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Assessment of Some Physico-chemical Parameters and Heavy Metals Level of an Ammonium-N Rich Industrial Effluent

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Abstract: Industrial effluents are laden with high concentrations of ammonia-N and heavy metals, considered as an urgent problem in developing populated countries due to their difficulty of safe disposal. The objective of this investigation was to evaluate the seasonal variation in water quality of a wastewater receiving drain from Eldelta for fertilizers and chemical industries (EFCI) company using some physico-chemical parameters between Spring 2018–Winter 2019. The parameters included water temperature, pH, total dissolved salts(TDS), electric conductivity(EC) biological oxygen demand(BOD), chemical oxygen demand(COD), dissolved oxygen(DO), total alkalinity, NO2-N, NO3-N, NH4-N, dissolved reactive phosphorus(DRP), total dissolved phosphorus (TDP), chlorides and heavy metals (iron, zinc, copper, lead, nickel, cadmium and manganese). The results shown significant ($P \leq 0.05$) increase in water pH (9.79± 0.01), NH4-N (185.76± 0.14 mg l-1), nitrate-N (1.95± 0.03 mg l-1), nitrite-N (2.93± 0.09 mg l-1), total alkalinity (1998.02± 0.03 mg CaCO3 l-1), dissolved oxygen (4.97±0.06 mg l-1), biological oxygen demand(18.05±0.02 mg l-1), chemical oxygen demand (18.9± 0.09 mg l-1), total dissolved salts(7.51±0.16 g l-1), EC(12.79±0.26 ms cm-1) and copper (0.339±0.002 mg l-1) in the winter, while DRP(0.39± 0.003 mg l-1), TDP (0.66± 0.002 mg l-1) and chlorides (3591.07±0.03 mg l-1) in summer. Thus, the high concentrations of chemical parameters investigated especially NH4-N and copper indicates the toxic state of the effluent discharged from (EFCI) company in winter season.

keywords Physico-chemical properties, industrial effluent, Ammonia toxicity.

1.Introduction

Water is among the most constituents that provide the Earth with the capacity of supporting life. It is regarded as our lifeline, which is required for all living things in the world. Water is obtained from two principal natural sources: surface water such as freshwater, lakes, rivers, streams, and groundwater such as borehole water and well water [1]

With an ever-increasing population and industrialization, the world faces a global water quality crisis in surface water resources as there are small fractions of world freshwater available for direct human consumption and other living organisms'uses. The other fractions are being contaminated enormously due to the high pollution rates by one or more of domestic effluent, agricultural activities and industrial effluents [2]

Industrial wastewater contamination is considered as being thieved issue in developing populated countries, particularly on natural water bodies that lie near to the industrial area resulting in various levels of pollutants that can be released directly into water through sewer line making such water resources unsuitable for drinking, irrigation, and aquatic life. The type of industrial pollutants varies depending on the type of industry, for example; the fertilizer industry generates massive amounts of wastewater containing high quantities of nitrogen-rich compounds, nitrate, and heavy metals whereas, discharging nitrogenous effluents into water bodies favors eutrophication and consequently hazards impact on aquatic life and human health [3].

Ammonia nitrogen is a common toxicant derived from industrial effluents that can exist in either ionized form (ammonium, NH_4^+) or unionized one (ammonia, NH_3). Increasing pH favors formation of the toxic ammonia (NH_3), while the decreasing favors NH_4^+ formation [4-6]. In this regard, NH_3 is documented to be more toxic than NH_4^+ as it can readily diffuse through the gill membranes of aquatic animals, causing growth inhibition, immune suppression as well as high mortality [7-9]. Moreover, the ammonium nitrogen assimilation process destroys the carbon and nitrogen balance in plants besides other autotrophic organisms[10].

In this concern, water quality assessment is an essential issue for estimating the toxicity of industrial wastewater on humans, animals and plants' life. Water quality is the physical state of water, including; temperature, concentrations of total suspended solids (TSS), colour, odor and turbidity besides chemical characteristics of water including; pH, biochemical oxygen demand (BOD), chemical oxygen demand (COD), nutrients (nitrate and phosphorus components), metals such as copper, zinc, cadmium, lead and mercury [11] in addition to biological quality assessment[12].

Based on this information, the present investigation aims to assess the degree of contamination of effluent from El-Delta for Fertilizers and Chemical Industries (EFCI) company based on physico-chemical properties and evaluate its toxicity using standard algal biotest.

2. Materials and methods

2.1 Study area

The wastewater which is receiving alkaline ammonia-rich industrial effluents from El-Delta for Fertilizers and Chemical Industries (EFCI) company which produces primarily nitrogenous fertilizers. The area is located about 2 Km north of Mansoura city (31° 04' 20.1" N, 31° 23' 57.5" E). The geographical location of this study area is shown in (Figure 1)

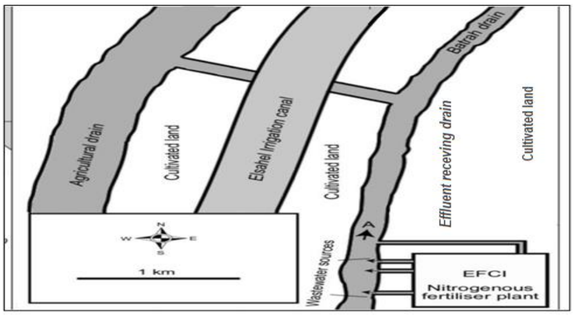

Fig .1. Schematic diagram showing the study area

2.2 The sampling program and sample preparation

Liquid samples were seasonally collected during the period from mid-spring, 2018 to mid-winter, 2019. Sample collection, handling, and processing were conducted according to EPA (1985). Four liters of each sample were filtered through GF/C glass fiber filters upon arrival to the laboratory. The first one liter was disposed of, and the others were stored at 4 ^oC in the dark to be used for distinctive chemical analyses

2.3 Field observation

Water temperature was measured using, YSI model 33 S.C.T. meter, electrical conductivity (EC) was measured directly using YSI model 33 S.C.T. meter, total dissolved salts (TDS) were measured directly using CORNING (Cole-Parmer model Check-mate 90). Hydrogen ion concentration (pH) was directly measured using a HORIZON ECOLOGY CO. PH meter Model 5995.

2.4 Chemical analyses

Biological oxygen demands (BOD_5), reactive silica, dissolved reactive phosphorus (DRP), chloride and total hardness, ammonia –N, total alkalinity as well as nitrate-N were estimated according to [13]. Also, nitrite – N was assessed following the method of [14, 15]. Total dissolved phosphorous (TDP), chemical oxygen demand (COD) were quantified according to [13] in addition to dissolved oxygen (DO), which was estimated by the modified method [16] as described by[17]. Heavy metals (iron, zinc, copper, lead, nickel, cadmium, and manganese) were analyzed following the direct aspiration into an air-acetylene flame using atomic absorption spectrophotometer type B U C K Scientific ATOMIC ABSORPTION SPECTROPHOTOMETER model ACCUSYS 211.

2.5 Statistical analysis

Values of each measurement represent the mean of three replicates ±SD.

3. Results and Discussion

3.1 Physical and chemical properties of the wastewater

3.1.1 Field observations

Field observations are listed in (Table 1) where water temperature exhibited a noticeable seasonal trend with the lowest value 17.97 ^{o}C recorded in winter and the highest 35.03 ^{o}C in summer with a mean annual value of (25.01±7.29 ^{o}C). The pH of water samples was almost alkaline with a mean annual value of (9.61±0.05), the highest value 9.79 was recorded in winter since, the lowest value 9.4 in summer. Electric conductivity (EC) showed a minimum value of 9.06 ms cm^{-1} recorded in summer, whereas the maximum value of 12.79 ms cm^{-1} was recorded in winter with a mean annual value of (10.84±1.61 ms cm^{-1}). Total dissolved salts (TDS) showed a minimum value of 5.87 g l^{-1} in summer, and the maximum one 7.51 g l^{-1}was measured in winter with a mean annual value of (6.62±0.75 g l^{-1})**.**

3.1.2 Laboratory analyses

Dissolved oxygen (DO) exhibited a minimum value of 2.06 mg l^{-1} that was recorded in summer and a maximum value of 4.97 mg l^{-1} in winter, with a mean annual value of (3.75±1.22 mg l^{-1}) (Table 1). Biological oxygen demand (BOD_5) values fluctuated between 14.89 ± 0.02 mg l^{-1} and 18.05± 0.02 mg l^{-1}, with an annual mean value of (16.27±1.37 mg l^{-1}). Its minimum value was recorded in summer and the maximum value in winter (Table 1). Chemical oxygen demand (COD) exhibited a minimum value of 15.02 mgl^{-1} was recorded in summer and a maximum value of 18.9 mg l^{-1} in winter, with a mean annual value of (16.69±1.7 mg l^{-1}) (Table 1).

Nitrite-N values ranged from 1.94 to 2.93 mg l^{-1} with a mean annual value of (2.53±0.42 mg l^{-1}), its minimum value was recorded in summer while the maximum value in winter. (Table 1). Nitrate-N concentrations ranged from 1.04 to1.95 mg l^{-1} with a mean annual value of (1.6±0.39 mg l^{-1}), the minimum value was recorded in summer, while the maximum value in winter (Table 1). Ammonium-N accounted for the major proportion of total soluble inorganic nitrogen (TSIN) whereas, the concentrations ranged from 177.32 to 185.76 mg l^{-1}, with a mean annual value of (182.07±3.6 mg l^{-1}), its minimum value was recorded in summer and the maximum value in winter (Table 1).

Dissolved reactive phosphorus (DRP) exhibited a minimum value of 0.31 mg l^{-1} was recorded in winter and the maximum value 0.39 mg l^{-1} in summer, with an annual average of (0.34± 0.04 mg l^{-1}) (Table 1). While total dissolved phosphorus (TDP) concentration ranged from 0.511 and 0.66 mg l^{-1}. The minimum value was recorded in winter and autumn, whereas the maximum value in summer with a mean annual average of (0.58± 0.08 mg l^{-1}) (Table 1).

N:P weight ratio is an important ecological parameter governing nutrient limitations (P and N) in aquatic ecosystems. Values ranged from 171.7 to 232.4, with a mean annual value of 205.2. The highest ratio was recorded in winter, and the lowest ratio was recorded in summer (Table 1).

Reactive silica concentration varied from 0.08 to 0.13 mg l-1 with mean annual value of (0.01±0.02 mg l^{-1}). The minimum value was recorded in winter and the maximum value in summer (Table 1). Chlorides minimum value 3508.35 mg l^{-1} was recorded in winter and the maximum value 3591.07 mg l^{-1} in summer with a mean annual value of (3552.36±39.08 mg l^{-1}) (Table 1).

Total hardness values ranged from 98.05 to 101.05 mg CaCO3 l^{-1} with a mean annual value of (99.79±1.5 mg CaCO3 l^{-1}), its minimum value was recorded in summer, but the maximum value in winter and autumn (Table 1). While the minimum value of total alkalinity 1948.05 mg CaCO3 l^{-1} was recorded in summer, and the maximum value 1998.02 mg CaCO3g l^{-1} in winter, with a mean of (1973.03±22.6 mg CaCO3 l^{-1}) (Table 1).

Regarding heavy metals, Iron concentration fluctuated between 0.06 to 0.149 mg l^{-1} with a mean of (0.113±0.039 mgl^{-1}), its minimum value was recorded in summer and the maximum value in winter (Table 2). Zinc

concentrations ranged from 0.052 to 0.150 mg l^{-1} with a mean annual value of (0.104±0.041 mgl^{-1}), its minimum value was recorded in summer and the maximum value in winter (Table 2). The lowest value of copper, 0.243 mg l^{-1} was recorded in summer, while the highest value 0.339 mgl^{-1} in winter with a mean value of (0.269 ± 0.05 mgl^{-1}) (Table 2). Lead concentration values ranged from 0.088 to

0.175 mg l^{-1}, with a mean annual value of (0.122±0.04 mgl^{-1}) its minimum value was recorded in summer and the maximum value in winter (Table 2). Nickel exhibited a minimum value 0.053 mg l^{-1} was recorded in summer and the maximum value of 0.142 mg l^{-1} in winter, with a mean value of (0.110±0.04 mgl^{-1}) (Table 2).Cadmium concentration values ranged from 0.031 to 0.065 mgl^{-1}, with a mean value of (0.047±0.02 mgl^{-1}), its minimum value was recorded in winter and the maximum value in summer (Table 2). Manganese showed the minimum value of 0.125 mg l^{-1} was recorded in winter and the maximum value of 0.222 mg l^{-1} in summer, with a mean value of (0.181±0.04 mgl^{-1}) (Table 2).

Table 1. Summary statistics of seasonal variations of physical and chemical water parameters investigated at Eldelta for fertilizers and chemical industries (EFCI) company (Spring 2018 – Winter 2019)

Parameter	**Unit**	**n[a]**	**Spring [b]**	**Summer [b]**	**Autumn [b]**	**Winter [b]**	**(Mean ± SD) [c]**	**Maxi.[d]**	**Min.[d]**
pH	-	4	9.51±0.02	9.4± 0.03	9.73± 0.02	9.79± 0.01	9.61±0.05	9.79	9.4
Water temperature	^0C	4	25.06±0.5	35.03± 0.06	21.97± 0.05	17.97± 0.06	25.01±7.29	35.03	17.97
Ammonium-N	mgl^1	4	181.76±03	177.32±0.03	183.42±0.03	185.76± 0.14	182.07±3.6	185.76	177.32
Nitrite-N	mg l^{-1}	4	2.54±0.03	1.94± 0.02	2.69±0.02	2.93± 0.09	2.53 ±0.42	2.93	1.94
Nitrate-N	mg l^{-1}	4	1.70±0.01	1.04± 0.03	1.71±0.03	1.95± 0.03	1.6 ±0.39	1.95	1.04
Dissolvedreactive phosphorus	mg l^{-1}	4	0.33±0.01	0.39±0.003	0.32±0.004	0.31± 0.009	0.34 ± 0.04	0.39	0 .31
Totaldissolved phosphorus	mgl^{-1}	4	0.62±0.05	0.66± 0.002	0.514±0.003	0.511±0 .02	0 .58± 0.08	0.66	0.511
N:P weight ratio		4	195.8	171.7	220.9	232.4	205.2±27.1	232.4	171.7
Reactive silica	mg l^{-1}	4	0.12±0001	0.13± 0.002	0.09±0 .002	0.08±0 .006	0.01 ±0 .02	0.13	0.08
Total alkalinity	$mgCaCO_3l^{-1}$	4	1961.01±002	1948.05±0.3	1985.03±0.03	1998.02±0.03	1973.03±22.6	1998.2	1945
Total hardness	$mgCaCO_3 l^{-1}$	4	99.02±o.3	98.05±0.02	101.047±0.05	101.05± 0.05	99.79±1.5	101.05	98.05
Chlorides	mg l^{-1}	4	3578.79±0.04	3591.07±0.3	3531.22±0.03	3508.35± 0.02	3552.36±39.8	3591.7	3508.5
Dissolved oxygen	mg l^{-1}	4	3.85±0.03	2.06± 0.02	4.11±0.02	4.97±0.06	3.75±1.22	4.97	2.06
Biologicaloxygen demand	mgl^{-1}	4	15.57±0.2	14.89± 0.02	16.55± 0.03	18.05± 0.02	16.27± 1.37	18.05	14.89
Chemicaloxygen demand	mg l^{-1}	4	15.97±0.6	15.02± 0.02	16.87± 0. 04	18.9± 0.09	16.69±1.7	18.9	15.02
Total dissolved salts	g l^{-1}	4	6.15±0.06	5.87± 0.08	6.93±0.06	7.51±0. 16	6.62±0.75	7.51	5.87
Conductivity	$mscm^1$	4	10.13±0.22	9.06± 0.08	11.36 ±0.22	12.79±0.26	10.84±1.61	12.79	9.06

4. Discussion

Physico-chemical assessment of water quality of any aquatic ecosystem is a very effective issue in assessing water quality and status. Consequently, seasonal variations of some reliable and pertinent water quality physico-chemical parameters were investigated along the study area during one year, the idea was to assess the seasonal variation of water quality during one year. The parameters included water temperature, pH, conductivity, TDS, BOD, COD, DO, total hardness, total alkalinity, chloride, NO_2-N, NO_3-N, NH_4-N, DRP, TDP, reactive silica, and some heavy metals were highly recommended as reliable and pertinent water quality measures[13, 18].

It is relevant to mention that the study area is a wastewater receiving drain that receives alkaline-ammonia-rich industrial effluents from El-Delta for fertilizers and chemical industries (EFCI) company that produces mainly nitrogenous fertilizers (Figure 1).

It's evident from data presented in Tables 1 and 2 that all effluent measurements are seasonality dependent. The results showed significant ($P \leq 0.05$) increase in water pH, conductivity, TDS, BOD, COD, DO, total hardness, total alkalinity, NO_2-N, NO_3-N, NH_4-

N. Also all the heavy metals increased in winter except manganese and cadmium which showed the maximum value in summer. The present results are in harmony with those obtained by [19, 20]. It has been reported that variation in physical and chemical parameters of industrial effluent is dependent on seasonality and industrial activity that might be high in winter, besides Egypt climate, which characterized by low precipitation during months of winter, leads to more concentrated effluent [21-24].

Table 1 indicated that water of the investigated area is alkaline with a pH range of 9.4-9.79 and total alkalinity range of 1948.05-1998.02 mg $CaCO_3$ l^{-1}, which may be attributed to the high concentration of ammonium-N discharged by the industrial activities, which reflects the high degree of the effluent deterioration. In this concern, pH is considered one of the most important factors affecting water quality, solubility, and toxicity of various water substances. Moreover, the increase in pH decreases the availability of free CO_2 and consequently, the presence of photosynthetic organisms like algae is significantly reduced [25].

A marked increase in the ammonium-N concentration of the effluent (Table 1) was observed during the study period especially in winter, the values ranged from 177.32 to 185.76 mg l^{-1}. The high concentrations of NH_4-N investigated signified an inferior and toxic state of the area of study. Our results are in harmony with those obtained in the same study area [20]. It has been reported that free ammonia at high pH is very toxic to aquatic biota than when it's in the oxidized form, reflecting the grossly polluted conditions of this effluent [26].

As revealed from current results (Table 1), the dissolved oxygen concentration of the effluent was relatively low during the year of the study. In this regard, the insufficient dissolved oxygen in the water affecting the biochemical oxidation of ammonia to nitrate and nitrite [27]. This assumption accommodates with the results of the low concentrations of nitrate and nitrite during the study. On the other hand, the COD and BOD results were relatively high during the year of study. This may contribute to the increased oxygen demand for the degradation of the organic wastes discharged, which led to depletion in dissolved oxygen.

As seen from results in Table 1, the concentration of the available phosphate-phosphorus (TDP) ranged between 0.511 and 0.66 mg l^{-1}, the minimum values recorded during the winter. Phosphorus determination is essential in measuringwater quality because of being a key element in eutrophication problems. In this study, the mean value of the TDP of the effluent is relatively higher as TDP value of any stream should not exceed 50 µg l^{-1} [28].

Since nitrogen and phosphorus are the primary limiting factors in eutrophication problems [29], it seems critical to calculating the N:P weight ratio of the effluent according to its importance as an ecological parameter governing nutrient limitations (N and P) in aquatic ecosystems. The results listed in Table 1 indicated that the maximum N:P ratio 232.4 recoded in winter, which proved that the effluent is highly rich in inorganic nitrogen (NH_4-N) than phosphorus.

The effluent’s heavy metal concentrations exhibited seasonal fluctuation (Table 2), demonstrating marked increase in Copper concentration in winter (0.339 mgl^{-1}), which indicates high involvement of Cu-rich materials in the industrial activities reflecting high contaminated study area. It has been widely known that heavy metals concentrations in surface water and sediments are influenced by source impute, the character of sediment, organic materials, temperature, and sometimes the mineral composition of underlying rock in the area where the surface water situated [30] .

Conclusion

Finally, it can be concluded that values of physico-chemical parameters investigated from Eldelta for fertilizers and chemical industries (EFCI) company raw effluents are seasonality dependant. The higher concentrations NH_4-N and copper indicated the potential toxicity of wastewater

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