QUALITY ASSESSMENT AND POTENTIAL ADVERSE IMPACT OF NUTRIENTS IN KHARTOUM REFINERY EFFLUENTS

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Abstract - This study assessed the effluent quality of Khartoum petroleum refinery in terms of nutrients (nitrogen, N and phosphorus, P) by testing the treated monitoring pond (MP) effluent on the basis of limitation guidelines, evaluated oxidation ponds (OPs) performance and investigated potential impact on the surrounding area in Khartoum North locality, Khartoum state, Sudan. Data analysis showed $T_{increase}$, NH_3– N and P_{total} quality parameters do not comply with the standard limits, whereas pH, NO_3–N, NO_2–N and P_{ortho} are in accordance. Average removal efficiency in oxidation ponds for $T_{increase}$ and NH_3–N was 100 and 97.23 %, respectively. In contrast, pH, NO_3–N, NO_2–N, P_{ortho} and P_{total}, increased by 1.80, 5900, 1284.60, 893.60 and 118.90 %, respectively. This study revealed possible groundwater contamination or adverse impact on the surrounding soils and farms through leaching or rain runoff. Thus, effluent management improvement is required and closer monitoring including the fate of contaminants is recommended.

Keywords - Groundwater, Nutrients, Oxidation ponds, Petroleum refinery effluents.

I. INTRODUCTION

Potential environmental hazards associated with petroleum refinery effluents (PRE) have attracted the attention of researchers and close proximity communities. Petroleum refineries consume large amounts of water [1], [2], consequently generate large volumes of effluents [3]-[5], with varying characteristics depending on the type of crude oil and complexity of refining process [1], [6], but in general comprising various inorganic, organic, nitrogen, and phosphorus compounds [1], [3]-[5], [7]. Discharge of ineffectively treated PRE leads to severe environmental impacts [3], [5]-[11], therefore, they require sufficient treatment and continuous monitoring [9] to meet the established regulations quality. Among the constituents of PRE often targeted for regulation and monitoring are nutrients: ammonia, nitrate, nitrite and phosphorus, which highly contribute to pollution load in PRE as reported by many authors [3], [5], [7]. Nutrient loading causes eutrophication in water bodies with consequences such as algal blooms, reduction in biodiversity, alteration of ecosystem services, and toxicity [12]-[14]. For example, ammonia is toxic to aquatic organisms [15], [16] and contributes to eutrophication resulting in oxygen deficiency. High nitrate concentrations are toxic to aquatic organisms, develop eutrophication, and, in drinking water, has been linked to various illnesses including, cyanosis, certain types of cancers, spontaneous abortions, thyroid disorders and diabetes [17]–[20]. Nitrite is highly toxic and responsible for methemoglobinemia (cyanosis) and also is suspected of causing certain cancers through the formation of nitrosamines [17]. In regards to soil, [21] reported that chronic high N inputs lead to several negative impacts, such as soil acidification, nutrients imbalance, soil microbes disturbance which affects soil fertility, and increased greenhouse gas emissions. Excess P inputs can cause eutrophication in water bodies leading to several other negative impacts [13], [22].

However, it is difficult to predict the fate of these pollutants in the environment, for example it is extremely complex to determine the environmental fate of ammonia because of the complexity of nitrogen cycle, nitrification factors (e.g., pH, temperature) and the physical behaviour of ammonia (e.g., volatilization, adsorption) [15]. The fraction of unionized ammonia (NH_3) in water, and hence the toxicity of ammonia, is positively influenced by pH and temperature [15], [16].

Khartoum refinery is the largest refinery in Sudan started processing 50,000 bbl/d of Nile blend crude in 2000 and expanded later to 100,000 bbl/d in 2006. The wastewater treatment system (300 m^3/h capacity) consists of API oil separator, dissolved air floatation uses aluminum chloride, activated sludge system and mechanical filter. The treated effluent is conveyed to the monitoring pond (MP) and then pumped into a series of oxidation ponds (OPs) outside the refinery. Although this poses a high risk of environmental pllution, only a few studies examined the effluent quality focusing only on the raw and MP effluents. Furthermore, the potential environmental impact has not previously been investigated.

Thus, the objectives of this research were (1) to assess the refinery effluent quality by comparative measurement of temperature ($T_{increase}$), pH, ammonia (NH_3–N), nitrate (NO_3–N), nitrite (NO_2–N), orthophosphate (P_{ortho}), and total phosphorus (P_{total}) in MP effluents (2) to evaluate OPs performance and (3) to investigate the potential impact of these pollutants on the surrounding environment by utilizing

geological, geographic, and topographic data and conducting field survey. The study will provide data base to mitigate negative impacts, thereby protecting the environment and human health, and enhance the effluent management in the study area. From other point of view, since there were no sufficient data to study the OPs performance, the study therefore, provided an opportunity to evaluate monitoring methodologies in such ponds environments.

II. MATERIALS AND METHODS

A.Study Area

The study area is a typical rural region situated between 15°48'–16°09' N and 32°34'–32°42' E in Khartoum North Locality of Khartoum State. The area (Fig. 1), comprises Khartoum refinery, Algaili town, and many villages along the eastern bank of the River Nile including farm sites. The refinery (16°07'44.5"N, 32°41'20.0"E, 412 m average elevation) is 65 km north of the capital city of Khartoum, 17 km north-east of Algaili Town , 12 km east of the River Nile and surrounded by many environmentally sensitive sites such as Wadramli Agricultural Scheme (10 km West) (Fig. 2).

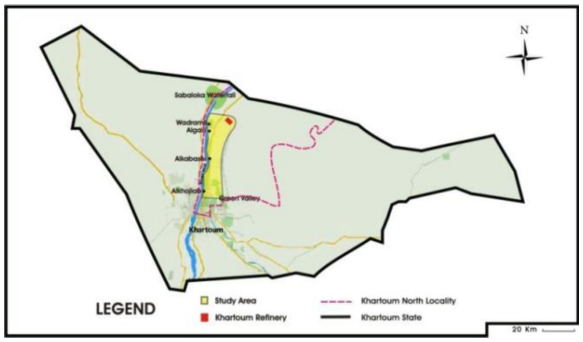

Fig. 1: Map of Khartoum State showing Khartoum refinery in the study area.

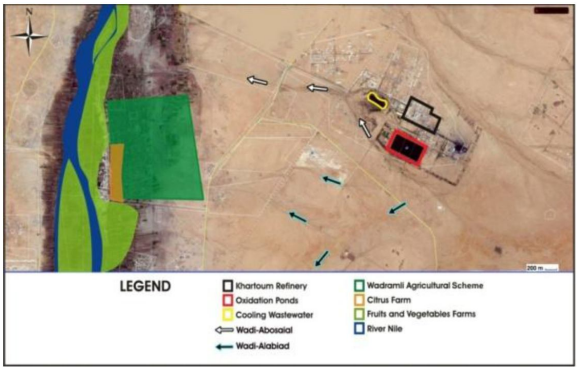

Fig. 2: Location map of Khartoum refinery and most near by environmentally sensitive sites, also the drainage streams can be seen.

The inhabitants are mostly engaged in agriculture, grazing, and poultry farms; therefore supply the capital city, Khartoum, with vegetables, fruits, dairy products, and poultry eggs and meat. The area is flat containing some isolated hills, rocky exposures and soil cover [23]. The whole area slopes gently to the west and drains into farm sites and the River Nile in a dendritic pattern as long shallow streams through which the area drams during the rainy seasons. These streams drain from high ridges in the east crossing the refinery site towards the west (Fig 2). The climate is dry semi-desert with low rainfall (200-300 mm average) in summer and cold dry winter. The maximum temperature reaches 45^0C in summer and declines to 31^0C in winter.

B.Sampling and Sampling Site

Effluent samples were collected from the MP and OPs (Fig. 3). MP was sampled three times on diverse dates; at 8 h intervals/d composited and analyzed for NH_3–N and P, this is repeated for three days, and composites of three days grabs were analyzed for NO_3–N and NO_2–N. Samples were taken from the center and near the two terminals below the surface.

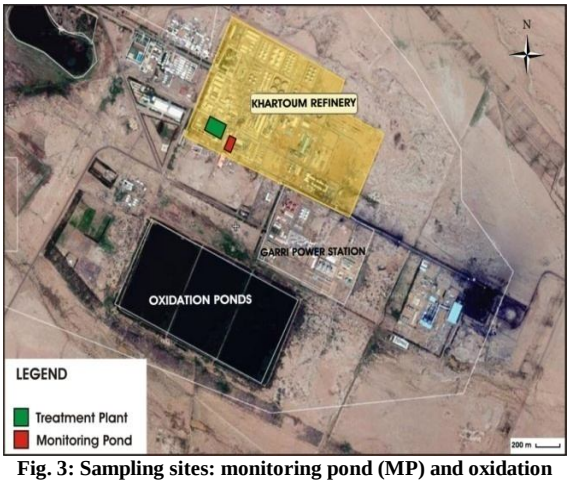

Fig. 3: Sampling sites: monitoring pond (MP) and oxidation ponds (OPs), the treatment plant can also be seen.

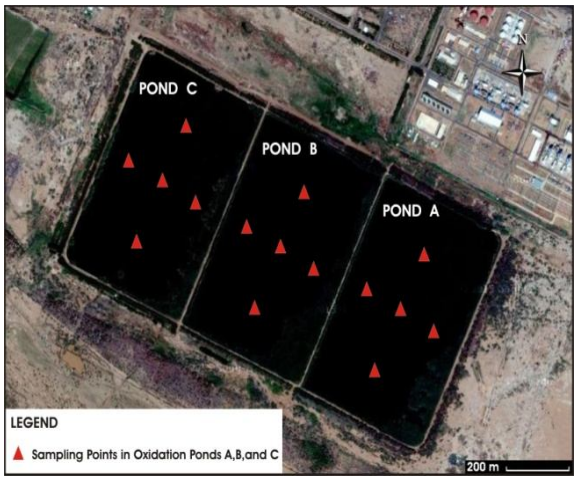

Fig. 4: Sampling points in the oxidation ponds (OPs).

The individual OPs (650 m x 420 m x 2-3 m water depth) were sampled from the surface, one-half the total depth, and the bottom at five points (Fig. 4) (composite of 15 grab samples each pond) using a

manual sampler provided with a glass bottle. The glass sampler and containers were decontaminated and labled, samples were preserved on site using analytical reagent grade chemicals and reagents and kept in ice (4°C) [24] before being transported to the laboratory for analysis.

C.Analyses

Effluent analyses were conducted at the Central Petroleum Laboratories (CPL), Khartoum, and the Water and Environment Laboratory, Khartoum refinery. For quality assurance all chemicals and reagents used were of analytical reagent grade. Contaminations were checked by running blanks and deionized distilled water was used throughout the experiments. Samples were analyzed by HACH DR/4000U spectrophotometer, CAMLAB limited, Cambridge for NH_3–N, NO_3–N, NO_2–N, P_{ortho}, and P_{total} , follow standard methods for the examination of water and wastewater [25]. Temperature and pH were measured immediately on site, by a mercury thermometer and a pH Ultrameter 6P, Myron L Company, Carlsbad , USA, respectively. All readings were made in duplicates and the average was taken.

III. RESULTS AND DISCUSSION

The data in the tables were compared with the effluent limitation guidelines, if specified, of the Ministry of Energy and Mining (MEM), Sudan [26], Environment Department of the World Bank (WB) [2], and the International Finance Corporation (IFC) of the World Bank Group [27]. The results were also compared with the Food and Agriculture Organization of the United Nations (FAO) guidelines for irrigation water [28] and the World Health Organization (WHO) guidelines for drinking water [29] to assess the effluent in terms of irrigation quality and suitability for discharge into freshwater bodies, respectively.

A. Assessment of the Effluent Quality

As shown in Table I, it is evident that MP effluent has quite high average $T_{increase}$,NH_3–N, and P_{total}, but acceptable pH and low levels of NO_3–N, NO_2–N, and P_{ortho}.

$T_{increase}$ ranged 7.5 –16°C and has high average value of 12°C above the WB standard limit of ≤ 3°C. This effluent could affect ecosystem composition, increase eutrophication rate, and increase toxicity of some compounds to aquatic life. Therefore, the effluent is not suitable for discharge into natural water bodies. The pH was alkaline ranging 7.9 – 9.45 and has an average value of 8.47 within the Sudanese standards and the WB standards, both of 6–9, but slightly higher than the guidelines for irrigation (6.5-8) [28], and higher than the findings of other authors in other countries [4], [7]. The reason for alkaline pH could be the inefficient pH control or insufficient neutralization of sour water and spent caustics.

Total ammonia–N (TAN) was fluctuating between 16.81 and 204.55 mg/L with an average value of 82.19 mg/L suggesting poor performance of the biological treatment unit where the most amount of N removal occurs [30]. The average value exceeded the Sudanese standard limit of 15 mg/L and was about 8 times above the WB guideline value of 10 mg/L (set for total N). The acute (1-h average) and chronic (30- day rolling average) aquatic life criteria for TAN in freshwater at pH 7.0 and 20°C, 17 and 1.9 mg/L respectively [16], were highly exceeded by the average TAN in the present study. The value was also higher than found in other studies in diverse countries [30]–[33]. Moreover, the calculated unionized (toxic form) ammonia–N (NH_3–N), as a function of pH and temperature [15], ranged from 2.47 to 162.54 mg/L with an average value of 55.93 mg/L (68.05 % of the TAN), which was expected in such hot alkaline effluent. This amount of NH_3–N is very much above the recommended criteria level of 0.016 mg/L NH_3–N for the protection of freshwater aquatic life in Canada [15]. In light of the above discussion, it is obvious that the effluent was poorly managed with respect to ammonia, and demonstrated significant toxic nature, therefore, it may greatly harm any receiving water body.

Table I : MP variables and compliance with PRE dischargecriteria, all units in (mg/L) except $T_{increase}$ (°C) and pH

Parameter	Average	MEM	WB/ IFC
$T_{increase}$	12.00	NS	≤ 3
pH	8.47	6 − 9	6 − 9
NH_3– N	82.19	15	TN=10
NO_3–N	0.01	NS	NS
NO_2–N	0.0026	NS	NS
P_{ortho}	0.48	NS	NS
P_{total}	2.64	NS	2.00

The average values of NO_3–N (0.01 mg/L, 0.0443 mg/L as NO_3^-) and NO_2–N (0.0026 mg/L, 0.0085 mg/L as NO_2^-) were far below the WHO recommended criteria levels of 50 mg/L (as NO_3^-) for short- term exposure and the tolerable limit of 3 mg/L (as NO_2^-), respectively. Also, the average nitrate was lower than the canadian aquatic life freshwater criteria of 13 mg/L as NO_3^- [34]. In addition, the effluent can be considered safe for use in agriculture in terms of nitrate which falls within the class of no restriction on use for irrigation (< 22 mg/L as NO_3^-) [28] . Low nitrate and nitrite levels suggest inefficient nitrification in the biological treatment unit. This inverse relationship between ammonia and nitrate levels was documented by [33] in UK. However, NO_3–N in the effluent was lower than that obtained in different countries as reported by [7], [30], and [32].

The results indicated P_{total} ranging from 1.45 to 4.25 mg/L with an average value of 2.64 mg/L, and P_{ortho} in the range of 0.057 to 1.28 mg/L and average value of 0.48 mg/L. The average P_{total} exceeded the WB/IFC guideline value of 2.00 mg/L and higher than the value recorded by [31], while P_{ortho} was lower than the value obtained by the same author. However, P released in Khartoum refinery effluent needs greater care.

B. Performance Evaluation of Oxidation Ponds

OPs are simple, economic, sustainable, and natural waste treatment and disposal method, specifically in hot climate regions. In many developing countries such as Sudan most refineries in rural areas where large land area is available have adopted this method. OPs in Khartoum refinery is a complete retention system in which the effluent flows by gravity through anaerobic, facultative, and maturation ponds, respectively in series. Table II shows the average results in the decrease or increase of OPs sysyem variables. The compliance of the final effluent is presented in Table III.

$T_{increase}$ removal efficiency for ponds A, B, and C were 50, 100, and 100 % , respectively. High pH was obtained through the system by intense algal photosynthetic activity. This pH increase diminished gradually from 28.7% in pond A to 1.8% in pond C within the acceptable discharge limits, but still above the FAO guideline for irrigation. 83 % of the NH_3–N was removed in pond A followed by 14.5 % extra purification added by pond B. Nevertheless, removal efficiency slightly decreased to 97.23 % in pond C , below the standard limits, may be due to effluent bypass from MP to pond C on many occasions or release of ammonia from settling organic solids at the anaerobic layer. In contrast, NO_3–N and NO_2–N levels were increasd by 429900 and 47592 %, respectively in pond A due to nitrification, then this increase declined to 11900 and 6053.8 %, and 5900 and 1284.6 % in ponds B and C, respectively. This decline can be explained by denitrification and algal uptake, but NO_3–N and NO_2–N concentrations were still higher than the influent. However, considering these results and the environmental factors (temperature, pH and mixing), it seems that nitrification and volatilization were the preferred ammonia removal pathway.

The P content was expected, although not effectively, to decrease in the OPs by sedimentation, and algal uptake. Instead P_{ortho} and P_{total} were increased by 889.6% – 918.8% and , 118.9 % – 143.6%, repectively suggesting desorption from sediment redox-sensitive iron hydroxides enhanced by pH increases, and release from organic sinks [22]. Moreover, the increase of P_{ortho} was more than 4 times the increase of P_{total} probably because of the inorganic dominating nature of the P released from sediments [22].

However, P_{ortho} and P_{total} (4.77 and 5.78 mg/ L, respectively) were higher than the WB standard limits for PRE discharge and the maximum permissible limit of P content in irrigation water set by the FAO, both of 2.00 mg/L, therefore, the effluent fits with neither discharge into freshwater nor irrigation with respect to P.

Table II : Performance of OPs system (% Removal or increase)

			E F F L U E N T S					
			Pond A		Pond B		Pond C	
Parameter (units)		Influent	Average	Efficieny	Average	Efficiey	Average	Efficiency
$T_{increase}$	(°C)	12.00	6.00	50 %	0.00	100 %	0.00	100 %
pH		8.47	10.90	28.70 %*	10.15	19.80 %*	8.62	1.80 %*
NH_3– N	(mg/L)	82.19	14.00	83.00 %	2.08	97.50 %	2.28	97.23 %
NO_3–N	(mg/L)	0.01	43.00	429900%	1.20	11900 %*	0.60	5900 %*
NO_2–N	(mg/L)	0.0026	1.24	47592 %*	0.16	6053.8 %*	0.036	1284.60 %*
P_{ortho}	(mg/L)	0.48	4.89	918.80 %*	4.75	889.60 %*	4.77	893.60 %*
P_{total}	(mg/L)	2.64	6.43	143.60 %*	5.93	124.60 %*	5.78	118.90 %*

* = % increase

Table III : Compliance of the final effluent in OPs system, all units in (mg/L) except $T_{increase}$ (°C) and pH

	LEGISLATED		*MEASURED*
Parameter	**MEM**	**WB/ IFC**	**Final effluent (Pond C)**
$T_{increase}$	NS	≤ 3	0.00
pH	6 – 9	6 – 9	8.62
NH_3– N	15	TN=10	2.28
NO_3–N	NS	NS	0.60
NO_2–N	NS	NS	0.036
P_{ortho}	NS	NS	4.77
P_{total}	NS	2.00	5.78

Based on this discussion, dredging ponds can mitigate reverse migration of P from the sediments, thus, improve the performance.

IV. POTENTIAL IMPACT

Potential environmental impact could be due to three main problems; mostly malfunctioning OPs (increase of P and most N species) due to mismanagement, construction defects reflected in lack of ponds liners

and fence, and improper location exemplified by the situation of the ponds in the course of seasonal streams on sloping area frequently affected by floods. Lack of liners has led to visible seepage in the vicinity of the ponds. Considerable effluent loss from seepage may occur depending on the effluent quality and soil properties as reported by many authors [35]. This main disadvantage of OPs [36] is well documented leading to nitrate contamination of groundwater [37], [38]. In addition, the ponds may overflow during periods of heavy rainfall leading to discharge of insufficiently treated effluent directly to nearby land. However, NO_3^- as negatively charged ion is more soluble and more prone to leach into groundwater than P which tends to be adsorbed on soil [13], [37] . Also as an open (unfenced) water body, OPs can be accessd by people and animals, therefore, there is some potential danger [35]. N and P can be washed by the seasonal streams when they cross the unprotected OPs area. It is important to remember that the area is flat gently sloping westward with a poor green infrastructure to slow down the runoff. In fact, this runoff was observed reaching the western part where the River Nile, farms and many villages are located. However, the runoff quality will be improved by soil filtration depending on the soil properties where P is strongly retained in the surface layer and ammonia is nitrified in aerobic soils to nitrite which, owing to its instability, will be oxidized to nitrate. Nitrate is stable and freely mobile although soil organic matter delays its movement [37]. But, however, land slope and lack of sufficient vegetation will increase surface runoff resulting in lower purification efficiency. Therefore, this may, by cumulative effect, create status of nutrient enrichment along the pathway and at the farm sites if it adds to fertilizer usage. Cosequently, soils and farms could be affected and may cause diffuse pollution to waterbodies. In view of OPs performance, there is need for proper management and closer monitoring of effluents in order to protect the surrounding environment and human health.

CONCLUSION

The treated MP effluent did not comply with petroleum refinery effluent criteria in terms of $T_{increase}$, NH_3–N, and P_{total} suggesting poor nitrification and insufficient P removal. OPs system proved effective in removing $T_{increase}$ and NH_3–N but increasd NO_3–N, NO_2–N, P_{ortho}, P_{total}, and pH values. Therefore, if the system continue to malfunction, it may act as pollution source rather than treatment system, leading to ptential groundwater contamination through infiltration, and surface runoff pollution to nearby soils and farms. Thus, the whole effluent needs better management and regular monitoring icluding the insite treatment and OPs system. OPs is recommended to be dredged, lined, fenced, and not receive bypass effluents. Costruction of monitoring wells in the periphery of OPs and sufficient training of the workers are strongly recommended.

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