Environmental Sustainability Study of Refinery Wastewater System Using Pinch Technology

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Abstract: Pinch technique was employed to study the potential of environmental sustainability in a Nigerian Refinery wastewater system. This was achieved by considering nine major water using units: cooling tower, ion exchangers, laboratory, SWS Desalter, FCC SWS, caustic treating, in-house water, fire service and boiler blowdown. In each of the operations, the water flowrate, and the inlet and outlet contaminants concentration were determined. The Pinch analysis software plotted the concentration interval diagram for quick determination of the mass load, cumulative mass load and the pinch point. The water pinched at BOD of 110ppm with average outlet contaminant concentration of 210ppm. About 50% reduction was observed for required fresh water flowrate after the water reuse optimization. Wastewater generation was also reduced by 38% considering reuse technique and 49% for regeneration reuse option. The final regeneration outlet concentration obtained was found to be 48ppm and within acceptable environmental standard.

Keywords: Pinch technology, wastewater, sustainability, optimization, refinery, pollution

دراسة الاستدامة البيئية لنظام الصرف الصحي في المصفاة باستخدام تقنية القرص

الملخص: تم استخدام تقنية القرص لدراسة إمكانات الاستدامة البيئية في نظام الصرف الصحي النيجيري لمصفاة التكرير. وقد تم تحقيق ذلك من خلال دراسة تسع وحدات رئيسية تستخدم المياه: برج التبريد، والمبادلات الأيونية، والمختبر، ومحلل SWS، وFCC SWS، ومعالجة المواد الكاوية، والمياه الداخلية، وخدمة الحريق، وتطهير سخانات المياه. في كل عملية من العمليات، تم تحديد معدل تدفق الماء وتركيز ملوثات المدخل والمخرج. قام برنامج تحليل القرص برسم مخطط فاصل التركيز لتحديد سريع للحمل الكتلي وحمل الكتلة التراكمي ونقطة الضغط. الماء المضغوط عند الطلب البيوكيميائي للأوكسجين ١١٠ جزء في المليون مع متوسط تركيز ملوث للمخرج ٢١٠ جزء في المليون. لوحظ انخفاض بنسبة ٥٠٪ تقريبًا في معدل تدفق المياه العذبة المطلوبة بعد تحسين إعادة استخدام المياه. كما تم تقليل توليد المياه العادمة بنسبة ٣٨٪ بالنظر إلى تقنية إعادة الاستخدام و٤٩٪ لخيار إعادة استخدام التجديد. وجد أن التركيز النهائي لمخرج التجديد الذي تم الحصول عليه هو ٤٨ جزء في المليون وضمن المعايير البيئية المقبولة.

1.Introduction

Water Pinch analysis can be applied for the optimal and more beneficial usage of process water (including wastewater) in process utility. It is the mass analogy to optimization of heat exchangers network via thermal Pinch analysis (Linnhoff et al., 1990). The idea of water pinch technology has been bought by many industries; especially oil refineries and the report have it that the volume of fresh water demand has been reduced from 60% to approximately 25% (Abubakar, 2016). The graphical the rigorous mathematical optimization approaches are usually applied in Pinch analysis processes. Pinch analysis consists mainly of two steps which are targeting and design. Targeting is a method of locating the water pinch, the minimum fresh water flow rate, and this is done before the network design or modifications. Composite curves/source and sink/purity profiles as well as excess water diagram with water cascade as a supplement can be displayed in a graph with the help of Pinch software (Wang and Smith, 1994).

Fresh water usage and capacities alongside the resultant wastewater in industries is being minimized with the help of Pinch analysis. This is important because it helps companies through systematic and technical analysis of water to meet the ever-increasing demand for fresh water and the stringent regulations for treatment and release of wastewater to the environment. The optimal reuse and regeneration of water including opportunities for effluent treatment can be identified with advanced algorithms in Pinch analysis. Reduction in feedstocks as well as recovery of economic products in outlet streams have been attributed to use of Pinch analysis (Lahnsteiner et al., 2012).

According to (Wang & Smith, 1994), wastewater optimization can be carried out in four ways;

1. **Changes in Process:** This involve process reconfiguration aim at inherent water demand minimization, a clear illustration of this is the conversion of wet cooling tower to dry air coolers.
2. **Water Reuse:** Water effluent from one process can be used in other process without any treatment if the quality of that water is considered fit for the other operations without compromising the quality requirement of the operations. This technique dose not only reduced the volume of the fresh water require but also reduce the volume of the waste water generated which in turn reduce the environmental contaminations and also reduction in overall operational cost.
3. **Regeneration reuse:** Wastewater can be regenerated by subjecting it to one or two water treatment processes to completely or partially reduce the level of contamination that

made it unfit to be reused in other water using processes. The mass-load of contaminants as well as the volumes of required fresh water and wastewater can be minimized by regeneration. (Khezri et al., 2010)

4. Regeneration Recycle: Wastewater quality can be improved by regeneration by suggesting the waste water through one on two treatment processes so that it can be recycled. In regeneration recycle, the regenerated water may be reused in other water using activities where the water stream was previously used. The introduction of the concentration interval diagram as well as the concentration composite curve, the concentration interval diagram and the freshwater pinch usually helps with the analyses. The work of Wang and Smith (1994) was used to calculate the lowest flow rates of both fresh inlet water and that after regeneration process.

In a typical oil refinery, over 2,000 products can be extracted from crude oil by using several unit operations including distillation, cracking, alkylation, in addition to polymerization, coking, hydrotreating, and others. In most of these processes, wastewater is been generated daily in the refining process which is based on the operations that produce the polluted water. Wastewater is mainly grouped as process and non-process types. The wastewater from the refining operations that has been in touch with the hydrocarbons is called is known as the process type while those from surface water runoffs, washing of machines, storage and office facilities as well as cooling towers is called non-process wastewater (Al-Shamrani et al., 2002). The streams usually given separate treatment for best outcome for the avoidance of pollution by harsh contaminants in substantial volume of water (Peng et al., 2008). Process wastewater is the result of the presence of water as suspension or emulsion when crude oil is produced from oil wells (particularly aging ones) and transported to the refinery (Edomwonyi-Otu and Angeli 2019, 2015). Moreover, liquid or gaseous water is also used specifically for enhanced oil recovery processes in aging wells (Cheryan and Rajagopalan, 1998). The application of gaseous and liquid water as a diluent and as a stripping fluid in distillation, cracking and desalting operations contributes to the amount of process wastewater in refineries (IPIECA, 2010).

The formation of oil layer in water bodies resulting from discharged wastewater that contains oil and grease is a source of danger to the aquatic life. This oil layer reduces the amount of light that can penetrate to maintain production of oxygen and other photosynthetic activities. The population of the ecosystem is also negatively impacted as the amount of oxygen that can be dissolved from the surrounding air is drastically reduced by the oil layer. Nacheva (2011) and Chao & Liang (2008) further confirmed that the health of the environment and life in general is at risk because of the poisonous nature of the compounds in the oil-contaminated water that has been unabatedly discharged to the environment. Some of the compounds in the oil-contaminated water include phenols, benzene, ethylbenzene, xylenes, sulfides, as well as suspended solids (SS), ammonia and other polyaromatic hydrocarbons (PAH)(IPIECA, 2010). The chronically toxic nature of phenols when consumed even in small amounts has bee known to result in impairment of sight, diarrhea, mouth souring and dark urine people in addition to life threatening consequences for aquatic life (Andreozzi et al., 1999). More worrying is the fact that the solubility of the compounds in water can serve as a ready media for the synthesis of even more toxic substances (Guerra et al., 2011). Bathing or showering with oil-contaminated water can result in the absorption of benzene, toluene, ethylbenzene and xylenes (BTEX) into the body through the skin leading to anemia and cancer. The presence of ethylbenzene, xylene and toluene in the body can cause improper functioning and damages to the liver, kidney and the nervous system (Peng et al., 2008).

The usual refinery practice for wastewater discharge to water bodies follows a two-step process to eliminate suspended oil from the accumulated wastewater. This is accomplished with the help of API separators and then the dissolve air flotation (DAF) unit. The equalization system receives the water from the secondary oil/water separation unit and levels out its concentration. The effluent from the equalization unit is then fed to the aeration tank clarifier for biological treatment and finally to tertiary treatment before release (Guerra et al., 2011). Products from the refinery include; liquefied petroleum gas (LPG), automotive gas oil (AGO), premium motor spirit (PMS), kerosene, fuel oil, sulfur. The lubrication oil complex produces base oils, asphalt/bitumen and waxes (KRPC, 2002) as additional products.

1.1 Objectives

The objective of this work is the application of water pinch analysis to Kaduna Refining & Petrochemical Company (KRPC) water management system. This system will reduce the KRPC freshwater demand that has resulted in a lot of water diversion from the Kaduna River. It will also reduce the amount of wastewater generation which are usually discharged into the environment without due regard to the attendant consequences.

2. Materials and Methods

2.1 KRPC Water Supply System: The following steps were taken to carry out the pinch analysis: KRPC water distribution network was analyzed from their water facility beside River Kaduna at Kamazo. The water then undergoes screening to remove solids debris, wooden piece etc, and thereafter sent through 13km network of pipes to a 750m^3 reservoir. It is then sent to clarifiers A, B and C, and then to the high rate filters, cooling tower, service water, ion exchange and to the activated filtration system before it is certified to be drinkable. The flowrate of water to the cooling tower, ion exchange, laboratory, desalter, fluid catalytic cracker (FCC), caustic treating, in-house, fire service and boiler blow down were obtained. The inlet and outlet water samples were collected from each of the unit using cleaned fresh plastic bowls that were properly rinsed with both tap and distilled water at least twice. The samples were then labeled appropriately and transported to the laboratory where it was refrigerated at 4^0C prior to analysis.

The parameters of the raw water determined were chemical oxygen demand (COD), conductivity, total hardness, biological oxygen demand (BOD), turbidity and total solid (TS) (Edomwonyi-Otu and Adelakun 2018). For the purpose of this study, BOD was selected as the limiting parameter. BOD is the measure of oxygen required to oxidize the organic matter present in sample water. The result obtained for BOD was used in the water pinch software developed by James Manna of Virginia Polytechnic Institute and State University. Pinch point, mass load, cumulative mass load, concentration interval diagram, concentration composite curve, preliminary network design and evolution network design were determined and constructed with the aid of the water pinch software. The experiments were carried out at a Civil Engineering Water Laboratory to improve the quality of treated effluent and to determine the appropriate treatment scheme for recycle/reuse of treated water. The treatment routes investigated were sand filtration and activated carbon column. The experimental setup for sand filtration and activated carbon column process was assembled in the same laboratory to carry out the recycle studies on effluents.

2.2 Regeneration and Recycling Process

2.2.1 Sand filtration: The sand used as a filter media was screened between 0.8 - 1.2mm particle size. The sand was thoroughly washed with tap water to remove all the dirt: both organic and inorganic matter, until the water became clear. The washed sand was oven-dried (Gallenkamp TM OV-420) at 100°C to remove the moisture/water content. The filtration experiment was carried out on secondary treated effluent of KRPC wastewater in a bench scale laboratory model (batch mode). The sand filter consisted of a circular glass tube with a packed bed of sand and gravel. The size of column was 8cm diameter by 78cm height. The reason for the choice of the size of the sand used was to ensure that rate of filtration was not too slow. The size of the sand at different layers is as seen in Table 1. The sand was placed on wool and perforated plate. The sand filter was fed from top through gravity with secondary treated effluent and the filtrate was collected at the bottom. The filtered effluent was analyzed for pH, SS, COD, BOD, chloride, nitrate, alkalinity, turbidity, total dissolved solids (TDS), TS, oil and grease and some heavy metals.

Table 1: Sand filtration

Layer	Size (mm)	Height (cm)
Top	0.8	6
Middle	1.2	6
Bottom	2.0	6

2.2.2 Granular activated carbon (GAC): The granular activated carbon used for this work was obtained from Alpha Chemicals in Kaduna State, Nigeria. The activated carbon was washed with tap water to remove impurities. The washed activated carbon was oven-dried (Gallenkamp TM OV-420) at 100°C to remove the moisture/water content. The adsorption test was conducted on sand filtrate in a bench scale laboratory model (batch mode). The filtrate effluent was also analyzed as in Section 2.2.1.

2.2.2.1 Adsorption capacity of GAC: The batch adsorption experiment was performed by contacting 1.6g, 2.8g, 4.0g, 4.8g, and 6g of GAC in 160ml of filtered effluent in 5 sets. Finetech Magnetic stirrer at 150rpm was used to provide continuous stirring of the mixture for the study duration for improved mixing and to enhance the degree of contact. Each set was removed from the shaker after 40 minutes and pH of 7 to 8 (Cheng 2008; Zheng et al., 2018). The completely mixed activated carbon-effluent system was passed through the Whatman filter paper. The filtrate effluent was also analyzed as in Section 2.2.1 to determine optimum dose.

2.2.2.2 Determining the effect of contact time on adsorption capacity: Samples of 160ml wastewater were added to the five different GAC dose (4g) in 250 ml Pyrex flasks. The contents were then agitated at a constant speed for different contact times of 12, 24, 36, 48, and 60 minutes. The filtrates were collected separately and also analyzed as in Section 2.2.1 to determine optimum contact time.

3. Results and Discussions

3.1 Assessment of unit flow rate and quality requirement : To carry out the pinch analysis, BOD was analyzed across the nine major water unit operations. BOD was considered because it is one of the most important water quality parameters, and it helps in the determination of the amount of organic matter in a given sample of water. It also provides useful clue on the effect discharged wastewater will have on the receiving environment. Table 2 shows the change in BOD across the nine operations considered. It can be observed that operations such as desalters, FCC, and caustic treating units generated effluent with higher content of BOD, while operations such as boiler blowdown, ion exchanger, laboratory and in-house water, contributed far less to BOD in the effluent water. The limiting inlet value of BOD was compared to the design specification and as can be seen when BOD as a single contaminant is considered, KRPC wastewater effluent agrees with the design specification (KRPC, 2002).

Table 2 Limiting water data for BOD

Operations	Limiting flowrate (te/hr)	Limiting inlet concentration (ppm)	Limiting outlet concentration (ppm)	Mass load (kg/hr)	Design specific ation
Cooling water (Operation 1)	96	45.00	94.00	4.90	100
Ion Exchangers (Operation 2)	178	17.00	110.00	16.64	50
Laboratory (Operation 3)	12	13.00	74.00	0.38	50
SWS Desalter (Operation 4)	29	94.00	420.00	9.48	180
FCCSWS (Operation 5)	10	94.00	380.00	2.86	180
Caustic treating (Operation3) (Operation 6)	10	94.00	410.00	2.40	180
In house water (Operation 7)	7	7.00	18.00	0.42	95
Fire service (Operation 8)	38.10	86.00	420	3.40	180
Boiler blow down (Opera 9)	50	4.0	9.0	0,18	0

Fig. 1 is the concentration interval diagram (CID) for the limiting data for BOD in Table 2. The CID was constructed by matching the inlet and outlet contaminant concentrations with the flowrate of water across the nine operations. CID allowed for easy determination of mass load and subsequently the cumulative mass load. From the CID constructed, the flow rate of the fresh water requirement was reduced from 430 te/hr to 214 te/hr which was in agreement with the similar work carried out on Tehran Oil Refinery by Mohammadnejad et al., (2011). The concentration composite curve (CCV) of Fig. 2 was constructed by using the cumulative mass load generated from concentration interval diagram of Fig. 1. The pure water line was plotted with an assumption that inlet concentration of the water is equal to zero and the outlet concentration is maximal. The pinch point indicated at the point where the pure water line made a tangent to the concentration curve. This is indicated at 110ppm which was in agreement with the KRPC design specification. The pinch point is also the concentration critical point, and above this value, water is discouraged from been used (Ipsital 2010).

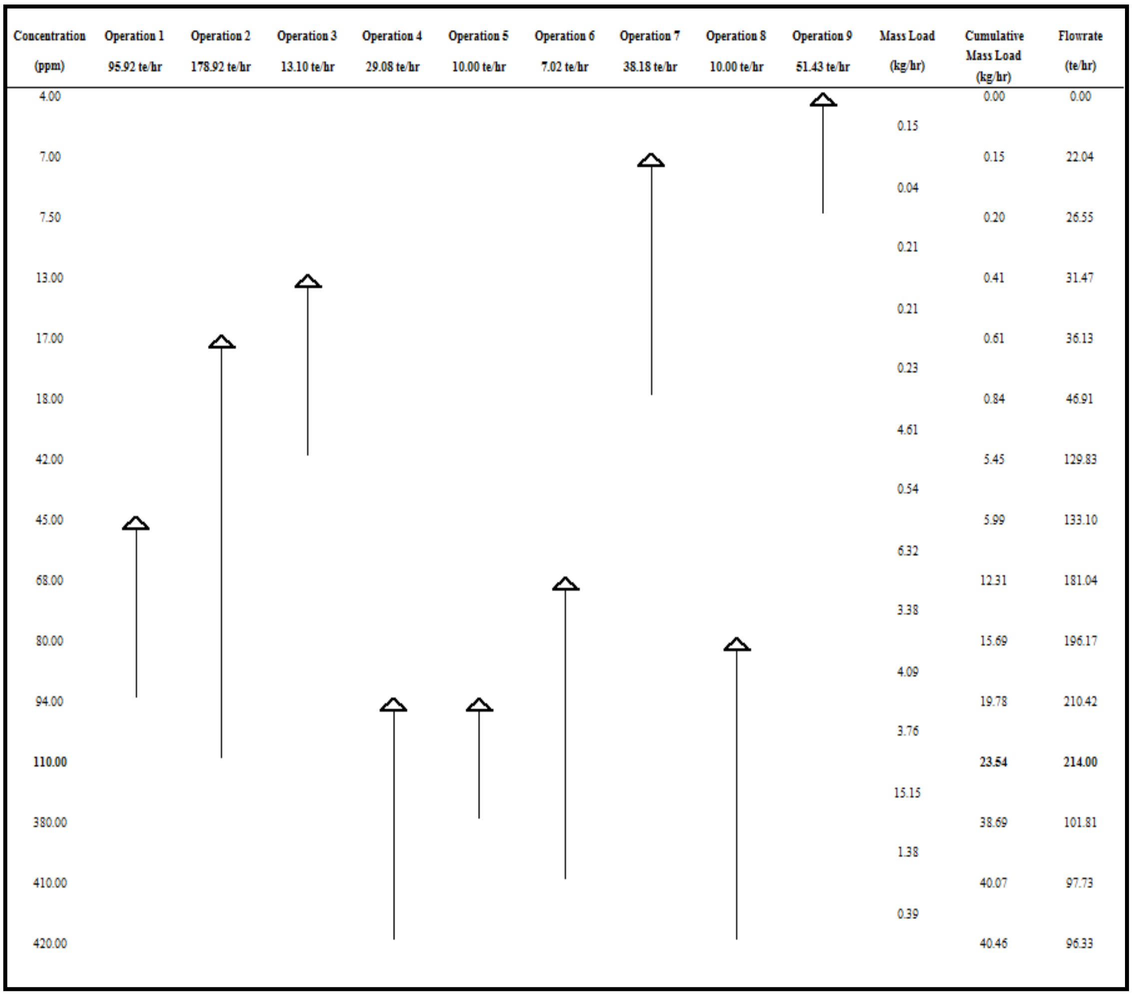

Figure 1. Concentration Interval Diagram for BOD

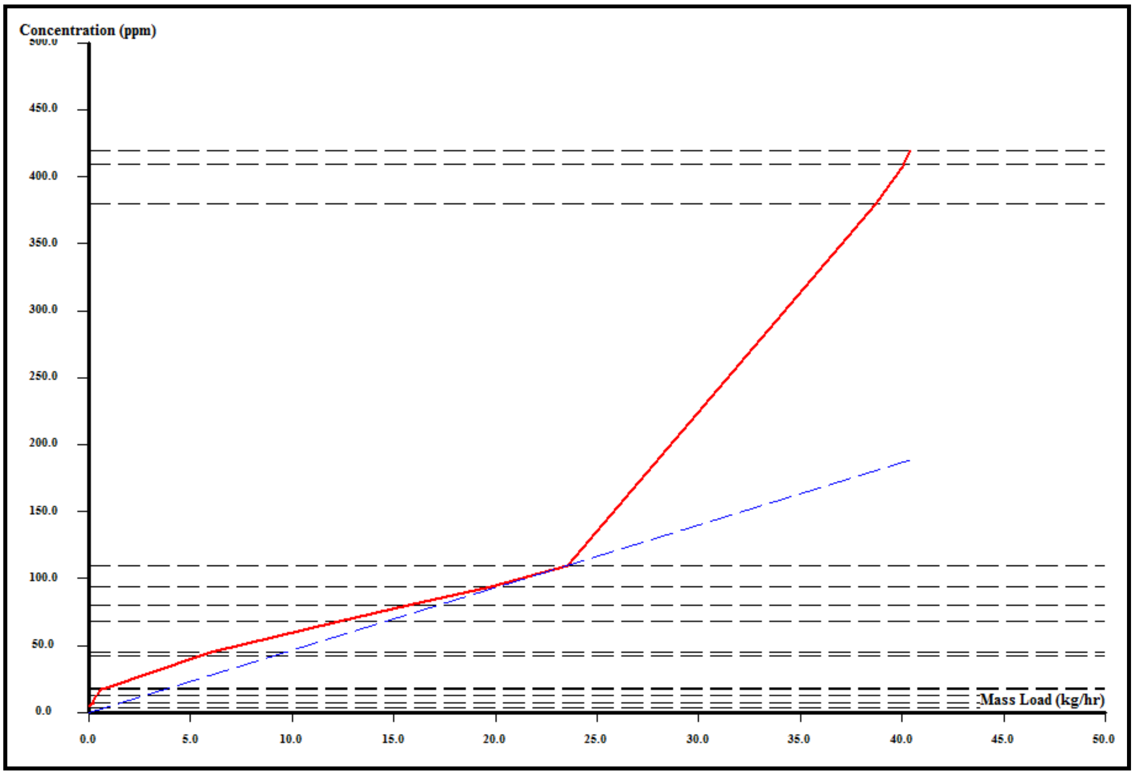

Figure 2. Concentration Composite Curve for BOD

Fig.3 is the evolution networks design for limiting data of Table 1. It was constructed from the concentration interval diagram of Fig. 1 and the concentration composite curve of Fig.2. It shows that operations one to nine makes use of the fresh water but the sources from the operations 2, 3, 7 & 9 formed the major sink to operations 1, 4, 5, 6 & 8. Hence, this provides an explanation for the 50% reduction in the volume of the fresh water need. Fig.3 also showed final networks for BOD as a single parameter. It can be seen that operation 3 required 50te/hr of fresh water before optimization. However, after optimization the volume of fresh water required was completely replaced by the effluent from operations 2, 3 & 9.This is due to the fact that the outlet of operations 2, 3 & 9 are less contaminated and the average outlet concentration was below the pinch point and can therefore be reused (Bush and Frankz, 1996). Operation 2 also had 30% of its fresh water requirement replaced by the outlet of operation 1, 7 & 9. Operation 3 requires 9.05te/hr of fresh water as its only source since no other outlet from any operation is reusable when BOD is the only parameter considered. Operations 4, 5, 6, & 8 have 50% of their required fresh water replaced by flows from operations 1, 2, 3, 7 & 9, and their outlet is highly contaminated and hence are not fit for reuse in any other operation (Mohammadnejad et al., 2011).

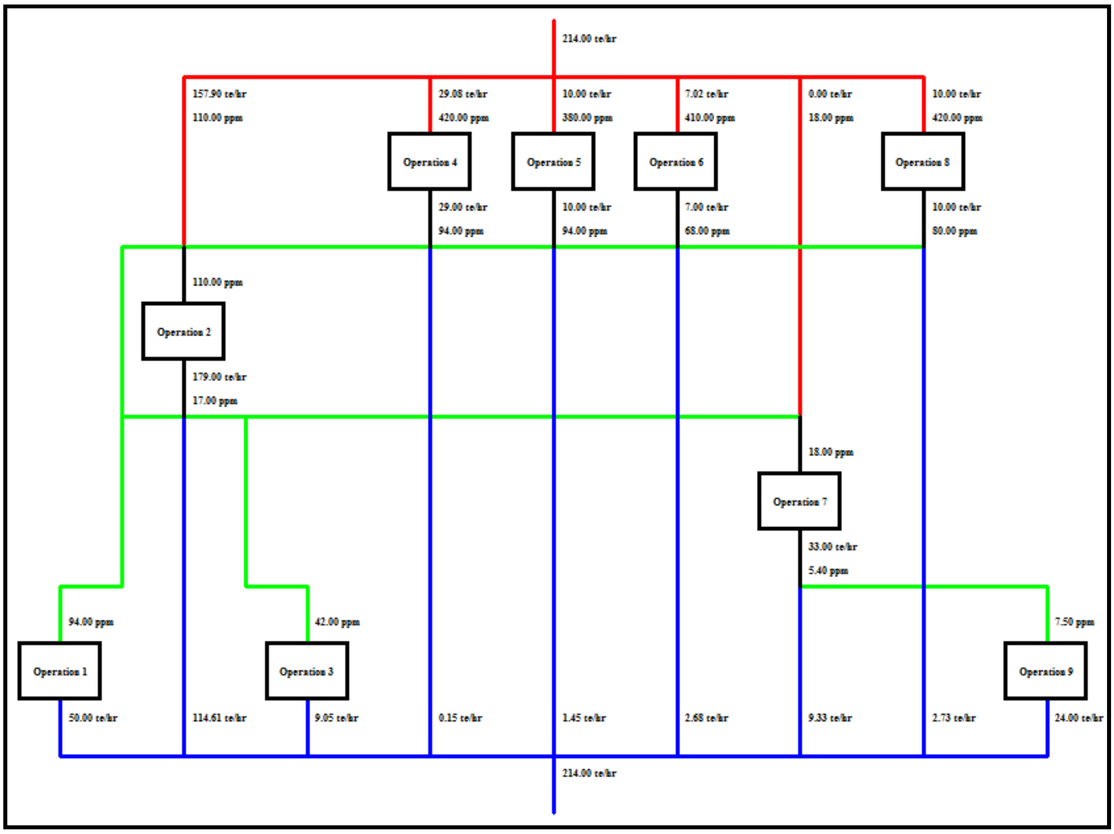

Figure 3. Network Evolutions for BOD

To determine the effect of regeneration on the environment, the wastewater was subjected to sand filtration process after which the filtrate was treated with activated carbon. Table 3 shows the physicochemical parameters and quality of the treated effluent water leaving/discharged from KRPC to Romi River, Kaduna.

Table 3 Physicochemical parameter of the effluent

S/No	Parameters	Value
1	Temperature (T^0C)	27.70
2	pH	7.60
3	Turbidity (NTU)	63.20
4	Total solid (mg/l)	450.10
5	BOD_5 (mg/l)	430.00
6	COD (mg/l)	720.65
7	Oil and grease (mg/l)	15.02
8	Total hardness (mg/l)	71.02
9	Conductivity (µs/cm)	400.63

It can be seen that the effluent from KRPC did not meet up with the discharge guideline by National Environmental Standard and Regulation Enforcement Agency (NESREA) as shown by turbidity, oil and grease content of the effluent water. Hence, the need to investigate the suitable processes to make the wastewater meet the NESREA guidelines for effluent discharge (NESREA 2010).

3.2 Sand filtration: The effluent water parameters were compared with the design specification and it was observed that the effluent water can only be used for fire services which requires water of lower quality. However, this is rarely used because fire outbreaks are not common hence the need to subject the effluent to further treatment so as to enhance it usability.

Table 4 Physicochemical parameter of the Sand filter effluent

S/No	Parameters	Experimental Value	Design specification	NESREA
1	Temperature(T^0C)	26.50	30	
2	pH	7.80	8	6 - 9
3	Turbidity(NTU)	9.90	20	$<$ 40
4	Total solid(mg/l)	147.50	200	2000
5	BOD_5(mg/l)	205.50	50	30
6	COD(mg/l)	573.00	100	1000
7	Oil and grease(mg/l)	5.60	10	10
8	Total hardness (mg/l)	58.12	180	-
9	Conductivity(μs/cm)	260.00	110	400

Table 4 shows the performance of the sand filter which consists of a circular glass tube that was filled with sand of different sizes. The glass tube used was 5cm wide and 78cm high, and was filled with sand of 2mm, 1mm and o.8mm diameter respectively to a height of 6mm. The filter is categorized as slow filter since the flowrate is less than 0.017gpm (Cheryan and Rajagopalan, 1998). It was observed that the filter media reduced the turbidity from 63.20 to 9.90 NTU, equivalent to 84% turbidity removal while the TS and grease contaminant concentration were reduced by 72 and 80% respectively. Similarly, the COD and BOD removal were 20 and 19% respectively, as shown in Table 4. The sand filter effluent was compared with the KRPC water design specification and it was observed that the water was now fit for reuse for other service purposes including fire service. The BOD content was too high to be fit for use in most of the operations and hence, the sand filter effluent was subjected to activated carbon treatment.

3.3 Activated Carbon: The result of the activated carbon treatment is shown in Table 5. As can be seen, the COD, conductivity, total hardness, BOD, turbidity and total solid contaminant concentration were reduced by 64, 39, 65, 52, 28, and 39% respectively. The result obtained was within acceptable limits and corroborates the report by Amuda and Ibrahim, (2006), who treated industrial wastewater by using natural adsorbents.

Table 5: Adsorption capacity of GAC

S/No	Parameters	1.6g (GAC)	2.8g (GAC)	4g (GAC)	4.8g (GAC)	6g (GAC)
1	Temperature(T^0C)	27.50	28.00	28.10	28.00	28.02
2	pH	7.60	7.50	7.20	7.50	7.50
3	Turbidity(NTU)	7.48	7.10	5.10	5.10	5.98
4	Total solid(mg/l)	105.04	103.00	75.10	74.25	75.00
5	BOD_5(mg/l)	101.00	93.00	54.45	44.03	43.06
6	COD(mg/l)	216.04	210.00	80.0.65	80.5.22	89.94
7	Oil and grease(mg/l)	1.79	1.47	1.02	1.00	1.00
8	Total hardness (mg/l)	23.32	20.99	18.59	18.60	18.60
9	Conductivity(μs/cm)	194.00	184.00	172.00	174.00	173.04

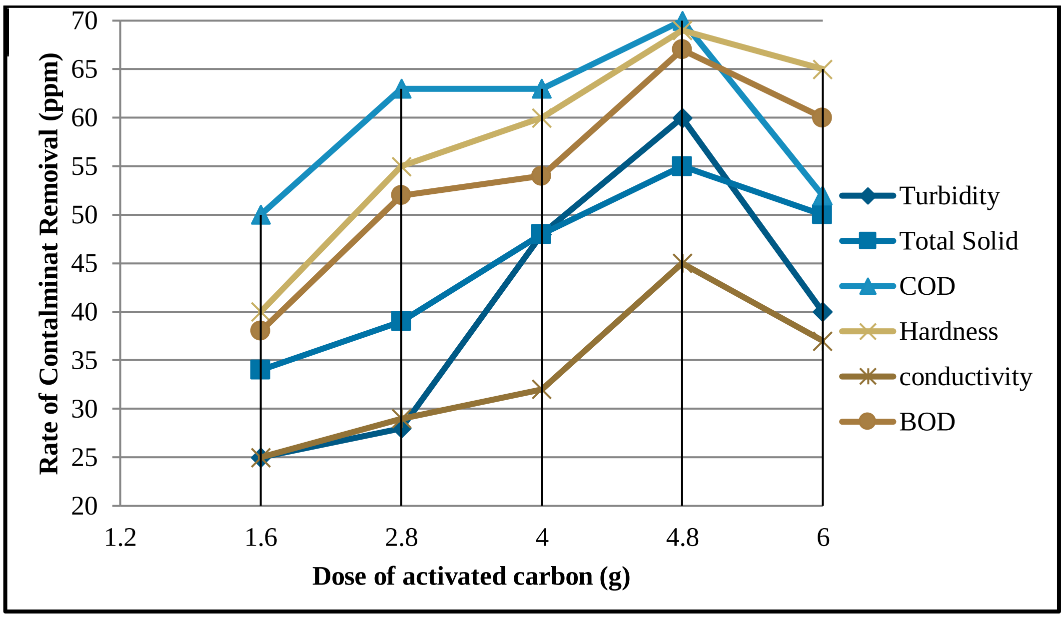

Figure 4. Adsorption capacity of GAC

Fig.4 presents the removal of COD, conductivity, total hardness, BOD, turbidity and TS. The dose was varied for 60 minutes (Couper et al., 2010). It can be seen that the percentage contaminant removal increased with the dose (g), particularly from 4g, to an optimum of 4.8g. This may be attributable to an increased amount of the replaceable sites and increased surface area (Edison et al., 2011). However, as the dose increased beyond 5g, the absorption rate started to decline. An evidence of saturation of the pores of the activated carbon.

3.3.1 Contact time: To obtain the optimum contact time of the activated carbon on the wastewater, batch experiment was conducted at different times; ranging from 12 minutes to 60 minutes (Bessarabov and Twardowski, 2002). Fig. 5 shows contact time versus absorption capacity of activated carbon. COD and BOD are our main targets for the activated carbon treatment since effluent from sand filter would have been reusable in most of the processes except that their concentration was too high. As can be observed, the optimum contact time was 36 minutes for all parameters and particularly the COD and BOD. While the COD removal decreased sharply after 24 minutes, the BOD removal decreased steadily and both parameters plateaued from 36 minutes. This may be due to the saturation of the pores of the GAC and it thereafter attained equilibrium (Edomwonyi-Otu et al., 2013; Cheng 2008).

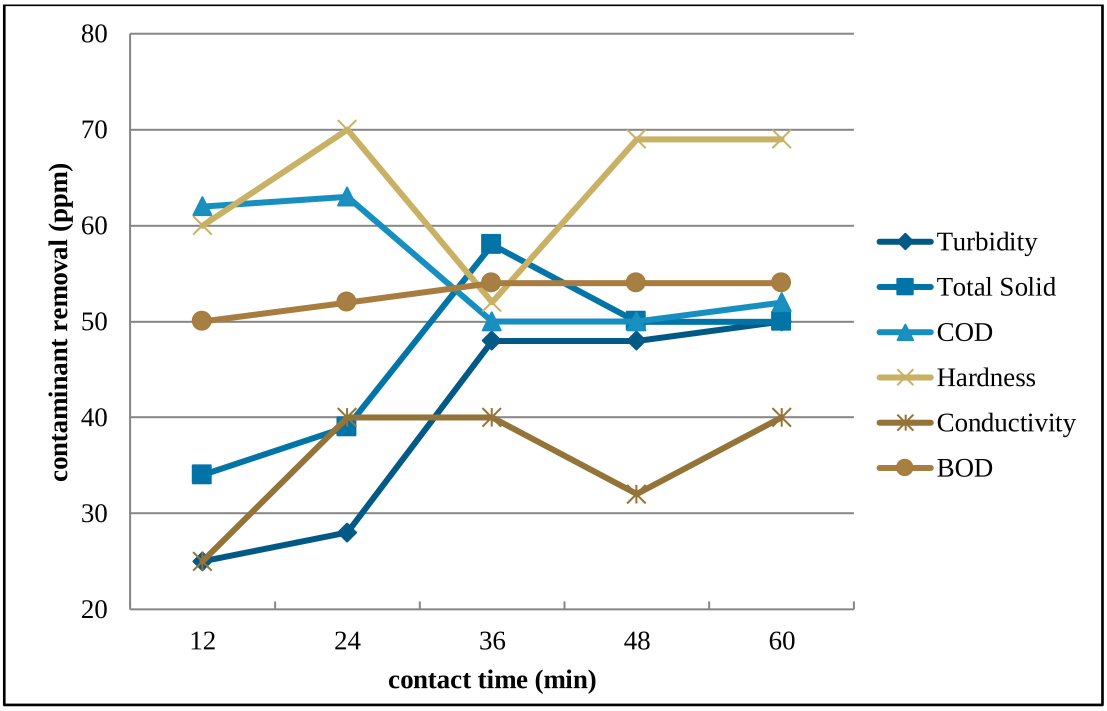

Figure 5. Contact time of wastewater with activated carbon

In pinch analysis, the recommended regeneration concentration C_0, is usually taken to be the pinch point (Lahnsteiner et al., 2012). In this work, two regeneration processes were carried out; sand filtration and activated carbon. The combination of these processes can increase savings by further reducing the volume of fresh water demand by 15%. From the regeneration processes carried out, the optimum regeneration concentration for the limiting parameter, BOD was 50ppm. This was added to initial flowrate for each unit operation and matched with each contaminant concentration to construct CID in Fig.6. This was used to determine the flowrate at 162.95te/hr and pinch point at 110ppm.

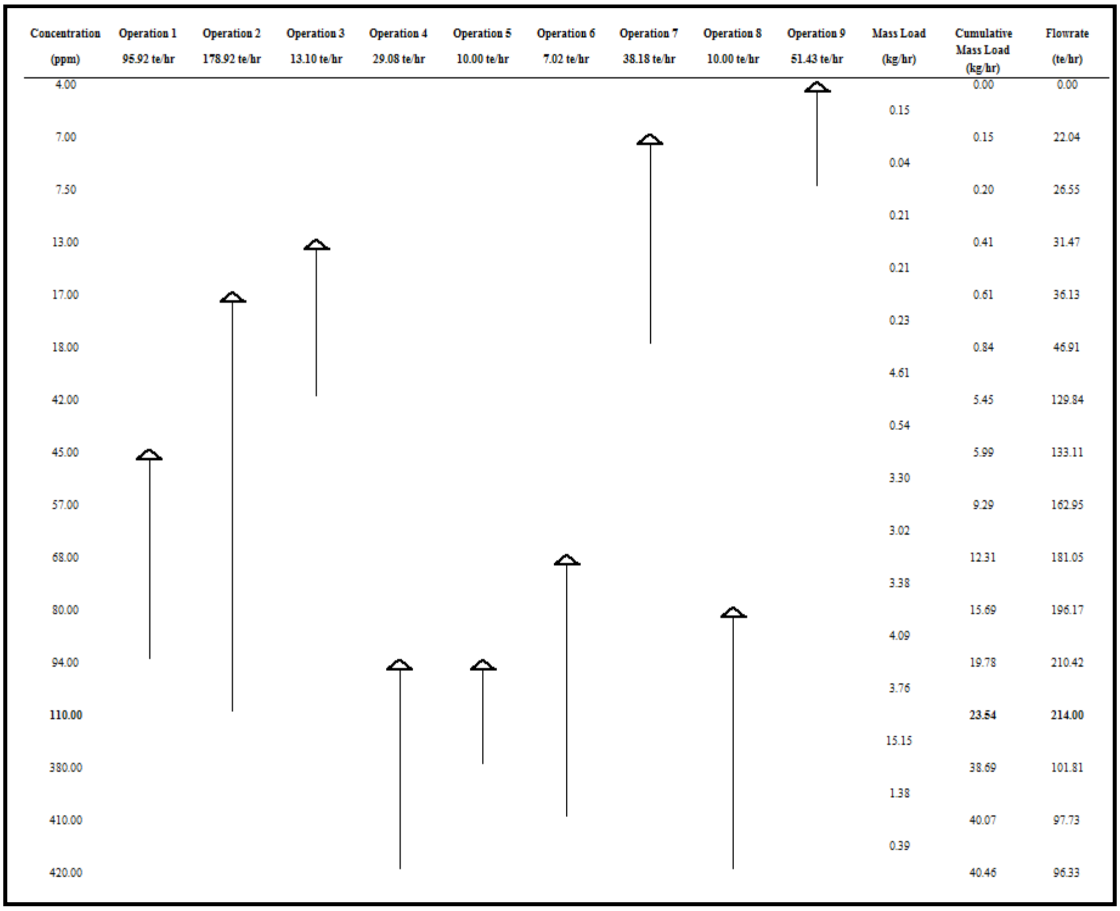

Figure 6. CID for BOD Regeneration

Fmin = 162.95te/hr; Freshwater pinch at 110.00 ppm; Average outlet concentration is 254.58 ppm

4. Conclusions

The application of water pinch analysis as a tool for environmental sustainability was demonstrated on Kaduna Refining and Petrochemical Company (KRPC) water system. Water reuse and regeneration approaches were considered. The water reuse approach showed reduction of fresh water demand from 430te/hr to 214.86te/hr equivalent to 50% reduction in the volume of fresh water required with an average outlet concentration of 201ppm. After consideration of the regeneration technique, the wastewater was reduced by 38%, and 49% for regeneration reuse option. This resulted in reduced cost of wastewater treatment and environmental contamination. The final regeneration outlet concentration was found to be 48ppm and falls within the limit of environmental regulation as designated by NESREA (40 - 50ppm, NESREA 2010). Hence, the water reuse and regeneration approaches are recommended for KRPC water supply system for the purpose of optimal fresh water utilization and environmental sustainability.

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