0.42), which indicated the precipitation of these metals as carbonate. Bicarbonates is positively correlated (n= 24, p< 0.01) with Ni²⁺ (r=0.55), (n=24, p<0.05) with Zn²⁺ (r=0.44), TN (r=0.44), TSS(r=0.48), and temperature (r=0.47). The high positive correlation (n= 24, p< 0.01) between chloride and sulphate with the major cations (r=0.99) indicated that a large amount of the major cations was presented in chloride and sulphate forms, these findings are in a consensus with the results those obtained by Goher et al [31].
3.2.2. Nutrient Salts

Nutrients of concern with respect to water quality are nitrogen and phosphorous. Excess nitrogen and phosphorous in lakes and streams can cause algal blooms and eutrophication [32]. Nutrient in surface water is connected to the natural conditions and anthropogenic effect [31]. Ammonia, nitrates, nitrite and total nitrogen were found in the ranges of (0.05-2.15) mg/l, (0.00-288.90) µg/l, (0.03-1.06) mg/l and (0.86-5.14) mg/l, respectively. Ammonia, Nitrite and Nitrate show a high significant difference (p<0.01) among the seasons and sites. While TN values show a temporal significant difference (p<0.05).

Phosphorous is a nutrient limited and needed for the growth of all plants, aquatic plants and Phytoplankton alike. Once phosphorus accumulates within a lake, it can cycle through the water column and promote algal blooms indefinitely [33]. Phosphorus forms showed an irregular distribution pattern, with a high spatial significant difference (p<0.01). Orthophosphate and TP varied in the ranges of (1.10-78.42) and (32.77-232.0) µg/l, respectively. These results declared that Qarun Lake is considered a eutrophic system; Mueller and Helsel [34] cited that a lake with a concentration exceeding 0.020 mg of phosphorus are already considered eutrophic.

Phosphorous and nitrogen are important for the conservation of the productivity of the lake; conversely, the high levels cause algal blooms, harmful to most aquatic organisms [35], which leads to oxygen depletion and cause fish mortality [31].

Reactive Silicate fluctuated between 2.11-6.70 mg/l with a spatial and temporal significant difference (p<0.01 and p<0.05, respectively). According to Abdel-Satar et al [36], the dissolution of sediments and silicate rocks in addition to the absorption by diatoms control the silica levels. Generally, the high concentrations of the nutrient salts were recorded in the stations in front the discharging point of the drains, especially stations 5 and 1.

The corresponding values in the drains were found much higher than the lake and changed in the ranges of (1.20-0.49) mg/l, (0.50-3.39) µg/l and (0.22-1.69) mg/l, (2.11-6.70) mg/l, (76.24-259.6) µg/l, (164.22-489.67) µg/l and (5.98-10.42) mg/l, for ammonia, nitrites, nitrate, total nitrogen, orthophosphate, total phosphorus and reactive silicate, respectively.

The obtained results showed a high positive correlation among the different nutrient forms (r = 0.68-0.93 n=24, p<0.01). Moreover, the positive correlation with different heavy metals (r = 0.59-0.73 n=24, p<0.01). These observations are in compatibility with that reported by both Goher  et al and Abdel-Satar et al [31,36] and indicate that the different wastes are the common source of these parameters.

3.2.3. Heavy metals

Heavy metals not only enter the aquatic ecosystem through erosion, atmospheric deposition and anthropogenic activities but also it increased due to industrial effluents, domestic sewage, and mining [37]. So, presence excess of them in the water environment, especially lakes and rivers caused a hazard to humans by their toxicity and potential pollution to the food chain. Unlike many organic wastes, trace metals cannot be converted biologically into harmless products [38].

The results of the studied metals (iron, manganese, zinc, chromium, copper, lead, nickel and cadmium) showed high significant variations among the locations and seasons. Where the highest contents were recorded at the stations facing the outlet of the drains. Otherwise, the metal levels in Qarun Lake water have increased during the hot period, which may be accredited to the metal liberation from the bottom sediment to the water column due to the degradation of organic matter under the effect of the high temperature and the microbial activity [9]. Inversely, the lower metals content in water during cold period; which is witnessing algae blooms; may be due to uptake of it by phytoplankton and the dead phytoplankton settling to the bottom sediment leaving the water poor in the trace elements, in addition to settling of metals from water column to the sediments under slightly high pH values [24]. The results declared that the levels of Fe^{2+}, Cr^{6+} and Cd^{2+} in Qarun Lake water exceeded the guidelines for aquatic-life of CCME [29].
Iron and manganese are the greatest common metals found in nature. They varied in Qarun Lake water between 111.91-481.24 and 11.00-40.85 µg/l, respectively. Iron and manganese concentrations in surface water are mainly controlled by redox conditions, the type and amount of dissolved organic matter and water pH. The bio-essential element iron is not toxic itself, but it enhances the uptake of As (III) in some aquatic organisms and inhibits those of As (V) [39]. Further, zero valiant iron has been tested by Gheju, [40] as a promoter of the reduction of the heavily toxic and mobile Cr (VI) into the less toxic Cr (III), a process which depends mainly of the conditions of the environmental of the aquatic system.

According to Ruttner [41], the distribution dynamics of iron in the aquatic system depended on DO and is usually present as insoluble Fe(OH)_3 or ferric oxide. The ferrous form can only exist in the depletion of oxygen and the ferric form is almost completely insoluble. In other words, at oxygenated water iron is precipitated as ferric form, while in the insufficiency of oxygen and the water containing CO_2 comes in contact with iron in the ferrous form, in this case, ferrous bicarbonate goes into solution; however, at the oxidation occur insoluble ferric hydroxide ions precipitated as follows:

\[ 4Fe(HCO_3)_2 + 2H_2O + O_2 \rightarrow 4Fe(OH)_3 + 8CO_2 \]  (4)

Also, in water contains ferrous sulfate which is unstable in presence of dissolved oxygen, ferrous sulfate and sulphuric acid (formed by the action of microorganisms) react under the presence of oxygen to produce ferric sulfate, which is quickly hydrolyzed to ferric hydroxide. Manganese is very close to iron in the economy of rivers, lakes and behave in much the same manner. The chemistry of manganese is appreciably complicated due to its existence in different oxidation states [24].

The distribution dynamics of zinc, chromium, lead, copper nickel and cadmium follow the distribution of manganese and iron and were varied in ranges of (13.60-38.36), (44.09-10.32), (3.59-12.65), (7.06-17.06), (11.87-36.41) and (0.43-1.49) µg/l, respectively. The positive significant correlations (r= 0.42–0.71; n =24, p< 0.01) among each pairs of the heavy metals indicated the association behavior and the common sources. Also, the statistical analysis showed a negative correlation (n=24, p<0.01) between the most studied metals with dissolved oxygen (r = -0.42: -0.66) and with pH (r = -0.78: -0.75), which indicate the effect of high dissolved oxygen and pH in the precipitation of the different metals into the bottom sediment these findings are in agreement with many studies [2,24].

3.3. Water quality index (WQI)

The quality of Qarun Lake water was investigated according to Oregon Water Quality Index (OWQI) module, which was developed by the Oregon Department of Environmental Quality (ODEQ), for the purpose of summarizing and evaluating water quality trends and status, in the late 1970s and updated several times since then [42]. The Oregon Water Quality Index is a single number that express water quality by integrating values of 8 parameters (temperature, dissolved oxygen, BOD, pH, (ammonia + nitrate nitrogen), total phosphorus, total solids and fecal coliform). The OWQI comforts to estimate the efficiency of the management activities of the water quality. It may also be to progress ecological indicators, such as the percentage of river and lakes monitoring sites with significantly improving water quality, or the percentage of sites with excellent water quality [42]. OWQI is classified to 5 categories (Table 4) [17].

In the current study, six parameters were used to calculate the OWQI for fishing usage. The variables included temperature, DO, BOD, pH, (ammonia + nitrates) and total phosphorus. The obtained results indicate that WQI for Qarun Lake water changed from 17.05 to 67.4 at the different stations. Therefore, Qarun Lake water during all seasons is classified as very poor for the Fishing utilization at all stations, except station 6 that is categorized as poor in winter and spring (Figure 2).

3.4. Metal quality indices

Two different indices are designed to evaluate the metal contamination of Qarun Lake water, the first one is the Pollution Index (PI), that independent on the effect of the individual metal. While the other
index, Metal index (MI), based on the effect of the total metals level. In the present study, the acceptable limits of the trace metals obtained by CCME [29] for aquatic life protection were used as maximum allowable concentration (MAC) value.

Table 4. Categories of OWQI

| OWQI Value | Class   |
|------------|---------|
| 10-59      | Very poor |
| 60-79      | Poor     |
| 80-84      | Fair     |
| 85-89      | Good     |
| 90-100     | Excellent|

Figure 2. OWQI and its categorizations of Qarun Lake water for fishing utilizations.

3.4.1. Pollution Index (PI)

The pollution index (PI) was used in our study to determine the grade of trace metals toxicity in water samples. It is based on individual metal calculations and categorized to five classes (Table 5) according to Caeiro et al [43].

The results indicate a various pollution degree of the studied metals for aquatic life in Qarun Lake. Pollution index exhibited that Mn, Ni and Zn have not polluted effect for aquatic life usage. On the other hand, Cu and Cr showed slight pollution to moderate effect at all station. Cd showed slightly pollution effect at stations 1, 5 and 6, while Fe showed the same effect at stations 1 and 4. Finally, Pb cause strongly pollution effect at all stations (Table 6).

Table 5. Categories of water pollution index

| Class | PI Value | Class            |
|-------|----------|------------------|
| 1     | ≤ 1      | No effect        |
| 2     | >1-2     | Slightly affected|
| 3     | >2-3     | Moderately affected|
| 4     | >3-5     | Strongly affected|
| 5     | >5       | Seriously affected|

3.4.2. Metal Index (MI)

It is based on a total trend evaluation of the present status. By increasing concentration of a metal compared to its respective maximum allowable value (MAC), the worse impact of the quality of the
water appeared. MI value >1 is the warning limit [18]. According to MI values, all selected sites in Qarun Lake are suffer from seriously metal pollution for the Aquatic life utilization (Table 7).

**Table 6.** Pollution index of the measured metals in the Qarun Lake water according to guideline levels of aquatic life utilizations.

| Station | Fe PI value | Fe Effect | Mn PI value | Mn Effect | Zn PI value | Zn Effect | Cu PI value | Cu Effect |
|---------|------------|-----------|-------------|-----------|-------------|-----------|-------------|-----------|
| 1       | 1.14       | slightly  | 0.67        | No        | 0.83        | No        | 2.14        | moderate  |
| 2       | 0.56       | No        | 0.43        | No        | 0.71        | No        | 1.96        | slightly  |
| 3       | 0.69       | No        | 0.31        | No        | 0.57        | No        | 1.53        | slightly  |
| 4       | 0.67       | slightly  | 0.38        | No        | 0.55        | No        | 1.56        | slightly  |
| 5       | 1.18       | No        | 0.70        | No        | 0.55        | No        | 2.18        | moderate  |
| 6       | 0.49       | No        | 0.31        | No        | 0.48        | No        | 1.77        | slightly  |

| Station | Ni PI value | Ni Effect | Cr PI value | Cr Effect | Pb PI value | Pb Effect | Cd PI value | Cd Effect |
|---------|------------|-----------|-------------|-----------|-------------|-----------|-------------|-----------|
| 1       | 0.53       | No        | 2.18        | moderate  | 3.47        | strongly  | 1.27        | slightly  |
| 2       | 0.41       | No        | 1.74        | slightly  | 3.54        | strongly  | 0.97        | No        |
| 3       | 0.30       | No        | 1.84        | slightly  | 3.39        | strongly  | 0.99        | No        |
| 4       | 0.27       | No        | 2.08        | moderate  | 3.99        | strongly  | 0.90        | No        |
| 5       | 0.40       | No        | 2.11        | moderate  | 4.03        | strongly  | 1.13        | slightly  |
| 6       | 0.42       | No        | 1.67        | slightly  | 3.90        | strongly  | 1.09        | Slightly  |

**Table 7.** Metal index of the measured metals in Qarun Lakes water for aquatic life utilizations.

| Stations | MI value | Rank |
|----------|----------|------|
| 1        | 11.73    | Polluted |
| 2        | 9.78     | Polluted |
| 3        | 9.07     | Polluted |
| 4        | 9.88     | Polluted |
| 5        | 10.96    | Polluted |
| 6        | 8.44     | Polluted |

3.5. Application of removal of toxic metal from wastewater discharged into Qarun Lake using synthesized nanocomposite

In the present study, the prepared Ni-Al-CO$_3$ layered double hydroxide (LDH) with Ni:Al ratio(3:1) based nanocomposites with alginate and chitosan beads were assessed to remove the metals from the different wastes that discharge into Qarun Lake. The characterization of the synthesized nanocomposites, that previously utilized for removal trace metal from aqueous solution and the optimum conditions of these materials for the its adsorption process have discussed in details in El-Rouby et al., [22].

For the raw wastewater, the results revealed that all nanocomposites (alginate, chitosan alginate, LDH alginate and LDH-chitosan- alginate beads) recorded 100% removal efficiency for all studied metals; (Fe$^{3+}$, Mn$^{2+}$, Pb$^{2+}$, Zn$^{2+}$, Cu$^{2+}$, Cd$^{2+}$, Cr$^{6+}$ and Ni$^{2+}$) for El-Bats Drain, El-Wadi Drain and pump station (Table 8).

On the other hand, the application of heavy metal removal using nanocomposites from the concentrated sample of raw wastewater declared that LDH-chitosan-alginate beads recorded the highest removal efficiency for all studied metals from the different wastes. Where, iron exhibited the most adsorbed ion with a removal ratio of 98.587, 98.765 and 98.333 % for El-Bats, El-Wadi and pump station wastewater respectively by LDH-chitosan-alginate beads, while nickel recorded the
lowest one with 82.588, 85.819 and 85.70 % removal ratio using alginate beads from for El-Bats, El-Wadi and pump station wastewater, respectively (Figure 3). According to the total ions that were adsorbed with the different adsorbents, the adsorption capacity of the prepared nanocomposites were in the order of LDH-chitosan-alginate > chitosan-alginate > LDH - alginate >alginate beads. LDH-chitosan-alginate beads exhibited the maximum adsorption capacity (qe) 5.056 mg/g for El Bats Drain wastewater; in contrast, the alginate beads recorded the lowest one of 2.987 mg/g for the pump station wastewater (Table 9). Our studies are in agreement with Rahmanian et al., [44], and Asiabi et al., [45] that confirmed that LDHs proved high removal efficiency for heavy metals.

It is worth mentioning that the synthesized nanocomposites considered an excellent adsorbent to remove different heavy metals from the various wastewaters. All prepared nanocomposites (alginate, LDH-alginate, Chitosan alginate and LDH-Chitosan-alginate beads) give efficiency removal reached to 100% of raw wastewater in all studied drains as illustrated in table.8. However, by application of these adsorbents on the concentrated wastewater samples, the removal efficiency was in the range of (98.833-92.353), (97.835-90.235), (97.039-88.981) and (94.456-82.588) % for LDH-chitosan-alginate, chitosan-alginate, LDH-alginate and alginate beads, respectively (Table 9). The total adsorption capacity (q_e) mg/g of the prepared adsorbents for all heavy metals removed by these adsorbents was found in the ranges of (4.568-2.987), (4.773-3.143), (4.858-3.210) and (5.056-3.319) for alginate, LDH-alginate, chitosan-alginate and LDH-chitosan-alginate, respectively in all wastewater samples as represented in table.10.

Table 8. The Removal efficiency % of the metals by the synthesized nanocomposites from the raw wastewater.

| metal Drain | Adsorbent               | Fe  | Pb  | Cu  | Zn  | Cd  | Mn  | Ni  | Cr  |
|-------------|-------------------------|-----|-----|-----|-----|-----|-----|-----|-----|
| El-Bats     | Concentration µg/l      | 657 | 57  | 21.8| 56.6| 1.8 | 65.2| 44.8| 45.3|
|             | Alginete                | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 |
|             | Chitosan- Alginate      | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 |
|             | LDH/ Alginate           | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 |
|             | LDH/chitosan/ Alginate  | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 |
| El-Wadi     | Concentration µg/l      | 519 | 53.94| 18.63| 52.11| 1.63| 50.36| 37.53| 31.06|
|             | Alginete                | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 |
|             | Chitosan- Alginate      | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 |
|             | LDH/ Alginate           | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 |
|             | LDH/chitosan/ Alginate  | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 |
| pump station| Concentration µg/l      | 429 | 46.76| 16.77| 40.91| 1.63| 54.32| 20.41| 25.64|
|             | Alginete                | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 |
|             | Chitosan- Alginate      | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 |
|             | LDH/ Alginate           | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 |
|             | LDH/chitosan/ Alginate  | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 |

Figure 3 illustrates the removal efficiency of heavy metals of concentrated samples (ten times) from (a) El-Bats Drain, (b) El-Wadi Drain and, (c) Pump station that discharged into Qarun Lake using different alginate nanocomposites beads. The results demonstrate that the removal efficiency of the prepared adsorbents are in the order of LDH-chitosan-alginate > chitosan-alginate > LDH-alginate > alginate beads. On the other hand, the removal of iron by LDH-chitosan-alginate beads recorded the highest one up to 98.587, 98.765 and 98.833 for the concentrated wastewater of El Bats, El Wadi and pump station drains, respectively. While, the lowest removal efficiency values obtained for Ni^{2+} using Alginate were 82.588% for El-Bats < 85.752 % for pump station drain < 85.819 % for El-Wadi Drain.
In the present study, the prepared adsorbents were assessed to eliminate the trace metal from the raw wastewaters and 10 times concentrated wastewater samples of the different drains discharging into Qarun Lake under the finest condition of ambient room temperature, 2g/l adsorbent dose, 2h contact at 300 rpm agitation speed.

Table 9. The Removal efficiency % of the metals by the synthesized nanocomposites from the concentrated wastewater.

| Drain                      | Adsorbent               | Fe       | Pb       | Cu       | Zn       | Cd       | Mn       | Ni       | Cr       |
|----------------------------|-------------------------|----------|----------|----------|----------|----------|----------|----------|----------|
| El Bats Drain Water        | Concentration µg/l      | 7220.0   | 620.00   | 226.00   | 621.80   | 18.90    | 690.00   | 473.00   | 482.70   |
|                            | Alginate                | 88.698   | 86.048   | 89.533   | 88.437   | 87.778   | 90.116   | 82.588   | 86.418   |
|                            | Chitosan- Alginante     | 94.155   | 94.984   | 92.965   | 93.036   | 93.704   | 95.158   | 90.235   | 90.870   |
|                            | LDH/ Alginante          | 92.641   | 92.339   | 90.664   | 90.962   | 92.434   | 93.420   | 88.981   | 89.584   |
|                            | LDH/chitosan/ Alginante| 98.587   | 96.952   | 96.062   | 95.529   | 95.238   | 97.212   | 94.497   | 92.353   |
| El Wadi Drain Water        | Concentration µg/l      | 5500.0   | 580.00   | 194.00   | 553.70   | 17.20    | 530.00   | 393.00   | 326.00   |
|                            | Alginate                | 88.291   | 91.845   | 92.629   | 90.946   | 88.721   | 91.485   | 85.819   | 87.847   |
|                            | Chitosan- Alginante     | 94.891   | 95.793   | 97.835   | 95.720   | 94.128   | 95.019   | 90.659   | 92.595   |
|                            | LDH/ Alginante          | 92.782   | 93.931   | 96.959   | 94.618   | 92.791   | 92.906   | 89.870   | 91.525   |
|                            | LDH/chitosan/ Alginante| 98.765   | 98.552   | 98.608   | 97.773   | 95.756   | 97.079   | 94.631   | 94.433   |
| Pump station               | Concentration µg/l      | 4560.0   | 490.00   | 179.00   | 431.10   | 17.00    | 570.00   | 218.00   | 271.10   |
|                            | Alginate                | 87.105   | 92.469   | 93.799   | 91.048   | 88.824   | 94.456   | 85.752   | 91.479   |
|                            | Chitosan- Alginante     | 95.022   | 96.449   | 97.709   | 96.381   | 94.353   | 96.298   | 92.922   | 94.419   |
|                            | LDH/ Alginante          | 92.434   | 96.082   | 97.039   | 95.662   | 94.059   | 95.719   | 91.225   | 93.298   |
|                            | LDH/chitosan/ Alginante| 98.833   | 98.776   | 98.659   | 97.926   | 96.000   | 97.349   | 95.133   | 95.876   |

Table 10. Adsorption capacity (qₑ) mg/g of the prepared adsorbents for the different wastewater.

| Adsorbent                  | El Bats Drain | El Wadi Drain | Pump station |
|----------------------------|---------------|---------------|--------------|
| Alginate                   | 4.568         | 3.598         | 2.987        |
| Chitosan alginate          | 4.8578        | 3.836         | 3.210        |
| LDH alginate               | 4.773         | 3.760         | 3.143        |
| LDH chitosan alginate      | 5.056         | 3.976         | 3.319        |

The obtained experimental results were confirmed with FTIR spectra for the LDH-chitosan-alginate bead before and after the adsorption process. Figure 4. (a-c) and table 11 displayed FTIR spectra of LDH-chitosan-alginate bead before and after adsorption of Cu²⁺ and Cd²⁺ cations. Where, the shifts and changes in the intensity of characteristic bands of the LDH-chitosan bead spectrum after adsorption -as compared with the spectra of it before adsorption- can be counted on with regard to confirming the interaction processes during adsorption, which is indicative of deprotonation of the functions group. The band at 3418 cm⁻¹ declined to 3421, 3428.6 cm⁻¹ after adsorption of Cu²⁺ and Cd²⁺, respectively, suggesting that the bonded OH groups exerted a significant role in Cu²⁺ and Cd²⁺ adsorptions. Appearance of some new peaks at 2379 cm⁻¹ and 2171 cm⁻¹ for copper and cadmium, respectively as confirmed with Mahmoud et al [13] that referred to presence of υ(C=O) of the amide group CONHR of the chitosan and aliphatic groups, specifically CH₂ and CH in cadmium and metal adsorption.
Figure 3. Efficiency removal of heavy metals of concentrated samples (ten times) of (a) El-Bats Drain, (b) El-Wadi Drain and, (c) Pump station discharged on Qarun Lake using different alginate nanocomposites beads.

Figure 4. FT-IR spectra of Ni–Al LDH- chitosan – alginate beads (a) before adsorption, (b) after adsorption of copper Cu$^{2+}$ and (c) after adsorption of cadmium Cd$^{2+}$ from different aqueous solutions.
4. Conclusion
Qarun Lake is an inland closed saline lake about 80 km southwest of Cairo. The unique source of the lake water is the agricultural wastewater of El Fayoum province. Due to the evaporation process that led to the concentration of the impounded drainage water that effect on the water quality and the environmental conditions of the lake. The status of the degraded lake water was confirmed with the results of WQI. The obtained WQI data classified Qarun Lake water as very poor water for fishing usage. On the other side, the metal pollution indices indicated that Qarun Lake suffers from different degree of metal contamination. Novel synthesized nanocomposites were used to eliminate the trace metals from the different wastewater that discharge into the lake.

The study showed that the iron is the most adsorbed one of the studied metals (Fe, Mn, Pb, Zn, Cu, Cd, Cr and Ni). Furthermore, the synthesized LDH-chitosan–alginate beads recorded the maximum removal efficiency > chitosan–alginate > LDH-alginate > alginate. It is worth mentioning that the synthesized nanocomposites considered an excellent adsorbent to remove different metals from the various wastewaters.

Table 11. FT-IR spectra assignment of Ni–Al LDH- chitosan – alginate beads (a) before adsorption, (b)after adsorption of cupper Cu²⁺ and (c) after adsorption of cadmium Cd²⁺ from different aqueous solutions.

| Assignment                                                                 | References |
|----------------------------------------------------------------------------|------------|
| 3418 cm⁻¹ Shift to 3421 cm⁻¹                                               | [46]       |
| stretching OH vibration mode                                               |            |
| 2977 cm⁻¹ Shift to 2926 cm⁻¹                                               | [47]       |
| Antisymmetric streching vibration mode of – CH₃                            |            |
| 2379 cm⁻¹ Shift to 2373 cm⁻¹                                               | [13,48]    |
| is calculated by υ(C=O) of the amide group CONHR of the chitosan.         |            |
| & adsorption for cadmium and cupper.                                       |            |
| 2171 cm⁻¹                                                                  | [13]       |
| For Cd²⁺                                                                  |            |
| 1634 cm⁻¹ Shift to 1622 cm⁻¹                                               | [49,50]    |
| N-H bond stretching vibration & (NH₂ bending).                             |            |
| 1422.7 cm⁻¹ Shift to 1422.6 cm⁻¹                                           | [47]       |
| Carboxyl group symmetric stretching vibration                               |            |
| 1094.5 cm⁻¹ 1109 cm⁻¹                                                     | [50]       |
| skeletal vibration including the COO stretching.                           |            |
| 1047 cm⁻¹ Shift to 1040.6 cm⁻¹                                             | [51]       |
| –CH- OH in cyclic alcohols and C-O stretch                                 |            |
| 877 cm⁻¹ Shift to 813.8 cm⁻¹                                               | [48]       |
| Shift to 815.8 cm⁻¹                                                        |            |
| attributed to ω(C=H) from the polysaccharide’s structure                   |            |
| 755 cm⁻¹ Shift to 633 cm⁻¹                                                 | [27,52]    |
| Overlap between deformation of water molecules band in interlayer at 770 cm⁻¹ and at 680 cm⁻¹ of carbonate ions & at 633 cm⁻¹ ensuing from metal–oxygen bonds M-O vibration in the brucite-like. |            |

References
[1] Liu J, Dorjderem A, Fu J, Lei X and Macer D 2011 Water Ethics and Water Resource Management. (UNESCO)
[2] Abdel-Satar A M, Goher M E and Sayed M F 2010 Recent environmental changes in water and sediment quality of Lake Qarun, Egypt J. Fish. Aquat. Sci. 5 56–69
[3] Dardir A A and Wali A M A 2009 Extraction of salts from lake Quaroun, Egypt: Environmental and economic impacts Glob. Nest J. 11 106–13
[4] Reemtsma T and Jekel M 2006 Organic pollutants in the water cycle: properties, occurrence, analysis and environmental relevance of polar compounds (John Wiley & Sons)
[5] Doherty V, Ogunkuade O and Kanife U 2010 Biomarkers of oxidative stress and heavy metal...
levels as indicators of environmental pollution in some selected fishes in Lagos, Nigeria. *Am. J. Agric. Environ. Sci.* **7** 359–65

[6] Liu Y, Liu J, Zhang A and Liu Z 2017 Treatment effects and genotoxicity relevance of the toxic organic pollutants in semi-coking wastewater by combined treatment process. *Environ. Pollut.* **220** 13–9

[7] El-Sayed M and Salem W M 2015 Hydrochemical assessments of surface Nile water and ground water in an industry area – South West Cairo. *Egypt. J. Pet.* **24** 277–88

[8] Farombi E O, Adelowo O A and Ajimoko Y R 2007 Biomarkers of oxidative stress and heavy metal levels as indicators of environmental pollution in African cat fish (Clarias gariepinus) from Nigeria Ogun River. *Int. J. Environ. Res. Public Health* **4** 158–65

[9] Goher M E, Hassan A M, Abdel-Moniem I A, Fahmy A H and El-sayed S M 2014 Evaluation of surface water quality and heavy metal indices of Ismailia Canal, Nile River, Egypt. *Egypt. J. Aquat. Res.* **40** 225–33

[10] Tesh S J and Scott T B 2014 Nano Composites for Water Remediation: A Review. *Adv. Mater.* **26** 6056–68

[11] Zhang Y, Wu B, Xu H, Liu H, Wang M, He Y and Pan B 2016 Nanomaterials-enabled water and wastewater treatment. *NanoImpact* **3** 22–39

[12] Moaty S A A, Farghali A A, Moussa M and Khaled R 2017 Remediation of waste water by Co–Fe layered double hydroxide and its catalytic activity. *J. Taiwan Inst. Chem. Eng.* **71** 441–53

[13] Mahmoud R, Moaty S A, Mohamed F and Farghali A 2017 Comparative Study of Single and Multiple Pollutants System Using Ti–Fe Chitosan LDH Adsorbent with High Performance in Wastewater Treatment. *J. Chem. Eng. Data* **62** 3703–22

[14] Moaty S A A, Farghali A A and Khaled R 2016 Preparation, characterization and antimicrobial applications of Zn–Fe LDH against MRSA. *Mater. Sci. Eng. C* **68** 184–93

[15] Shadrin N V, El-Shabrawy G M, Anufriieva E V, Goher M E and Ragab E 2016 Long-term changes of physicochemical parameters and benthos in Lake Qarun (Egypt): Can we make a correct forecast of ecosystem future? *Knowl. Manag. Aquat. Ecosyst.* 18

[16] Ibrahim L A and Ramzy E M 2013 Water quality and its impact on Tilapia zilli (case study) Qarun lake-Egypt. *Int. Water Technol. J.*, **3** 170–91

[17] El-Shabrawy G M, Anufriieva E V, Germoush M O, Goher M E and Shadrin N V 2015 Does salinity change determine zooplankton variability in the saline Qarun Lake (Egypt)? *China J. Oceanol. Limnol.* **33** 1368–77

[18] Cude C G 2001 Oregon Water Quality Index a Tool for Evaluating Water Quality Management Effectiveness 1. *JAWRA J. Am. Water Resour. Assoc.* **37** 125–37

[19] Caeiro S, Costa M H, Ramos T B, Fernandes F, Silveira N, Coimbra A, Medeiros G and Painho M 2005 Assessing heavy metal contamination in Sado Estuary sediment: an index analysis approach. *Ecol. Indic.* **5** 151–69

[20] Bakan G, Özoçoş H B, Tülek S and Cüce H 2010 Integrated Environmental Quality Assessment of Kızılırmak River and its Coastal Environment. *Turkish J. Fish. Aquat. Sci.* **462** 453–62

[21] Tamasi G and Cini R 2004 Heavy metals in drinking waters from Mount Amiata (Tuscany, Italy). Possible risks from arsenic for public health in the Province of Siena. *Sci. Total Environ.* **327** 41–51

[22] El-Rouby W M A., Goher M E., Noaemy S G. E-D S I Efficient Water decontamination Using Nanocomposite of Layer Double Hydroxide Beads. Under publication

[23] Y A-A T Drains impact on water quality of manzala lake and photocatalytic removal of some chemical pollutants via using modified graphene nanomaterials (B.Sc.Thesis, Fac. of Sci. Benha University)

[24] E G M Chemical studies on the precipitation and dissolution of some chemical elements in Lake Qarun. (PDh Thesis, Fac. Sci. Al-Azhar Univ.Cairo, Egypt.)

[25] Khalil M T, Fishar M R, Shakir S H, Amer A S and Nassif M G Impact of Drainage Water on
Macrobenthos Structure of Lake Qaroun, El-Fayoum, Egypt

Fisher M R, El-Mageed A A, Elwa S E A-E A S and B R E. Environmental factors affecting life cycle of benthic invertebrates in Lake Qaroun, Egypt. *J. Egypt. Acad. Sci. Environ. Develop.* (D- Environ. Stud. 6) 9-32.

Ahmed A A A, Talib Z A, Bin Hussein M Z and Zakaria A 2012 Zn-Al layered double hydroxide prepared at different molar ratios: Preparation, characterization, optical and dielectric properties. *J. Solid State Chem.* 191 271–8

Rostom N G, Shalaby A A, Issa Y M and Afifi A A 2017 Evaluation of Mariut Lake water quality using Hyperspectral Remote Sensing and laboratory works *Egypt. J. Remote Sens. Sp. Sci.* 20 S39–48

Saffran K, Cash K, Hallard K, Neary B and Wright R 2001 Canadian water quality guidelines for the protection of aquatic life *CCME water Qual. Index* 1 31–4

E-S M H K 2010 Quantitative assessment and treatment of some industrial pollutants along the river Nile at Giza region (Ph.D. Thesis, Fac. of Sci. Benha University)

Goher M E, Mahdy E-S M, Abdo M H, Farida M, Korium M A and Elsherif A A S Water quality status and pollution indices of Wadi El-Rayan lakes, El-Fayoum, Egypt *Sustain. Water Resour. Manag.* 1–14

Kavita U, Piyush M and Gupta A K 2010 Studies on the physico-chemical status of two ponds at Varanasi and Bhadohi under biotic stress. *Plant Arch.* 10 691–3

Edwards A C and Withers P J A 2008 Transport and delivery of suspended solids, nitrogen and phosphorus from various sources to freshwaters in the UK *J. Hydrol.* 350 144–53

Mueller D K, Helsel D R and Kidd M A 1996 *Nutrients in the nation’s waters: too much of a good thing?* (US Government Printing Office Washington, DC)

Sahni K and Yadav S 2012 Seasonal variations in physico-chemical parameters of Bharawas Pond, Rewari, Haryana *Asian J. Exp. Sci* 26 61–4

Abdel-Satar A M, Ali M H and Goher M E 2017 Indices of water quality and metal pollution of Nile River, Egypt *Egypt. J. Aquat. Res.* 43 21–9

Bahnasawy M, KHIDR A A and Dheina N 2011 Assessment of heavy metal concentrations in water, plankton, and fish of Lake Manzala, Egypt *Turkish J. Zool.* 35 271–80

Goher M E, Hassan A M, Abdel-Moniem I A, Fahmy A H, Abdo M H and El-sayed S M 2015 Removal of aluminum, iron and manganese ions from industrial wastes using granular activated carbon and Amberlite IR-120H *Egypt. J. Aquat. Res.* 41 155–64

Khang H V, Hatayama M and Inoue C 2012 Arsenic accumulation by aquatic macrophyte coontail (Ceratophyllum demersum L.) exposed to arsenite, and the effect of iron on the uptake of arsenite and arsenate *Environ. Exp. Bot.* 83 47–52

Gheju M 2011 Hexavalent chromium reduction with zero-valent iron (ZVI) in aquatic systems *Water, Air, Soil Pollut.* 222 103–48

Ruttner F 1963 *Fundamentals of limnology* (University of Toronto Press)

Sarkar C and Abbasi S A 2006 Qualidex— a new software for generating water quality indices. *Environ. Monit. Assess.* 119 201–31

Federation W E and Association A P H 2005 Standard methods for the examination of water and wastewater *Am. Public Heal. Assoc. Washington, DC, USA*

Rahmanian O, Maleki M H and Dinari M 2017 Ultrasonically assisted solvothermal synthesis of novel Ni/Al layered double hydroxide for capturing of Cd (II) from contaminated water *J. Phys. Chem. Solids* 110 195–201

Asiabi H, Yamini Y and Shamsayei M 2017 Highly selective and efficient removal of arsenic (V), chromium (VI) and selenium (VI) oxyanions by layered double hydroxide intercalated with zwitterionic glycine *J. Hazard. Mater.* 339 239–47

Vijayalakshmi K, Devi B M, Latha S, Gomathi T, Sudha P N, Venkatesan J and Anil S 2017 Batch adsorption and desorption studies on the removal of lead (II) from aqueous solution using nanochitosan/sodium alginate/microcrystalline cellulose beads *Int. J. Biol. Macromol.* 104 1483–94
[47] Ruan X, Chen Y, Chen H, Qian G and Frost R L 2016 Sorption behavior of methyl orange from aqueous solution on organic matter and reduced graphene oxides modified Ni-Cr layered double hydroxides Chem. Eng. J. 297 295–303

[48] Negrea P, Caunii A, Sarac I and Butnariu M 2015 THE STUDY OF INFRARED SPECTRUM OF CHITIN AND CHITOSAN EXTRACT AS POTENTIAL SOURCES OF BIOMASS. Dig. J. Nanomater. Biostructures 10

[49] Kumar N, Reddy L, Parashar V and Ngila J C 2017 Controlled synthesis of microsheets of ZnAl layered double hydroxides hexagonal nanoplates for efficient removal of Cr (VI) ions and anionic dye from water J. Environ. Chem. Eng. 5 1718–31

[50] Peniche C, Argüelles-Monal W, Davidenko N, Sastre R, Gallardo A and San Román J 1999 Self-curing membranes of chitosan/PAA IPNs obtained by radical polymerization: Preparation, characterization and interpolymer complexation Biomaterials 20 1869–78

[51] Nayak P L and Sahoo D 2011 Chitosan-alginate composites blended with cloisite 30B as a novel drug delivery system for anticancer drug paclitaxel Int. J. Plast. Technol. 15 68–81

[52] Jitianu M, Gunness D C, Aboagye D E, Zaharescu M and Jitianu A 2013 Nanosized Ni-Al layered double hydroxides Structural characterization Mater. Res. Bull. 48 1864–73