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Human health risk assessment of industry impact in Kikinda industry zone

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ABSTRACT

In industrial zones such as the municipality of Kikinda (presented in this manuscript) it is necessary to monitor environmental pollution and take measures to protect the environment from the effects of harmful polluting and toxic substances (especially from heavy metals). The risk assessment model developed by the US EPA was used to assess the health risks posed by emissions of heavy metals in the air in Kikinda industry zone. It can be concluded that no increased level of risk was identified from heavy metals content in the air from industry systems in the area of the industrial zone in Kikinda, however, it is necessary to apply preventive measures in order to reduce the accumulation of heavy metals in the environment due to activities that are constant in that area.

1. Introduction

Most heavy metals (Cd, Pb, Ni, As, Cr, Hg…) are harmful and dangerous substances which, in addition to polluting the environment, have a very toxic effect in higher concentrations, both on plants and animals and on human health. Therefore, in the last twenty years, public awareness has been developed of the need to monitor environmental pollution and take measures to protect the environment from the effects of harmful substances in general, and especially from heavy metals, because their concentration in soil, water, and air is getting bigger every day. The data indicate that about 150,000 tons of nickel from natural sources and 180,000 tons originating from industrial activities are released into the environment annually, primarily during the emission of fossil fuel combustion, industrial production, and industrial waste rich in nickel (IARC, 1990).

The International Committee on Nickel Carcinogenesis in Man in 1990 suggested that the risks of developing respiratory tumors were associated with exposure to soluble nickel concentrations above 1 mg/m^3, and exposure to less soluble forms at concentrations above 10 mg/m^3. The Committee could not determine with certainty the level at which exposure to nickel becomes substantially hazardous. About 2 % of workers in the nickel industry are exposed to dust particles containing nickel in concentrations from 0.1 to 1 mg/m^3 (Ilić et al., 2007). Exposure to nickel compounds can cause a variety of adverse effects on human health. Nickel allergy in the form of contact dermatitis is the most common reaction.

Although the accumulation of nickel in the body through chronic exposure can lead to pulmonary fibrosis, cardiovascular and kidney disease, the greatest danger is associated with the carcinogenic effects of nickel.

Human exposure to nickel is most often experienced through inhalation and ingestion and is particularly high in metallurgical workers engaged in nickel processing. In developed environments and large cities, atmospheric

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nickel concentrations are associated with dust generated by the combustion of fossil fuels in power plants and automobiles, and can reach 120-170 ng/m^3 compared to 6-17 ng/m^3 in less industrialized areas. (Norseth and Piscator, 1979)

Anthropogenic sources produce about three-quarters of total arsenic emissions into the atmosphere. Significant amounts of arsenic come from the combustion process of fuels (coal and heavy oils), the iron and steel industry, and the production of copper and zinc. The largest natural sources of arsenic are: volcanic activity, fires, mineral decomposition processes, and the activity of microorganisms (in wetlands).

Arsenic mainly occurs in fine fractions of suspended particles (up to 2.5 μm in diameter), which can be transported over long distances and as such can easily penetrate the respiratory system. Almost all forms of arsenic in the air are in the form of particles with an aerodynamic diameter of up to 10 μm.

Previous experimental animal studies and epidemiological studies on the human population have demonstrated the toxic and carcinogenic properties of arsenic. According to the IARC classification, inorganic trivalent arsenic is classified in group I, which means that it has been proven to be carcinogenic to humans, while pentavalent inorganic arsenic and organic arsenic, as well as their compounds are classified as toxic substances. (IARC, 2012) The WHO has estimated that daily intake of water containing 20 mg/L of arsenic for 70 years will increase the likelihood of cancer by 5 % (WHO, 2011).

The degree of toxicity of arsenic depends on the inorganic or organic form and the state of oxidation of arsenic. Prolonged exposure to even low concentrations of arsenic can cause lung cancer and bleeding, cardiovascular, pulmonary, immune, and neurological disorders. The complete mechanism of arsenic action in the body is not yet known. Chronic arsenic poisoning can be the result of the accumulation of arsenic compounds in the body. One of the symptoms of chronic toxicity in humans, resulting from oral exposure to arsenic, are skin lesions. They are characterized by hyperpigmentation, hyperkeratosis, and hypopigmentation.

Vascular disease of the black foot, which causes gangrene of the lower extremities, has also been detected in humans with chronic arsenic exposure (Sharma and Sohn, 2009). Acute toxicity is associated with the chemical form and oxidative state of arsenic. In adults, the lethal dose of arsenic was estimated at 1-3 mg As/kg (De Zuane, 1997). Characteristics of severe acute toxicity include gastrointestinal distress, vomiting, diarrhea, anuria, convulsions, coma, and death. Lead as a pollutant can be detected in all basic environmental factors and biological systems. Sources of lead contamination are combustion products in metallurgy and chemical industry, industrial wastewater, landfills, and traffic. In atmospheric precipitation, the total lead content ranges from 1-50 μg/dm^3 (Goyer and Clasen, 1995).

From the atmosphere, soil, and water (surface and groundwater), lead is introduced and retained in plants, and further through the food chain and drinking water reaches the human body. In addition to food and drinking water, lead can also be ingested through air contaminated with fossil fuel combustion products (Goyer and Clasen, 1995). The introduced lead is deposited mostly in the bones, then in the liver, kidney, spleen, nervous tissue, and muscles. A blood lead concentration of 60 μg/dL was considered safe during the 1960s. Over time, by studying the toxic effects of lead, the acceptable content in the blood was reduced to 25 μg/dL and then to 10 μg/dL in 1991. Regardless of these changes, subclinical symptoms of lead exposure also occur at a content of less than 10 μg/dL. However, a harmless level of lead in the body has not yet been defined (Ahamed and Siddiqui, 2007).

According to the physic - chemical properties, Pb^{2+} -ion can easily replace Ca^{2+} -ion in calcified tissues (bones and teeth), but also in various soluble complexes of this metal with bioligands in biological fluids and tissues.

Lead in bones contributes to the development of osteoporosis, decreased bone mass, changes in structure, and increased bone resorption in the elderly (Kaličanin et al., 2004).

Daily amount of ingested lead, orally and by inhalation, can be around 0.3 mg. It is partially eliminated from the body by excretion, but it also accumulates, so that about 250 μg/dm^3 can normally be found in the blood. An increase in the levels of this metal in the blood is moderately risky for values (250-490 μg/dm^3), highly risky for (500-690 μg/dm^3), and urgent with more than 700 μg/dm^3 in body fluid (Munoz and Palermo, 2006).

Lead from drinking water is probably more absorbed than lead from food. According to some studies, adults absorb 35 to 50 % of the ingested metal, and the percentage of absorption for children can be higher than 50 %. In addition to age, the absorption of lead is also affected by the general physiological state of the organism (Flora et al., 2006). Death from acute human poisoning can occur with the intake of 25 to 30 g of soluble lead salts. Chronic exposure to this heavy metal leads to mental retardation, psychosis, hyperactivity, weight loss, and muscle weakness and paralysis. Increased presence of this metal is attributed, in some cases, to the appearance of hypertension, cardiac arrhythmias, and malignant changes in the digestive tract, lungs, and kidneys (Counis, 1998).

Volcanic activity is one of the reasons for the occasional increase in the concentration of cadmium in the environment, primarily in the air. Permanent sources of cadmium contamination are related to its application in industry, as an anticorrosive reagent, stabilizer in PVC products and the production of tires, paint pigment, and in the production of Ni-Cd batteries. Although some cadmium - containing products can be recycled, much of the pollution with this metal is the result of inadequate disposal and uncontrolled incineration of cadmium-

containing waste (Jarup, 2003). The biggest source of inhaled cadmium intoxication is smoking. Total global cadmium emissions are estimated at about 7,000 tons per year (Stoeppler, 1991). The maximum permissible values of cadmium for workers are much lower, under German law for example they are 15 μg/dm^3. For comparison, in non-smokers, the average concentration of cadmium in the blood is 0.5 μg/dm^3 (Godt et al., 2006).

Unlike acute, chronic intoxication leads to the development of some diseases such as chronic obstructive pulmonary disease, kidney disease (nephrotoxicity) and bone (arthritis, osteoporosis), anemia, growth disorder, and others (ATSDR, 2012).

Normal blood cadmium levels in adults are less than 1 μg/dm^3. Although cadmium spreads through the blood throughout the body, the largest accumulation (50 to 60 % of the body load of cadmium) is in the kidneys and liver. The load of cadmium, especially in the kidneys, mostly increases linearly with age, up to 50-60 years of age, after which the level of cadmium in the kidneys remains constant or very little decreases (Webb, 1979). Highly toxic effect of cadmium is the result of its interactions with the necessary micro and macro bioelements, especially with iron, calcium, copper, and zinc (Brzoska and Moniuszko-Jakoniuk, 1997). Cadmium poisoning can be acute or chronic. Acute poisoning occurs by inhalation of vapors or particles of cadmium salts (oxides, chlorides, sulfides, sulfates, carbonates, and acetates). Symptoms of acute cadmium exposure include nausea, vomiting, loss of smell, taste and appetite, and abdominal pain (Wentz, 2000).

Chronic poisoning can occur after prolonged exposure to cadmium by inhalation or oral administration, and systematic exposure to cadmium leads to increased calcium excretion, which poses an increased risk of kidney stones and bone damage (Godt et al., 2006). Emissions of toxic trace elements can come from a variety of sources in urban areas, including vehicle emissions, industry and other activities (Harrison et al., 1981). Industry is considered to be one of the most important anthropogenic sources of emissions of trace elements into the air (Niragu and Pacyna, 1988) and is considered an activity with an extremely adverse impact on the environment. Huge amounts of dust with elevated levels of trace elements are released into the air during industrial activities (Csavina et al., 2012).

One of them is the industrial zone in Kikinda. Despite this, limited attention has been paid to industrial zones. Therefore, it is necessary that the risks to the environment and human health in industrial zones are assessed in a timely manner and, accordingly, appropriate protection measures are planned and taken.

Numerous health risk studies related to heavy metals in the air have been done in densely trafficked areas, mining areas, and industrial complexes (Ferreira-Baptista and De Miguel, 2005; Zheng et al., 2010a; Zheng et al., 2010b; Csavina et al., 2012).

One of the industrial giants whose influence is also considered from the health aspect of the population is RTB Bor in Serbia (Mrazovac Kurilić et al., 2019; Mrazovac Kurilić et al., 2020). Based on the results from Bor, the alarming situation in Kikinda cannot be expected, but the emphasis can certainly be placed on the cumulative effect and its reduction.

The aim of this paper is to assess the current state of air quality and impact on health, i.e. health risk assessment in the industrial zone of Kikinda for timely preventive steps to reduce harmful effects.

2. Materials and methods

2.1. Study area

Kikinda is a municipalty located in northeastern part of Serbia (and Vojvodina), on the border of Romania (Figure 1 a) and b).

a)

b)

Figure 1. a) Kikinda on the map of Serbia b) industrial zone of Kikinda - map

Data from the Kikinda industrial zone were used to analyze the risks to the environment and human health.

Kikinda is an industrially developed area and it occupies an important place in the economic development of the Republic of Serbia. Industry in the municipality of Kikinda is a priority area and is based largely on the available raw material base, production capacity, and quality human resources. Industrial production is very diverse, and the available production capacities are mainly of a processing character with a high degree of product finalization. There are several IPPC and SEVESO plants operating in the Kikinda industrial zone, which are very important and important from the aspect of environmental protection, because an integrated permit is obtained for the operation of such plants. The following plants belong to the IPPC and SEVESO groups:

Foundry "Kikinda" metal industry; foundry "Le Belier Kikinda" production of aluminum castings for the automotive industry; building materials industry - "Toza Marković"; "MSK" Kikinda, methanol - vinegar complex; petroleum and chemical industry - NIS "North Banat"; "Bell Chemicals" oil and lubricant refinery; "Blik Produkt"; food industry - "Banini", "Prima Produkt", „Kikindski mlin", "Mokrin imlek"; "G-Graphix", "Grindex", "Agroseme" and fodder factory. Plants belonging to IPPC and SEVESO plants have a major impact on the environment.

2.2. Sampling and analysis

Measurements were made during 2019, from January to December. The used monitoring station was a part of the local network of automatic monitoring of ambient air quality (part of sepa.gov.rs) in AP Vojvodina, which was managed by the Provincial Secretariat for Urbanism and Environmental Protection. Measurements were performed daily based on a 24 h sample.

Sampling of suspended particles of PM_{10} fraction in ambient air in automatic station in Kikinda was performed by a reference sampler of suspended particles of the manufacturer DIGITEL, model LVS DPA 14, Switzerland. Determination of mass concentration was performed by gravimetric method in accordance with the standard SRPS EN: 12341:2015. Determination of lead, cadmium, nickel, and arsenic was performed by an automatic absorption spectrophotometer in accordance with the standard SRPS EN: 19402:2008, (Inductively coupled plasma mass spectrometry ICP-MS).

2.3. Human health risk assessment model

The risk assessment model developed by the US EPA was used to assess the health risks posed by emissions of trace elements in the air in Kikinda. The research was performed for two groups of people: adults and children, and the following exposure categories were used: adults and children 1) inhalation through the mouth and nose; 2) swallowing through the mouth; and 3) skin contact through exposed skin.

According to the Human Health Assessment Manual (Part A) (US EPA, 1989) and the Dermal Risk Assessment Supplementary Guidelines (Part E) (US EPA, 2004), the hazard ratio (dimensionless, HQ) was used to assess non-cancerous risks of trace element emissions in air (equations 1-3), where RfD was the appropriate reference dose.

HQ < 1 means that there are no adverse health effects, while HQ > 1 indicates that adverse health effects are likely to occur due to the action of a particular element.

$$HQ_{ing} = \frac{(C_{95\%UCL} \cdot IngR \cdot EF \cdot ED \cdot CF)}{(BW \cdot AT \cdot RfD_{ing})} \quad (1)$$

$$HQ_{inh} = \frac{(C_{95\%UCL} \cdot InhR \cdot EF \cdot ED)}{(BW \cdot AT \cdot PEF \cdot RfD_{inh})} \quad (2)$$

$$HQ_{dermal} = \frac{(C_{95\%UCL} \cdot SA \cdot SL \cdot ABS \cdot EF \cdot ED \cdot CF)}{(BW \cdot AT \cdot RfD_{dermal})} \quad (3)$$

The hazard index (dimensionless, HI) is equal to the sum of the HQs and is used to assess the overall potential non-carcinogenic risk of different pollutants through the three types of exposure described above. HI < 1 indicates that there is no significant risk of non-carcinogenic effects. If HI > 1, then there is likely to be a non-carcinogenic effect on the health of residents of a particular category (US EPA, 1989).

According to the classification made by the International Agency for Research on Cancer (IARC), As, Cd, and Ni have been characterized as elements of increased carcinogenic risk (IARC, 2014). The lifespan of carcinogenic risks can be estimated by equation 4 where SF is the appropriate slope factor.

$$R = \left(\frac{(C_{95\%UCL} \cdot EF \cdot SF_{inhal})}{(AT \cdot PEF)} \cdot \frac{InhRchild \cdot Edchild}{(Bwchild)} + \frac{(InhRadult \cdot Edadult)}{Bwadult} \right) \quad (4)$$

Any carcinogenic risk in the range of 10^{-6}-10^{-4} (dimensionless) is considered acceptable (US EPA, 1989). All exposure factors for these models are shown in the Table 1. RfD and SF values of all examined elements (Ferreira-Baptista and De Miguel, 2005; Zheng et al., 2010a; Zheng et al., 2010b) are shown in Table 2.

Table 1
Exposure factors and their values for the human health risk assessment model (US EPA, 2004)

Factor	Meaning	Values for adults	Values for children	Unit of measure
BW	Average body mass	70	15	kg
IngR	Ingestion frequency	100	200	mg/day
InhR	Inhalation frequency	20	7.6	m^3/day
PEF	Particle emission factor	$1.36 \cdot 10^9$	$1.36 \cdot 10^9$	m^3/kg
SA	Surface parts of the skin that touch air particles	5700	2800	cm^{-2}
SL	Skin adhesion factor	0.07	0.2	mg/cm^2day
EF	Exposure frequency	180	180	day/year
ED	Duration of exposure	24	6	Year
ET	Exposure time	24	24	Hour/day
AT (non-carcinogenic risk)	Average time	ED · 365	ED · 365	day
AT (carcinogenic risk)	Average time	70 · 365	70 · 365	day
ABS	Dermal absorption factor	0.03 (As); 0.001 (other)	0.03 (As); 0.001 (other)	-
CF	Conversion factor	$1 \cdot 10^{-6}$	$1 \cdot 10^{-6}$	kg/mg

Table 2
Reference dose (RfD) and slope factor (SF) values for the health risk assessment model

	Ing RfD	Inhal RfD	Dermal RfD	Oral SF	Inhal SF	Dermal SF
Pb	3.50E-03	3.52E-03	5.25E-04	-	-	-
Cd	1.00E-03	1.00E-03	1.00E-05	-	6.30E+00	-
Ni	2.00E-02	2.06E-02	5.40E-03	-	8.40E-01	-
As	3.00E-04	3.01E-04	1.23E-04	1.5E+01	1.51E+01	3.66E+01

2.4. Statistical analysis

$C_{95\%UCL}$ (upper exposure concentrations, mg kg^{-1}) is considered a "reasonable maximum exposure" (US EPA, 1989; US EPA, 1992; Zheng et al., 2010a; Zheng et al., 2010b; Hu et al., 2011), which is the upper limit of the 95 % confidence interval for the mean. A 95 % confidence limit (UCL) was calculated using the adjusted central limit theorem (CLT) (Singh et al., 1997; US EPA, 2002). Although the approach was developed for normally distributed large data sets, the theorem does not say how many samples are sufficient for normality. $C_{95\%UCL}$ was calculated using the equation 5:

$$C_{95\%UCL} = \overline{X} + \left[z_\alpha + \frac{\beta}{6\sqrt{n}} (1 + 2 \cdot z_\alpha^2) \right] \cdot \frac{S.D.}{\sqrt{n}} \quad (5)$$

where: $\overline{X}$ = arithmetic mean; S.D. = standard deviation; β = skewness; α is the probability of type I error (false positive result) and its value is 0.05; for $Z\alpha$ = (1−α) quantile of standard normal distribution.

For a confidence level of 95 %, $Z\alpha$ = 1,645; n = number of samples.

All statistical analyzes were performed in the software package Statistica 8.

3. Results

Heavy metals concentrations were detected during 2019, as a result of monitoring under the jurisdiction of the state monitoring network. Measurements in the industrial zone of Kikinda showed the presence of heavy metals (Ni, As, Pb, and Cd). All concentration values below the detection limit were calculated as the detection limit.

In Table 4 are shown values of non-carcinogenic and carcinogenic risk of analyzed elements.

Table 3
Basic statistics of measured parameters - Kikinda (2019) (www.sepa.gov.rs)

mg/kg	Pb	Cd	Ni	As
MIN	0	0	3.15E-06	2.31E-07
MAX	4.69E-05	1.54E-06	1.43E-05	6.92E-06
MEAN	6.05E-06	2.42E-07	3.47E-06	8.17E-07
SD	5.73E-06	1.73E-07	1.46E-06	6.84E-07
SKEW (β)	4.109609	3.507945	5.713115	4.624892
$C_{95\%}$	**7.61E-06**	**2.854E-07**	**3.953E-06**	**10.163E-07**

Table 4
Calculated HQ, HI, and R values for each trace element measured in air in Kikinda (2019)

	HQ ingestion		HQ inhalation		HQ dermal		HI	
	A	**Ch**	**A**	**Ch**	**A**	**Ch**	**A**	**Ch**
Pb	1.532E-09	1.430E-08	2.240E-13	3.971E-13	4.073E-11	2.667E-10	1.57E-09	1.46E-08
Cd	2.011E-10	1.877E-09	2.957E-14	5.243E-14	2.810E-11	5.251E-10	2.29E-10	2.40E-09
Ni	1.392E-10	1.300E-09	1.988E-14	3.525E-14	2.057E-12	1.347E-11	1.41E-10	1.31E-09
As	2.387E-09	2.227E-08	3.498E-13	6.202E-13	2.322E-11	1.520E-10	2.41E-09	2.24E-08

*A - adults; Ch - children

Table 5
Calculated R values for each trace element measured in air in Kikinda (2019)

	Ring	Rinh	Rder	Ri
Cd	-	921.81E-16	-	921.81E-16
Ni	-	170.24E-15	-	170.24E-15
As	7,815.55E-16	7,867.65E-16	19,069.94E-16	3.48E-12

4. Discussion

Linear correlation coefficients between analyzed heavy metals showed low interdependence between metals, lower than 0.75, (except between As and Pb), which implied anthropogenic origin of these elements in atmosphere (Table 6).

Table 6
Correlation between measured heavy metals

	Pb	Cd	Ni
Cd	0.509	1	
Ni	0.135	0.071	1
As	0.859	0.277	0.128

Based on quantitative values, it can be concluded that no increased level of risk was identified by technical-technological systems in the area of the industrial zone Kikinda.

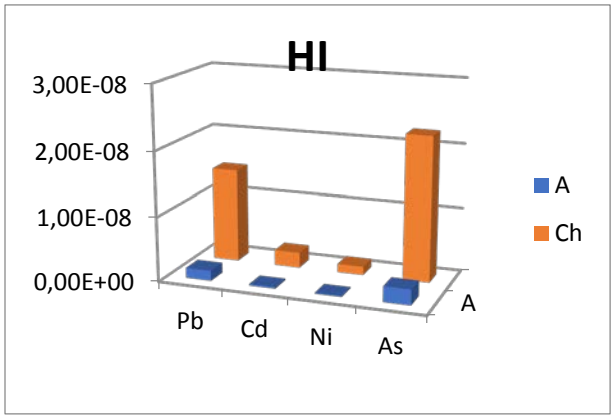

Figure 2. Graphical representation of HI values for each analyzed element, for adults (A) and children (Ch)

The Figure 2 shows a significantly higher value of HQ in children, which implied a significantly higher non-carcinogenic impact of harmful elements on the younger population. Also, the most significant influence of As and Pb was noticeable.

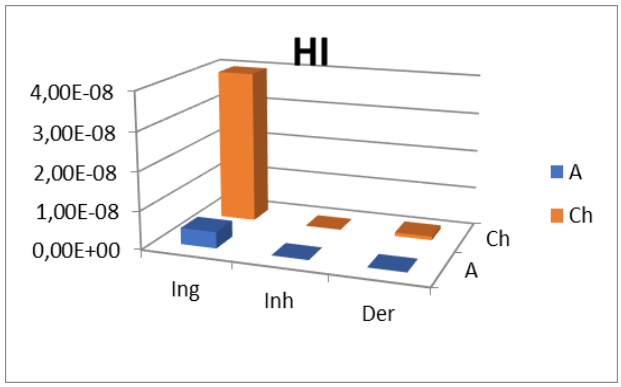

Figure 3. Graphical representation of HI values depending on the way of intake, for adults and children

Based on the graphic presentation, the dominance of oral intake of harmful elements by the intensity of action can be observed, also with a far more pronounced effect on the younger population.

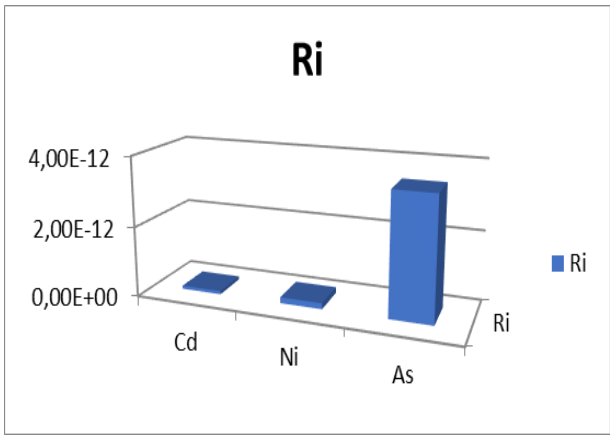

Figure 4. Graphical representation of R values for each analyzed element

In the case of carcinogenic risk, As can be pointed out as the biggest influence. The most significant was the dermal effect, in case of carcinogenic risk.

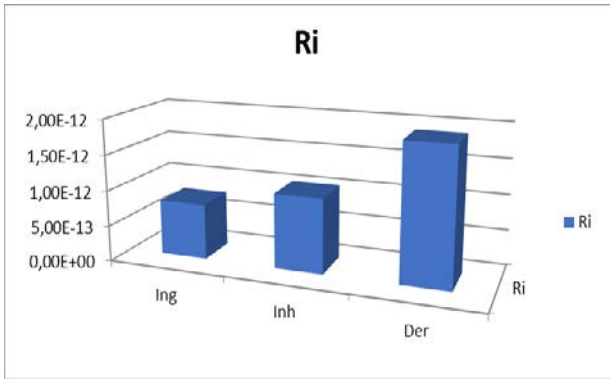

Figure 5. Graphical display of HQ values depending on the way of intake

Compared to other localities that were mainly developed industrial and mining centers (Luanda - Angola, mega city Nanjing - China, Bor - Serbia...) for which the human health risk was assessed, it can be said that the situation in the industrial zone of Kikinda is far safer and not in an area of increased health risk.

By comparing with other results from authors from different parts of the world, it can be concluded that similar findings and results have been reached.

In Wanshan district of Guizhou province in China, oral ingestion was the main pathway affecting the carcinogenic risk and hazard quotient (HQ) of heavy metals in air. The total carcinogenic risk of twenty-five sampling points was between 1.219×10^{-6} and 3.446×10^{-4}, and the total - HQ was between 0.37 and 43.56. (Wu et al., 2020)

In Tehran, based on the study of Zarandi et al., 2018, the rank order of exposure pathways based on health risk was ingestion > inhalation > dermal contact. Moreover, the significant health risks for Tehran residents due to heavy metals bound $PM_{2.5}$ (HQ > 1; carcinogenic risk > 1.00E−06) were noted based on the health risk assessment. Carcinogenic risk of PAHs bound $PM_{2.5}$ was 4.16E−07 that demonstrated that there was no considerable risk (< 1.00E−06).

Also, in Tehran, The average risk of carcinogenic at urban stations in the spring for As, Cd, and Cr was 2.25×10^{-9}, 2.09×10^{-12}, and 2.05×10^{-11} (Anoushiravan et al., 2018).

In Delhi, India, hazard quotient (HQ) values indicated that ingestion was the major pathway of road dust heavy metal exposure to human beings. Hazard index values showed that there was no probable non - carcinogenic risk of the heavy metals present in the road dust of the area. Children were found vulnerable to the risks of road dust metals. (Roy et al, 2019)

The purpose of this assessment is to prevent population from unrestrained development of the industry and the danger of a cumulative effect. In that sense, it is necessary to think about long-term monitoring of the health risk trend of heavy metals in order to be able to take adequate protection measures.

5. Conclusion

Monitoring of the air quality in the industrial zone in Kikinda showed the presence of heavy metals. During the analysis of the presence of heavy metals in the atmosphere in the industrial zone of Kikinda, no increased risk to the environment and human health from the presence of nickel, cadmium, arsenic, and lead compounds was noticed. As the most significant impact the impact of arsenic can be singled out, in the case of carcinogenic and non-carcinogenic risk, as well as in the case of adults and children. The most significant way of intake of heavy metals into the body for non-carcinogenic risk was ingestion, while for carcinogenic risk the effect through the skin was dominant. The greatest danger was the ability of heavy metals to accumulate in the human body.

How to prevent environment pollution and human health deterioration from heavy metals?

- Application of process technologies with low emissions, especially in new plants;
- Waste gas treatment (secondary measures of reduction) by means of filters, scrubbers, adsorbers, etc.;
- Modification or preparation of raw materials, fuels, or others materials for production (e.g. use of raw materials with low heavy metal content);
- Best management practices, such as good maintenance by space, preventive plant maintenance programs, or primary measures, such as closing units that produce dust; and
- Appropriate environmental management measures for the use and disposal of certain products that contain Cd, Pb, and / or Hg.

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Procena rizika po ljudsko zdravlje od uticaja industrije u industrijskoj zoni Kikinde

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I Z V O D

U industrijskim zonama kao što je opština Kikinda (predstavljena u ovom radu) neophodno je pratiti zagađenje životne sredine i preduzeti mere za zaštitu životne sredine od uticaja štetnih zagađivača i toksičnih supstanci (posebno od teških metala). Model za procenu rizika koji je razvila Agencija za zaštitu životne sredine Sjedinjenih Država je korišćen za procenu zdravstvenih rizika koje predstavljaju emisije teških metala u vazduh u industrijskoj zoni Kikinde. Može se zaključiti da nije utvrđen povećani nivo rizika od sadržaja teških metala u vazduhu koji potiče iz industrijskih sistema na području industrijske zone u Kikindi. Međutim, neophodno je primeniti preventivne mere kako bi se smanjila akumulacija teških metala u životnoj sredini koja nastaje zbog aktivnosti koje se na tom području odvijaju konstantno.

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Raising environmental awareness through art projects

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ABSTRACT

The paper analyzes the importance of actively raising awareness about the significance of ecology and the preservation of our environment through various art forms. The role they play in the process is an important one, both in terms of educating the younger, and raising awareness among the older generations about environmental issues. Art strives for the preservation of culture and cultural heritage, and represents a permanent record of a certain age, a way of life, the social and political circumstances, human opinions, and socially relevant topics. Ranging from architecture, as the most frequently used type of art, via literature and film, to music which reaches the widest of audiences, it can convey any message to the greatest number of people, and each art form can give its own contribution to environmental issues. Socially engaged art is a frequent occurrence. Throughout history, art has been used as a call to rebellion, resistance, and change. Environmental topics have been increasingly more present in art over the past few decades, but are still not present enough. Great potential for the awakening of mankind in terms of the environmental challenges we are facing lies precisely in various art forms. Everyone has their own preference when it comes to art, which is why no art form should be neglected; instead, they should all be developed equally so as to encourage as many people as possible, spanning all generations, to consider the importance of environmental issues.

1. Introduction

Solving the environmental problems that have arisen is of crucial importance for the future quality of life and survival of both humanity and the flora and fauna. In many countries around the world, the increase of environmental awareness has become an important goal. This most often involves various campaigns aimed at reducing pollution, economic, and political measures, but also educating the population, especially the young (Mitić et al., 2018). Education of the population is usually done through various projects and workshops. It is necessary to start raising environmental awareness at the preschool age, then continue the development of environmental culture through further education, all in order to have a responsible community in the future. Ecological consciousness includes behaviors, motives, desires, and expectations in relation to the natural environment (Ilić et al., 2010).

Two projects for raising awareness about the importance of recycling were organized in the kindergarten "Star grove" in Belgrade, in the municipality of Zvezdara, and were named "I do not throw away, I create" and "The story of old looms". As part of these projects, children created new works of art, toys made of PET packaging, yarn for looms from old

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newspapers, as well as works of art by combining art techniques with old newspapers and packaging. (https://zvezdara.rs/oni-su-spojili-ekologiju-umetnost-i-tradiciju/?lang=lat).

In sports, medals made of recycled electronic material were made for the first time at the Vancouver 2010 Winter Olympics, and seven years later the Government of Japan issued a document requiring all citizens to donate old mobile phones, computers, and other electronic devices in order to collect a sufficient amount of gold, silver and bronze to make medals for the Olympic and Paralympic Games in Tokyo in 2020 (Šiljak et al., 2019).

Eco-fashion is becoming more and more popular in the world. Eco-fashion and eco-design are clothes made of materials that help preserve the environment. They are made without the use of materials of animal origin and are produced according to environmental standards, so that the production process itself does not disturb the environment in any way (Frfulanović-Šomođi and Savić, 2019).

Another problem we face today is the amount of information we receive daily. Excessive exposure to it leads to lethargy and a lack of interest in "difficult" topics such as climate change or pollution. Reading serious literary works, such as "Anna Karenina", "Doctor Zhivago", and others is often replaced by watching a film or a brief abridged version of the same story; thus, topics that are of vital importance cannot easily attract the attention of the general public if they are presented in the form of a scientific paper or a serious newspaper article.

The simplest way for a certain message to reach a large number of people and leave an impression is through various art forms.

Engaged art is not new. The theater in the Middle Ages was financed by the church. It featured plays with religious content (Adam and Eve, Noah's Ark, the birth of Christ) to convey messages to the illiterate (Raduški, 2017).

One of the most famous works of the Spanish painter Pablo Picasso is a painting called Guernica, painted as a reaction to the Nazi bombing of the Basque city of Guernica during the Spanish Civil War. Guernica depicts the pain and suffering of innocent civilians. Thus, this image became one of the greatest anti-war messages and a constant reminder of the destruction of war, and at the same time one of the greatest symbols of peace. (https://www.pablopicasso.org/guernica.jsp)

It is, therefore, not surprising that an increasing number of works from various types of art forms now contain an ecological message and call for social responsibility, that is, they carry a warning of a dark future if we continue to neglect nature.

This paper aims to show that raising environmental awareness should be approached responsibly at all levels and in all domains of social life. This inevitability also applies to art, but the ways of reaching this level of consciousness are slightly different, and they present a challenge, both for realization and analysis. For that reason, the topic warrants more attention.

The paper is structured as follows. After the introductory section, individual chapters outline ecology in various branches of art such as: architecture, literature, fine and applied arts, music, film, and theater. The final section contains the concluding remarks.

The paper is intended for the interested professional and scientific public, as well as for all those who could benefit from the elaboration of this insufficiently studied issue.

2. Ecology in architecture (green building)

When it comes to art forms, ecology has found its greatest application in architecture, an art form that has the greatest use-value. The concept of green or sustainable construction appeared with the first concepts of sustainable development in the 1960s and 1970s.

A green building is an innovation that stems from an awareness of the need to preserve the environment (Singh et al., 2020). It is a building that by its design, construction, or use reduces or eliminates negative impacts and has a positive effect on the climate and natural environment. It can be a house, an office building, a school, a hospital, a shopping mall, or any other building (https://www.worldgbc.org/what-green-building).

There are a number of features which can make a building 'green'. These include:

- Efficient use of energy, water, and other resources,
- Use of renewable energy, such as solar energy,
- Pollution and waste reduction measures, re-use, and recycling,
- Good indoor environmental air quality,
- Use of materials that are non-toxic, ethical, and sustainable,
- Consideration of the environment in design, construction, and operation process,
- Consideration of the quality of life of the occupants in the design, construction, and operation process; and
- A design that enables adaptation to a changing environment.

Very few of these so-called green buildings actually possess all of the aforementioned characteristics. Nevertheless, the goal of green architecture is full sustainability. This ecological approach to architectural design is based on the premise that it is possible to integrate these new systems into pre-existing natural functions (Ragheb et al., 2016). Alazm and El-khalidi (2018) have compiled a comprehensive list of the six

major elements of green building design, which can be found in Figure 1.

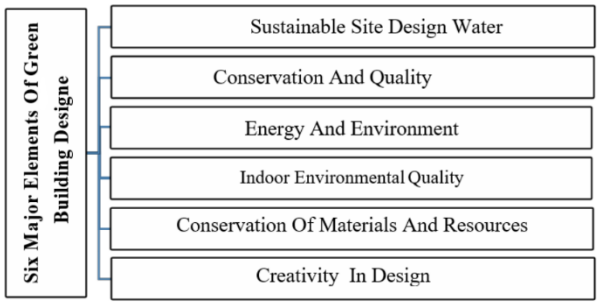

Figure 1. Six Major Elements of Green Building Design (Alazm and El-khalidi, 2018)

Just like the concept of sustainable development itself, the green building contains three important segments: the natural environment, the social aspect, and the economy. The beginnings of green buildings in the United States date back to the 1990s. In Europe, the number of green buildings doubles every three years, while in Serbia they are still in the development phase. A significant contribution to the topic of green architecture and the opportunities it provides is given by green building fairs held in Belgrade (https://balkangreenenergynews.com/rs/).

3. Ecology in literature

Twentieth century art has brought about a significant shift in how we as the audience perceive the artist. Artists are no longer merely individuals portraying feelings of amazement at something; they are now the ones intervening in the situation at hand. Such 'interventions' are evident in the works of Joseph Beuys, who through his work strives to encourage his audiences to look for and establish a new form of harmony between themselves and their natural environment (Verri, 2020).

Contemporary literature is increasingly more focused on topics related to the field of ecology and sustainable development. Most often, these are works of science fiction that consider the possible consequences for the planet if humanity continues with the trend of industrial development and the associated degradation of the environment.

Interesting books in this field that deal with the current situation are:

- "Last Chance to See" by Douglas Adams and Mark Carwardine which discusses species that are on the verge of extinction.
- Mike Hulme's "Why We Disagree about Climate Change: Understanding Controversy, Inaction and Opportunity", in which Hume, after 25 years as a scientist on climate change, Hulme uses an insider account of the origins of these changes. He, through aspects of science, economics, religion, psychology, sociology, and politics, seeks to explain why scientists disagree on climate change.
- "The End of the Line: How Overfishing Is Changing the World and What We Eat" by Charles Clover which reveals the hidden costs of bringing food to the table, both in households and restaurants, and reveals that 90 % of large fish in the oceans have disappeared in the past 50 years.
- "Sustainable Energy - Without the Hot Air" by David MacKay was written in the form of a case study on the topic of nuclear energy, fossil fuels, and the possibility of international exchange of renewable energy (https://fivebooks.com/books/ecology/).

4. Ecology in fine and applied arts

It is believed that different environmental content and the use of recycled materials can be important factors in raising environmental awareness among students. One of the most famous artists involved in recycling is certainly Mexican artist Alejandro Durán. He is known for his project "WASHED UP: Transforming a Trashed Landscape" in which he collects garbage that comes out on the Caribbean coast and makes sculptures out of it. Over the years, Alejandro has identified the garbage of 58 different nations from six continents (https://alejandroduran.com/statement).

A very famous work is the installation of the Bulgarian artist Christo Javacheff called "Running fence" (Figure 2). The fence was set up in America, starting from Highway 101, all the way to the exit to the Pacific Ocean. It is 39.4 kilometers long and 5.5 meters high, and was made of a piece of nylon (https://christojeanneclaude.net/artworks/running-fence/).

Figure 2. Running fence (https://christojeanneclaude.net/artworks/running-fence/)

Another example is the installation of the Finnish artist Tea Mäkipää, a sloping cabin that floats on a lake, while the sounds of family life can be heard from it, drawing attention to global warming (Brown, 2014).

With ecological concerns on the rise, Chinese artists have also joined the ongoing trend and shifted the focus of their work to global environmental concerns. One such artist, Cai Guo Qiang, achieved notoriety with a work titled "The Bund Without Us". The painting depicts what the riverfront of Shanghai would look like centuries in the future after it had been reclaimed by nature. Humans are nowhere to be found in the depictions (Carroll, 2017). Another example is the work of Mary Mattingly. Her series of photographs titled "Her House and Universe" depicts, among other things, the naked body of a human being pressed down by a huge ball of garbage wrapped in twine. The desired effect is to blur the lines between the human and the ball of trash, and to juxtapose both against the purity of nature. (Carroll, 2017)

5. Ecology in music

The song "Woodman! Spare that Tree" by George Pope Morris and Henry Russell from 1837 is considered the first ecologically engaging song. After that, this topic will run mostly through folk (traditional) music. However, it is not surprising that with the development of new musical genres, this theme spills over into new musical directions. Rock and pop music have been extremely influential for decades and reached the largest number of people, so many musicians have decided to spread environmental awareness through the music they create.

The famous rock band The Beach Boys had a series of songs focusing around the theme of preserving the environment, such as "Don't Go Near the Water", which was about ocean pollution or "A Day in the Life of a Tree" which was about air pollution.

The most popular music song of this kind was the 1995 "Earth Song" by 'the King' Michael Jackson. The song was accompanied by a high-budget video lasting seven minutes, which showed the destruction of the planet in several ways. Although the song was nominated for a prestigious Grammy Award and was number one on the charts in many countries, this song, like the rest of the video, is almost unknown to the American audience.

Live Earth, the largest international entertainment event that brought together musicians with the intention of raising environmental awareness, was established in 2007. However, this event was followed by numerous controversies because often the main sponsors of the event were companies that were considered the biggest polluters of all (Kahn, 2013).

Numerous artists are involved in environmental activism, and not only through the music they create. The famous musician Sting is one of the founders of the Rainforest Foundation, which deals with the preservation of rainforests and the rights of indigenous tribes living in them. This foundation supports projects of the sister organizations Rainforests UK whose work focuses on Africa, Rainforests US whose work focuses on South America, and Norwegian Rainforests whose work focuses on Asia. Although each has its own area to cover, all of these organizations operate internationally.

Since the 2000s, an increasing number of sound artists have become actively involved in contemporary environmental issues. This level and extent of activity has virtually led to the formation of a contemporary movement. Despite their activism, their work is yet to achieve the impact and recognition already achieved by artists working with other art forms.

An illustrative example of this contemporary movement is the staging of the "Ear to the Earth" festival in October 2006 in New York. The organizers of this five-day festival were Joel Chadabe and the Electronic Music Foundation. What was originally a means of promoting environmentally concerned sound art went on to become an annual event held for seven consecutive years. Another example is the EcoSono. It is an activist network established by Matthew Burtner in 2008, involved in raising awareness through sound art. It went on to develop into an annual educational event, the EcoSono Institute, aimed at achieving environmental sustainability (Gilmurray, 2017).

6. Ecology on film

The concept of the ecological film dates back to 2004, to the work of Scott MacDonald titled "Towards an Ecocinema". Later on, the ecological film has appeared in various genres: documentaries, animations, science fiction, as well as horror films.

In 2013, as part of the "Let's not pollute Serbia" movement, the educational film "Nature and Society" was made. It deals with solid waste, water supply, and wastewater. This film was realized through the program of support for the development of local self-government infrastructure, financed by the EU and implemented with the help of the Delegation of the European Union to Serbia.

The Belgian environmental organization "Wake Up" posted 10 documentaries on the Internet that were part of a festival called the "Green Up Film Festival". The idea of the organizers of this festival was to increase awareness of environmental issues through the film form. The films were divided by topics - biodiversity, food and agriculture, pollution, water, green economy, and energy. The film "New York, Green Revolution" spoke about the city of tomorrow, and "LoveMEATender" asked questions about the real cost of our meat consumption.

The film "Throwing in the World" highlghted the fact that a third of the world's food production ended up as garbage, while on the other hand, a billion people went hungry.

"Electronic Waste Land" provided a look at the 50 million tons of electronic waste generated each year and then shipped to poor parts of the world, while the focus of the film "Chemerical" was an American family trying to get rid of chemical cleaning products and cosmetics

(https://www.rts.rs/page/magazine/sr/story/411/film-i-tv/1581498/ekoloski-dokumentarci-na-internetu.html).

In his book "Hollywood Utopia: Ecology in Contemporary American Cinema", Patrick Brereton looks at films on nature and their impact on ecology, using films such as "Jurassic Park" and "The Emerald Forest" (Brereton, 2004).

Another interesting film is "An Inconvenient Truth", directed by Davis Guggenheim. The film is about the campaign of the former vice president of the United States Al Gore to raise the level of awareness about global warming. The film is actually an adaptation of a presentation that Gore gave more than a thousand times around the world.

Among the films that emphasize the ecological aspect is the 2016 film "Before the Flood" in which the co-producer and the narrator is Leonardo DiCaprio. The 2009 film "Home" produced by Luc Besson, was a great success, winning the Caesar Award for Best Documentary about the interests of large companies and the impact it can have on the environment (https://booksandideas.net/Towards-an-Ecological-Cinema.html). These examples tell us that more and more famous and influential people are trying to contribute to raising awareness about environmental protection through various art forms.

7. Ecology in theater

Although no theater projects that deal with the topic of ecology and the environment have achieved global popularity, it would be unfair to say that no efforts have been made to present ecology to the general public through this art form. According to Wendy Arons, "The attitude of humanity towards the environment has become worrying and this topic should be addressed by all who can have some influence, including theater artists" (Arons, 2007). Even though we are in the second decade of the 21st century, one gets the impression that these themes are underestimated in dramatic works. As much as the concept of ecology has been developed in architecture, design, fashion, it has been rather neglected in the sphere of theatrical art (Woynarski, 2015).

If there are projects of this type, they are usually realized in smaller theaters by smaller theater troupes (http://www.ashdendirectory.org.uk/directory.asp?searchTerm=allProductions), while it is almost impossible to find environmentally engaged performances on large stages.

Despite the fact that the fewest examples of socially engaged projects can be found in the theater, the very motif of nature in dramatic works is quite common. Some of the examples of works with themes of nature are Shakespeare's play – "A Midsummer Night's Dream", then "Waiting for Godot" by Samuel Beckett, and Chekhov's "The Cherry Orchard" (Cless, 2011). Another very interesting book is "Ecology and Environment in European Drama", written by Downing Cless, in which the author focuses on the motifs of nature in famous plays, from Greek tragedies to Berthold Brecht and Samuel Beckett (Cless, 2010).

8. Conclusion

The motif of nature has appeared in art for centuries. It can be found in Shakespeare's plays as well as popular 19th century music. With the development of industry, humanity has faced new problems, so the view of nature went beyond mere enjoyment, and the topic of connecting man with nature took on a whole new dimension. Industrialization has contributed to environmental degradation, manifested in increasing waste storage, forest destruction, and the associated extinction of plant and animal species, declining sources of drinking water, as well as ozone whole problems and global warming. All that contributed to the need to start looking at nature through the prism of its preservation. The accelerated progress of humanity in the 20th,and especially the 21st century has led to an alarming situation in the field of ecology and increased efforts to draw humanity's attention to common problems because they do not affect individuals but the entire planet. There are more and more thematic seminars, scientific papers, and appeals at the state level in this area, in addition to the adoption of the necessary laws to regulate the problem of the biggest polluters as much as possible at the state level.

In addition to trying to enlighten humanity, the importance of educating the youngest members of our society was emphasized. If taught from an early age to respect and care for the environment in which they live, future generations have a better chance of living a more responsible life both towards themselves and others. Educating children is most often done through creative workshops that frequently include art projects. In this way, children learn about their environment and the importance of caring for it through fun and creative work. As the situation and view of nature changed, so did the artistic contents, adapting to the new circumstances and needs. In addition to the already well-known socially engaged themes in the field of art, such as war and globalism, the influence of ecological themes on various art forms has been growing in recent decades. Ecology has had the greatest influence in the field of architecture, which, as an art form, has a pronounced use value, only to gain increased influence in the field of music, literature, and film.

Despite the efforts of many authors who have attempted to improve the situation with their books and articles, the field of the theater remains an underused resource in an attempt to support the ecological sanctuary. This area must be as relevant as possible in the coming period because the theater is a great place to convey very strong and impressive messages.

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Podizanje ekološke svesti kroz projekte u umetnosti

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I Z V O D

U ovom radu se razmatra pojava i važnost podizanja svesti o značaju ekologije i očuvanja životne sredine kroz različite umetničke forme. Veliku ulogu u tome mogu igrati različite umetničke forme, kako u vaspitanju novih, tako i u skretanju pažnje sadašnjih generacija na probleme očuvanja životne sredine. Umetnost teži očuvanju kulture i kulturnog nasleđa, i trajni je zapis određenog doba, načina života, društvenih i političkih dešavanja, ljudskog mišljenja i društveno aktuelnih tema. Od arhitekture kao najupotrebljivijeg vida umetnosti, preko književnosti i filma, do muzike koja ima najširu publiku, pa samim tim može preneti poruku do najvećeg broja ljudi, svaka umetnička forma može dati značajan doprinos ovoj temi. Društveno angažovana umetnost je česta pojava. Kroz istoriju, umetnost je korišćena kao poziv na bunt, otpor i promene. Ekološke teme u umetnosti su sve prisutnije poslednjih decenija, ali ipak još uvek nisu dovoljno česte. Velika snaga za buđenje čovečanstva po pitanju ekoloških problema sa kojima se suočavamo, leži upravo u različitim umetničkim formama. Svi imaju različite umetničke afinitete, pa iz tog razloga ne treba zanemarivati ni jednu umetničku formu, već ih podjednako razvijati, ne bi li značaj ekoloških pitanja podstakao na razmišljanje što veći broj ljudi, svih generacija.

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Characteristics, Treatment Techniques, and Operational Limitations for Refinery Wastewater: Review

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ABSTRACT

Large quantities of wastewater generate from refineries in the process of crude oil usage, distillation, and cooling systems. The wastewater samples need to be treated before disposing into the environment. Disposal of the untreated refinery wastewater causes problems for the water sources and environment. The aim of this work was to study the characteristics, treatment techniques, and limitations of refinery wastewater treatment. A number of tables were prepared to summarize and review wastewater characteristics, treatment process, and the operational limitations. Results revealed that values of some parameters such as biochemical oxygen demand (BOD), chemical oxygen demand (COD), phenols, oil and grease, and total suspended solids (TSS) were 40.25 mg/L to 8,000 mg/L, 80 mg/L to 21,000 mg/L, 3.5 mg/L to 128 mg/L, 12.7 mg/L to 50,000 mg/L, and 22.8 to 2,580 mg/L, respectively. Numerous treatment technologies were used for the treatment of refinery wastewater. Treatment techniques have benefits, weaknesses, and operational limitations. Most amount of the TSS, oil and grease, organic materials are eliminated in the primary and secondary treatment units. Tertiary/Advanced treatment units are necessary for removal of the remaining portions of the contaminants, heavy metals, nitrogen compounds, and phosphorus. Combination of physical, chemical and biological treatment techniques increase removal efficiency of the contaminants.

1. Introduction

Petroleum consists of oil and gas. Refinery is one of the sources of producing enough quantity of wastewater that is related to the source of hydrocarbon. Refinery can be defined as storage for producing petrochemical materials from crude oil. Petrochemical materials are possibly more than 2,500 products which include kerosene, gasoline, diesel, fuel oil, liquefied gas, and oil lubrication to use in industrial for variety purpose. The consequences of these petrochemical materials is the production of tremendous amounts of wastewater (Mustapha, 2018). The quantity and characteristics of produced wastewater are based on the configuration of the process. There is a high amount of wastewater produced during recycling of cooling water that is about 3.5-5 m^3/ton. Refinery is a kind of source of producing polluting wastewater that includes chemical oxygen demand (COD), biochemical oxygen demand (BOD), oil and grease, phenol, benzene, and heavy metals (such as lead, and chrome). However,

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refinery produces soft and solid waste that ranges between 3-5 kg/ton of petrochemical. In addition, about 80 % of this waste material is considered as a hazardous due to presence of some toxic heavy metals (Benyahia et al., 2006). Modifications and novelty in the treatment of petroleum refinery wastewater have been conducted by researchers. A three-step modification including ZnO nano particle loading, UV irradiation, and Polyether sulfone coating on membranes studied by Ratman et al. (2020). Authors reported that treatment technologies increased the rejection of organic matter from 16 % to 54 %. Jafarinejad et al. (2019) stated that membrane separation was low cost and efficient for the treatment of the refinery wastewater and petrochemical plants.

Radelyuk et al. (2019) studied effluent quality of three refinery wastewater treatment plants in Kazakhstan. The authors reported that characteristics of treated wastewater exceeded the disposal standards. In another research, powdered activated carbon augmented with the sequencing batch reactor (SBR) process for improving Kawergosk oil refinery wastewater treatment in Erbil City, Kurdistan Region-Iraq was studied (Aziz and Fakhrey, 2017). Rahi et al. (2021) studied thirteen refinery wastewater treatment plants in Iraq and they stated that effluent impacted the environment and water sources. The use of Microbial Fuel Cells for simultaneous degradation of pollutants in the refinery wastewater with electricity generation was studied by Sheela (2020). Recent global issue in some developing regions and countries is a contamination of land and water by petrochemical products. Furthermore, the ecosystem is polluted by untreated refinery products released into the environment. Consequently, refinery wastewater needs treatment before disposing to natural environment. Additionally, efficiency of various treatment technologies and operational limitations for treatment of refinery wastewater are other issue.

Subsequently, the objective of this research was to describe and discuss refinery wastewater quality, various treatment techniques and studying operation limitations of petroleum refinery wastewater based on the study and results of other researchers.

1.1. Collected Data

Data were collected from published works of other researchers and arranged in Table 1 that illustrated the characteristics of refinery wastewater. Refinery wastewater contains many impurities such as BOD_5, COD, total organic carbon (TOC), phenol, oil and grease, heavy metals, pH, Turbidity, Total suspended solids (TSS) etc.

1.2. Characteristics of Refinery Wastewater

Petroleum wastewater properties are different from a refinery to another refinery and from country to country that is based on drilling of crude oil, crude oil types, composition of crude oil and treatment strategy. It is dramatically influenced by the quantity and character of the material that causes the contamination by refinery (Aljuboury et al., 2017). Table 1 showed the different organic material types that found from petroleum. BOD refers to the quantity of organic substances in the water which causes the increase of pollution. When BOD is high then the pollution level is high. BOD is usually determined after 5 days at temperature 20 °C.

TOC represents the quantity of the organic carbon in the waste water which can be determine from the oxidation of carbonaceous (Catalytic combustion) and it measures the carbon dioxide (CO_2) production. Suspended solid is a type of the physical contamination.

The high ratio of the suspended solid makes biological alteration and aesthetic which increases the nutrients, metal quantity, fish kills and pesticide that goes in the water. Both nutrients such as nitrogen and phosphorous have the ability to make depletion of the oxygen. Ammonia (NH_3) refers to the ration of the nitrogen parts in the pollutant of the refinery wastewater that is highly harmful and toxic to the human health and aquatic life.

Other pollutants of wastewater are called heavy metals that include Iron (Fe), Copper (Cu), Cadmium (Cd), Vanadium (V), Nickel (Ni), Arsenic (As), Zinc (Zn), and Mercury (Hg). These have high ratio of toxic which leads to health problem to the human body (Abdelwahab et al., 2009). Wastewater from petroleum is composed of the pollutants composed of different organic materials and most of that material contains grease and oil which can make a barrier for oil pipes which has odors and is sticky (Mustapha, 2018). The compounds of phenolic has harmful influence to the environment because it has high toxicity and ability for long time to remain in the environment. Both sulphur and nitrogen are producing hydrogen sulphate and ammonia, respectively (Altas and Buyukgungor, 2008). The demand on the petroleum and products of petrochemical will increase fluid waste and its discharge to the water that leads to environmental pollutant (Zhao et al., 2006; Diya'uddeen et al., 2011).

The influence of this water discharge consists of toxic material accumulation, eutrophication, dissolved oxygen in to the sediment and water (Paul et al., 2021). The source contamination of drinking and ground water influences the health life in the community (Yuliwati et al., 2011). Shpiner et al. (2009) mentioned that the wastewater from petroleum included organic and inorganic materials. The organic wastewater from petroleum had grease, oil and dispersed oil, heavy oil, aromatic hydrocarbon, and phenols. The inorganic wastewater from petroleum had, for example, heavy metals and ammonia. Therefore, there are some small quantities of metals inside the crude oil which needs to be treated with a specific tool to separate it. Furthermore, hydrocarbon contains both carbon dioxide and sulphur which needs to be cleaned before going to the market

Table 1
Characteristics of petroleum refinery wastewater by the following researchers

Locations	Sulfide (mg/L)	Fe (mg/L)	pH	TSS (mg/L)	Turbidity (NTU)	Oil and grease (mg/L)	Phenol (mg/L)	TOC (mg/L)	COD (mg/L)	BOD_5 (mg/L)	Parameter
Sourwater refinery/ Rio de Janeiro, Brazil	-	-	8-8.5	-	22-52	12.7	98-128	-	850-1,020	570	Coelho et al. (2006)
Youbang Co., China	15-30	-	6.5-6.8	90-300	150-350	400-1,000	10-20	-	500-1,000	-	Zenga et al. (2007)
Oil recovery industry (Çorlu-Tekirdağ, Turkey	-	-	2.5	2,580	-	1,140	-	-	21,000	8,000	Dincer et al. (2008)
A petroleum refinery located in Alexandria, Egypt	-	-	8	22.8	-	-	13	-	80-120	40.25	Abdelwahab et al. (2009)
Petrochemical industry, Singapore	-	-	7.5-10.3	130-250	10.5-159.4	40-91	-	-	330-550	-	Khaing et al. (2010)
A Malaysian National Refinery	-	-	7	-	83	240	-	398	1,343	846	Hasan et al. (2012)
Petroleum refinery at Whitegate, County Cork, Ireland	-	-	7.6	105	42	946	-	-	364	-	Tony et al. (2012)
Petroleum company Tabriz, Iran	-	-	7.5	110	-	-	-	-	1,120	-	Farajnezhed et al. (2012)
Petroleum refinery, Perak, Malaysia	-	-	8.48	-	-	-	-	-	7,896	3,378	Gasim et al. (2013)
Petroleum refinery, hennai, India	180	-	-	375	-	50,000	20	-	1,250	625	Ibrahim et al. (2013)
Refineries, Malaysia	-	-	6.5-9.5	-	-	-	-	-	550-1,600	-	Aljuboury et al. (2014)
Oil Refining Co. in Iran	-	-	6.7	-	-	870	-	119	-	-	Saber et al. (2014)
Refinery, Rio de Janeiro, Brazil	-	-	8.5	150	-	-	-	-	1,250	-	Vendramel et al. (2015)
Kawergosk Oil Refinery, Erbil, Iraq	-	-	6.57-9.15	400-800	201.3-354	17.36	3.5	-	485	155	Aziz and Fakhrey (2016)
Local refinery, Doha, Qatar	14.5-16	-	8.3-8.7	30-40	-	-	8-10	-	3,970-4,745	-	El-Nass et al. (2016)
Not reported	142	-	8	75	-	-	70	-	1,494	718	Jafarinejad (2017)
Centre Treatment Oil ROM, Algeria	198	390	9.5	-	0.62	-	-	-	2,150	-	Zueva et al. (2020)

References

marketing. The toxicity depends on many factors, such as volume, variability, and quantity of the discharge (Nwanyanwu and Abu, 2010).

Table 1 illustrated that values of some parameters such as BOD, COD, phenols, oil and grease, and TSS were 40.25 mg/L to 8,000 mg/L, 80 mg/L to 21,000 mg/L, 3.5 mg/L to 128 mg/L, 12.7 mg/L to 50,000 mg/L, and 22.8 to 2,580 mg/L, respectively. Refinery wastewater contains high concentrations of the contaminants and they exceeded the disposal standards (Aziz et al., 2020).

Direct disposal of the refinery wastewater causes problems for the people, animals, and the environment.

Consequently, proper treatment is essential for the refinery wastewater prior disposal to the environment.

2. Treatment Techniques for Refinery Wastewater

Typical wastewater treatment processes are comprised of preliminary (such as screens, comminutor, grit chamber, flow equalization), primary (like oil trap, coagulation and flocculation, dissolved air flotation, sedimentation), secondary (biological,) and advanced (tertiary) treatment processes (Radelyuk et al., 2019; Jain et al., 2020; Rahi et al, 2021).

Different treatment techniques for the refinery wastewater is illustrated in Figure 1. There are three types of wastewater treatment from hydrocarbon which are biological, chemical, and physical. Therefore, petroleum wastewater represents a complicated problem that requires a specific technique.

The conventional method needs a several steps to treat the process. First step, consists of before treatment that includes physicochemical and mechanical treatment. Second step is a more modern treatment for previous wastewater.

Different treatment methods and the removal efficiency of the pollutants for petroleum refinery wastewater are shown in Table 2.

Details and discussion for the treatment techniques are shown in the following section.

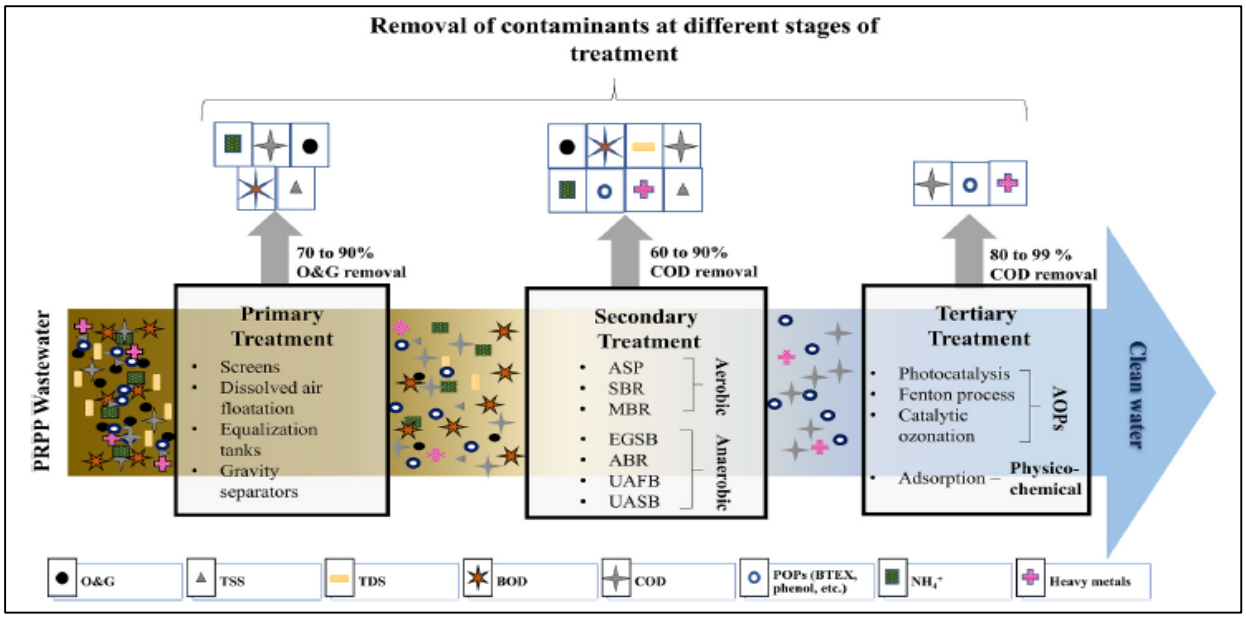

Figure 1. Different treatment methods and their target pollutants throughout the treatment of petroleum refinery wastewater (Jain et al., 2020)

Table 2
Different methods and removal efficiencies for petroleum refinery wastewater

No.	Treatment methods	Removed pollutants	Removal efficiency (%)	References
1	Aerobic biological	COD	86	Satyawali and Balakrishnan (2008)
2	Coagulation by ferric chloride	COD	52	Altaher et al. (2011)
3	Adsorption	Organic substances	62	Cavalcanti et al. (2012)
4	MBBR	Phenol	55 to 90 %	Mahmoudkhani et al. (2012)
		COD	62 to 63 %	
5	Electro-coagulation	phenol	100	El-Ashtoukhy et al. (2013)

Table 2 continued
Different methods and removal efficiencies for petroleum refinery wastewater

No.	Treatment methods	Removed pollutants	Removal efficiency (%)	References
6	Anaerobic biological	COD	82	Gasim et al. (2013)
7	Membrane bioreactor process	Heavy metal and iron	70 and 75	Malamis et al. (2015)
8	Physicochemical treatment	Total naphthenic acids (NAs)	16	Wang et al. (2016)
9	Activated sludge process	Naphthenic Acids (NAs)	73	Wang et al. (2016)
10	Biofilm reactor process	COD	81	Nasirpour et al. (2015)
11	Contact-stabilization process	COD	78.65 %	Ebrahimi et al. (2016)
12	Sequencing batch reactor (SBR) plus Powdered activated carbon (PAC)	Ammonia Turbidity Electrical conductivity Color	62 86 42 86	Aziz and Fakhrey (2017)
13	Returned activated sludge plus powdered activated carbon	COD BOD Oil and grease	79.05 95.07 95.27	Jafarinejad (2017)
14	Constructed Wetland	COD Oil	60-90 % 80 %	Jain et al. (2020)
15	Single chamber microbial fuel cells with air-cathode with additional voltage	Diesel range organics	89 %	Sheela (2020)
16	Bioelectrochemical	COD	17.84-63.10 %	Mohanakrishna et al. (2020)
17	Conventional Fenton Process	Furfural	99 %	González et al. (2021)

2.1. Physical Treatment

This treatment method is a process that is free from biological and chemical changes to treat the wastewater. Course screening is an example for removing large particle and sediment. Currently, physical technique for example sedimentation method is used for treatment to remove fine grains rather than biological method. Sedimentation method is used for separating both water and oil that is obtained. The process of changing liquid to solid state was used for reduction fine grains. Physical process was effective for treatment wastewater from petroleum due to their complexity and the other process can do better (Mikhak et al., 2019). Wang et al. (2016) reported that the maximum reductions for total naphthenic acids and aromatic naphthenic acids using physicochemical processes were 16 % and 24 %, respectively. While in the biological process the removal efficiencies were 65 % and 86 %, respectively.

2.2. Membrane Process

According to Malamis et al. (2019) and Razavi and Miri (2015), membranes were basically divided in two main types, i.e. synthetic and biological membranes. Both ultra-filtration and electrodialysis are tools of membrane technology that are increasingly applied. This technology was found as a useful for organic matter treatment and in terms of economic efficiency it is more acceptable for treating (Jyoti et al., 2013; Kulkarni and Goswami, 2014). Razavi and Miri, (2015) showed that the average removal efficiencies of COD, BOD_5, TSS, volatile suspended solids (VSS), and turbidity using hollow fiber membrane bioreactor were obtained 82 %,

89 %, 98 %, 99 %, and 98 %, respectively. The interactions between the membrane surface and suspended solid constituents in refinery wastewater strongly influenced the membrane in polyvinylidene fluoride hollow fiber membranes, which was approved by Yuliwati et al. (2011).

2.3. Coagulation/Flocculation

This process is one of the most popular methods for treatment of wastewater to remove the material such as turbidity, COD, color, TSS (Farajnezhad and Gharbani, 2012). This treatment belongs to the pre-treatment that is used before membrane and biological treatment. This process can be also used in the final process treatment to eliminate the organic matter of non-biological origin in hydrocarbon (Farajnezhad and Gharbani, 2012). The flocculation method is used for treatment of wastewater from petroleum to bring the large removable material that includes the total phosphate, TSS, and COD. On the other hand, this process is not accurate to remove full wastewater treatment caused by level of efficiency to eliminate the organic matter (Hassan et al., 2012).

Applied the ferric chloride and aluminum chloride are used to remove wastewater from petroleum (Farajnezhad and Gharbani, 2012). They noticed that from two above parameters the aluminum chloride was more effective than ferric chloride. The changing of the pH was significant for the removal of color of the hydrocarbon while the effect of the COD was based on the properties of the petroleum and coagulant types that included metals of inorganic origin, such as ferrous sulfate and aluminum sulfate. El-Naas et al. (2009b) achieved 30 % of COD reduction at the ambient temperature, whereas at 60 °C, 53 % of COD reduction was reached.

2.4. Adsorption

The main advantages of using adsorption process are affordable cost, adaptability, and simplicity (Kulkarni & Goswami, 2013). Cavalcanti et al. (2012) studied analysis of adsorption by used organ clay for eliminating liquid waste from petroleum wastewater. They mentioned that the organophilic clay had significant effective adsorption for reducing the material with maximum toxicity for example phenols and compounds of BTEX. Technology of adsorption refers to the activated adsorption of carbon that is mainly used for ammonium, toxicity and organic compounds in petroleum treatment wastewater (Wang et al., 2007).

Activate carbon is highly influencing the reducing remain organic compounds after treatment from biological method. Therefore, pollutant of the low molecular weight is highly adsorbed (Wang et al., 2007).

This process has limited work due to consumption of carbon activated columns (Renou et al., 2008; El-Naas et al., 2009a).

2.5. Physicochemical Treatment

Physical-chemical method is combined with previous method physical techniques for example filtration and absorption and chemical techniques for example ozonation and oxidation for treatment petroleum wastewater (El-Naas et al., 2016).

After the mechanical process, the physicochemical step collected fine grains that deposited within large grains to easily reduce by the process of floatation, sedimentation and filtration.

2.6. Chemical Treatments

This treatment consists of utilities chemical reactions to enhance the quality of water. This treatment is usually used for petroleum wastewater treatment that is called neutralization. Neutralization comprises of the base or acid to change the level of the pH. The base material is lime that is used in the neutralization of acidic waste. According to Sun et al. (2008), a microwave-catalytic wet air oxidation method gained more than 90 % of COD removal and increase in BOD_5/COD ratio at 30 min from 0.04 to 0.47 to treat petroleum wastewater at 150 ℃with 0.8 MPa.

2.7. Biological Treatment

There is a number of micro-organisms used for treating wastewater to fix the last product. Part of the most micro-organisms waste is changed to water, CO_2 and other products (Zhao et al., 2006). There are several biological methods used for treating wastewater of the petroleum, for example soft reactors and biofilm reactors to eliminate organic compound pollutants (Melamane et al., 2007; Manyuchi and Ketiwa, 2013). Biological oxidation is based on the components of the wastewater from petroleum. However, this method has some disadvantage, such as high soft production and low space to COD removal (Jou and Huang, 2003). Biological process is divided into two types which are anaerobic and aerobic that depend on availability of oxygen dissolved (Zhao et al., 2006). In the anaerobic method, biochemical and chemical products reactions lead to change color and odor of the water. So, the availability of oxygen is very crucial to eliminate that process to change the odor and color (Attiogbe et al., 2007).

2.7.1. Aerobic Biological Treatment

The main objective of this process is to change organic material and refusing materials from wastewater to the

CO_2, water and biological product (Zhao et al., 2006). This type of reactor has the degradation efficiency of about 78 % and 94 % removal of the total organic carbon and oil, respectively from wastewater of the petroleum refinery. This method showed the enhancement of the COD reduction (Satyawali and Balakrishnan, 2008). Furthermore, higher willing for toxic and loads of organic shock and losing biomass was recorded.

2.7.2. Anaerobic Biological Treatment

One of the most popular methods for its economic efficiency and removal of organic component is called anaerobic biological treatment. Organic component is changed to methane (CH_4), CO_2 and wet material during this process. Due to high efficiency, this process is widely applied (Lettinga et al., 2001). The use of anaerobic up-flow of the wet beds is dramatically increased for treatment in petroleum wastewater due to simple and clear design, easy construction with highly maintenance (Rastegar et al., 2011). According to Gasim et al. (2013), the anaerobic method could easily be used for treatment of the petroleum wastewater because it could remove about 82 % of COD. Wang et al. (2016) determined that 70 % of COD was removed, as well as 72 % of the total oil which was obtained from up-flow sludge beds of anaerobic reactor for heavy oil treatment wastewater. It contained tremendous amount of the polar organic and potential efficiency for petroleum wastewater treatment. However, up-flow sludge beds of anaerobic (UASB) reactor had to be used within few organic loads and long duration time of the petroleum wastewater treatment (Wang et al., 2016). Zou (2015) illustrated that removal of NH_3-N, oil, and COD from the complex oil wastewater were 90.2 %, 86.5 %, and 90.8 %, respectively. The combinations of the UASB and biofilm reactor for treatment of the petroleum wastewater resulted in COD removal of 81.075 % (Nasirpour et al., 2015).

2.7.3. Aerated Lagoons

Biological process for the treatment of wastewater from petroleum is normally organized in wet or soft aerated lagoon environment (Tellez et al., 2002; Ma et al., 2009). The activity of being a few times aerated in lagoon does not obtain the needs in fluid treatment. They require a large area caused by small concentration of biomasses (Ma et al., 2009).

2.7.4. Activated Sludge Process

This method is compacted and it should be considerable for the area of the building tanks and other construction of the sludge. Biotransformation of the acidic naphthenic from the sludge method was mostly under effect of the temperature. The average acidic naphthenic from the sludge during summer is higher than in the winter that is about 73 % and 53 %, respectively. It was caused by activity of the high Biotransformation microbial in the sludge system. There are some disadvantages of this method for example high amount of sludge product that needs more time and more energy (Renou et al., 2008).

2.7.5. Biofilm Reactor Process

This method has high efficiency for removing solid suspended materials (Rodgers et al., 2003; Vendramel et al., 2015). This method is known as a steady operated and flexible, with ability for difficult contaminants, and shock loads of the organic matters with large amount of the biomass existence (Galvez et al., 2003; Rodgers et al., 2003; Ibrahim et al., 2012). According to Vendramel et al. (2015), the removable amount of the COD and TSS that was about 91 % and 92 % respectively from anaerobic submerged fixed-bed reactor (ASFBR). The importance and quantity of the biofilm required more analysis in the reactor operations (Vendramel et al., 2015). The average efficiency for removing phenols in the petroleum wastewater is 98 % by utilities of the batch sequencing (Al Hashemi et al., 2015).

2.8. Summary of the Treatment Processes

Radelyuk et al. (2019) reported that the treated refinery wastewater in three treatment plants in Kazakhstan still contained surpassing concentrations of contaminants in their effluents. Rahi et al. (2021) studied effluent quality for thirteen refinery wastewaters in Iraq. The researchers stated that wastewater produced by the refineries contained high contaminants and caused problem to the people and the surrounding groundwater sources. Most suspended solids and oils, and a part of the organic matters were removed in primary treatment units. In the biological process, utmost remained parts of the organic matters are removed. For the removal of the remained organic material, nitrogen compounds, phosphorus and heavy metals further treatment techniques were required in the tertiary/advanced treatment process. Application of physical-chemical, physical-biological, and chemical-biological enhance removal efficiencies of the pollutants are needed (El-Ashtoukhy et al., 2013; Wang et al., 2016; Aziz and Fakhrey, 2017; Jafarinejad, 2017; Mohanakrishna et al., 2020; Sheela, 2020). Type of influent wastewater and the goal of the treatment decides the selection of the treatment process.

3. Limitations of Operational Parameters

Several operational parameters, laboratory and pilot plant studies were performed for the treatment of oily wastewater using aerobic and anaerobic bioreactors of various configurations and different pattern. Table 3

showed the works of other researchers for the treatment of petroleum refinery wastewater with different reactor configurations and removal efficiencies.

It can be seen from Table 3 that more than 90 % of pollutants (such as COD, hydrocarbon, oil, NH_3-N, and turbidity) were removed in the refinery wastewater.

Commonly, the biological treatment was efficient method for refinery wastewater treated, because it contained huge amount of organic matter and hydrocarbons.

Table 3
Operational conditions and reactor configuration for petroleum refinery wastewater

Wastewater type	Treatment Technique	Operational Conditions	Parameter (Removal efficiency)	References
Petroleum refinery wastewater	Two-stage SBR	Two stage operation with Methanol as co-substrate.	COD (97.5 %)	Lee et al. (2004)
Synthetic petroleum wastewater	MSBR	HRT values of 8, 16 and 24 h.	Hydrocarbon (97 %)	Shariati et al. (2011)
Petroleum refinery wastewater	MBBR	Volume 550 L, 85 % of the reactor was filled with Polyurethane elements and MLSS 1.400-1.700 mg/L	Phenol (55 to 90 % COD-(62 to 63 %)	Mahmoudkhani et al. (2012)
Refinery wastewater	Contact-stabilization process	4.19 hr HRT, flow rate 2.77-28.8 l/day	COD (78.65 %)	Ebrahimi et al. (2016)
Heavy oil wastewater	HA-MBBR O_3-BAC	E_uent concentrations of COD, oil and ammonia were 48, 1.3 and 3.5 mg/L.	COD (95.8), Oil (98.9 %) and ammonia (94.4 %)	Zheng (2016)
Petroleum refinery wastewater	SBR plus PAC	Cycle time 6 h, PAC dosage 10 g/L, Aeration 2 L/min	Ammonia (62 %) Turbidity (86 %) Electrical conductivity (42 %) Color (86 %)	Aziz and Fakhrey (2017)
Refinery wastewater	SBR	pH 9	Oil and grease (85 %)	Qarani et al. (2020)
Oil refinery wastewater	Coagulation with central composite design	Effectiveness of $Ca(OH)_2$ and $Al_2(SO_4)_3$	Turbidity (100 %), Total hydrocarbons (90 %) and COD (70 %)	Zueva et al. (2020)
Petroleum refinery wastewater	Single chamber microbial fuel cells with air - cathode with additional voltage	45 mWm^{-2} (control) to 12 mWm^{-2} (500mV)	Diesel range organics (89 %)	Sheela (2020)
Petroleum refinery wastewater	Bioelectrochemical	HRT 4-6 days, Voltage 330-577 mV, power density 274-832 mV/m^2, and specific power yield 0.66-2.95	COD (17.84-63.10 %)	Mohanakrishna et al. (2020)
Furfural-containg refinery wastewater	Conventional Fenton Process	Low temperature (20-40 °C), low hydrogen peroxide (< 38 g/L) and a H_2O_2/Fe^{2+} mass ratio lower than 109	Furfural (99 %)	González et al. (2021)

In this paper review of petroleum refinery wastewater using different physical, chemical and biological methods was presented. Among them, conventional treatment technics had drawbacks as they produced large oily sludge during treatment processes. Biological treatments particularly constructed wetland were found to overcome the limitations to treat petroleum refinery wastewater since it was not only high efficient in removing COD, phosphate, and nitrate, but also were quite efficient in the removal of phenols and other organic compounds without producing any significant amount of oily sludge (Jain et al., 2020). Each method has its advantages, disadvantages, and operation limitations.

4. Conclusion

Refinery wastewater contains huge amount of TSS, BOD, COD, oil and grease, phenols, heavy metals etc. which surpass the disposal standards. Thus, treatment is essential before disposal to the environment. Several treatment techniques were applied for the treatment of refinery wastewater. Each treatment method had its advantages, shortcomings, and operational conditions. A great part of the TSS, oil and grease, organic matters was removed in the primary and secondary treatment units. Removal of the remaining parts of the pollutants, heavy metals, nitrogen compounds, and phosphorus needed further polishing in the advanced/tertiary treatment units. Combination of physical, chemical, and biological treatment processes improves removal of pollutants.

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Karakteristike otpadnih voda iz rafinerija, tehnike prečišćavanja i njihova ograničenja: pregled

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Rafinerija
Postupci prečišćavanja
Otpadne vode

I Z V O D

Velike količine otpadnih voda nastaju u rafinerijama tokom postupaka prilikom kojih se koristi sirova nafta, postupka destilacije, kao i u sistemima za hlađenje. Uzorci otpadnih voda se moraju preraditi pre ispuštanja u životnu sredinu. Odlaganje neprečišćenih otpadnih voda iz rafinerija stvara probleme za izvore vode, kao i za životnu sredinu. Cilj ovog rada je bilo ispitivanje karakteristika otpadnih voda, tehnika za prečišćavanje, kao i njihovih ograničenja. Izrađen je niz tabela u kojima se rezimira i daje pregled karakteristika otpadnih voda, postupaka za prečišćavanje i operativnih ograničenja postupaka. Rezultati su pokazali da su vrednosti nekih parametara, kao što su biohemijska potreba kiseonika (BPK), hemijska potreba kiseonika (HPK), fenola, ulja i masti, kao i ukupne suspendovane supstance (TSS) redom iznosile 40,25 mg/L do 8.000 mg/L, 80 mg/L do 21.000 mg/L, 3,5 mg/L do 128 mg/L, 12,7 mg/L do 50.000 mg/L, i 22,8 do 2.580 mg/L. Prilikom prečišćavanja otpadnih voda korišćene su brojne tehnike za prečišćavanje. Svaka tehnika je pokazala svoju prednost, slabost, kao i operativno ograničenje. Većina ukupne suspendovane supstance, ulja i masti, kao i organskih materijala je bila elimisana u jedinicama za primarni i sekundarni tretman. Tercijarni/napredni postupak je bio neophodan za uklanjanje preostalih delova zagađivača, teških metala, jedinjenja azota i fosfora. Kombinacija fizičkog, hemijskog i biološkog postupka povećava efikasnost uklanjanja zagađivača.

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Applying mass balance dilution technique for wastewater disposal to Greater-Zab river in Erbil, Kurdistan Region-Iraq

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ABSTRACT

Treatment is essential for wastewaters prior to its disposal to the environment or water sources. Numerous wastewater treatment techniques are applied for the treatment of wastewater types. To date, dilution via mass balance approach has not been reported for treatment of various types of wastewaters in Erbil City, Kurdistan Region-Iraq. Consequently, the aim of this work was to examine the treatment of various types of wastewaters using dilution method by river water through applying mass balance approach. Characteristics of different types of wastewaters and Greater-Zab River water in Erbil City were studied. Slaughterhouse, tannery, municipal, landfill-leachate, dairy, and refinery wastewaters in Erbil City were used in the present work. Mass balance approach was applied to verify that dilution of various types of wastewaters using Greater-Zab river water. Dilution factor and required amount of river water were calculated. Temperature, biochemical oxygen demand (BOD), and Dissolved oxygen (DO) were studied using mass balance approach. Results revealed that dilution factor for Erbil wastewaters varied from 10.36 to 513.91. Mixing of wastewaters with Greater-Zab river water led to decreasing of DO in the river water by 3.525 % and increasing of BOD in the Greater-Zab River water. Dilution using various quantities of raw river water via applying mass balance approach resulted in decreasing the pollutants in the wastewaters to an acceptable level and it was regarded as a treatment process. Each type of wastewater needs a definite quantity of raw water for the treatment. Commonly, sedimentation is suggested prior dilution of wastewater with the Greater-Zab River water. Maximum discharge of 1,182 m^3/s is sufficient for treatment of all mentioned types of wastewaters in Erbil City.

1. Introduction

The surface waters that are contaminated by humans' bad use causes the main problem in supplying water for humans. The concentration of pollutants in wastewater related to any combination of surface runoff, storm water, domestic, industrial, commercial, and agricultural activities is called wastewater (Sagasta et al., 2017). The characteristics of wastewaters depend on the source of the wastewater such as domestic, industrial, dairy, municipal, slaughterhouse, refinery, landfill leachate, tannery, etc. (Aziz and Ali, 2018). Mainly, pollutants in the wastewaters exceed the standards for the disposal of wastewater. Consequently, treatment methods like

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natural (dilution and land treatment), artificial (primary and secondary treatment), and combined (primary treatment and effluent disposal by natural methods) are necessary (Punmia et al., 1998; Singh and Singh, 2003). Of course, each treatment method, such as dilution method, land treatment, physical, chemical and biological treatment has advantages and disadvantages (Punmia et al., 1998; Singh and Singh, 2003; Metcalf and Eddy, 2014; Qasim, 2017; Aziz and Ali, 2018; Aziz et al., 2020). On the other hand, initial cost, maintenance and operation coasts, chemicals, and sludge disposal are other problems for the artificial treatment processes. Therefore, examining dilution process for treatment of wastewaters using river water via applying mass balance approach is another option for the treatment processes.

Mass balance approach combine quality and quantity of waters/wastewaters before and after mixing (Davis and Cornwell, 2013). In literature, several investigations and analyses were done to solve various problems that were created by wastewaters and applying the concept of mass balance. Wentze et al. (2006) investigated, both experimentally and theoretically, the conservation of mass of wastewater organic chemical oxygen demand (COD) and nitrogen compounds along the link connecting the primary settling tank and anaerobic digester. It was found that the primary sludge characteristics verses the biodegradable and un biodegradable soluble and particulate COD and nitrogen compounds needed to be calculated from mass balances around the primary settling tank. Wooley (1981) described the process to determine solids mass and location throughout a treatment plant. The researcher explained how these values could be used to determine the solids mass balance around single treatment units and the entire system. This was done by applying an analytical solution of mass balance calculations. Assis (2016) analyzed the energy and material balances of wastewater including anaerobic biological treatment process with aerobic biological treatment in a recycled board mill. The comparison of the wastewater treatment plant running before and after the start-up of the biogas plant was studied. The plant systems with the anaerobic digestion showed an increased energy use coupled to an increased flow of wastewater. Ekama et al. (2011) studied the steady state modelling of mass balance to evaluate the municipal wastewater treatment process from input and output of a stream. Nowadays, the gradual growth of continuous flow models and stoichiometry has been estimated to have a higher precedence than further progressions of simulation models. Therefore, after validation, the experimentally performances of the first stage biodegradability and waste activated sludge under anaerobic and aerobic digestion conditions was determined. Slewa et al. (2018) studied impact of Alton Kopri slaughterhouse wastewater on the quality of Lesser-Zab river water in Kirkuk City, Iraq. They found that the Alton Kopri slaughterhouse wastewater affected on the Lesser-Zab water.

In the present research, different types of wastewaters in Erbil City, Kurdistan Region-Iraq were studied. To date, there is no central wastewater treatment plant in Erbil City and produced wastewater in some areas are treated using small treatment plant in the site. Additionally, a huge amount of Greater-Zab River water is available close to Erbil City. Applying different quantities of river water for dilution of wastewaters as treatment process in Erbil City was examined. Consequently, the current study was focused on the different types of wastewaters and mixing them with Greater-Zab River water through implementing the mass balance concept for the treatment purpose.

2. Materials and Methods

2.1. Plan of the work and location of wastewaters

In the present research, treatment of different types of wastewaters such as slaughterhouse, tannery, municipal, landfill-leachate, dairy, and Kawergosk oil refinery wastewaters in Erbil City, Kurdistan region-Iraq were studied, Figure 1. Data for various kinds of wastewaters were obtained from published works and are given in Table 1. Additionally, site visiting was conducted as well. Greater-Zab River water was proposed for dilution of wastewaters as treatment technique. Information for Greater-Zab was achieved through literature and site visiting. Mass balance approach was planned for using different amount of Greater-Zab river water for dilution of wastewaters. Further, information about biochemical oxygen demand (BOD) were studied and dissolved oxygen (DO) were estimated as 0.01 mg/L for all types of wastewaters. Details about wastewaters, Greater-Zab River, Mass balance approach, and DO information are given in the upcoming parts. Dilution factor for mixing of wastewaters with river water was calculated. Further, impacts of wastewaters mixing with river water on BOD and DO in the river water were studied.

2.2. Greater-Zab River Water

Location of Greater-Zab River is illustrated in Figure 1. Characteristics of Greater-Zab water are given in Table 2. The plan was to use different amounts of river water for dilution of different types of wastewaters in Erbil city for the purpose of the study.

2.3. Mass Balance Approach

The solution of mass balances was necessary to perceive the implications of the DO sag curve problem, Figure 2. The mass balances may be applied to explain for initial mixing of the waste stream and the river. For this purpose, three resistant changes such as DO, five-day biochemical oxygen demand (BOD_5), and temperature were not stable and constant as the pollutant water mixed with the river. The conservation of mass balance for

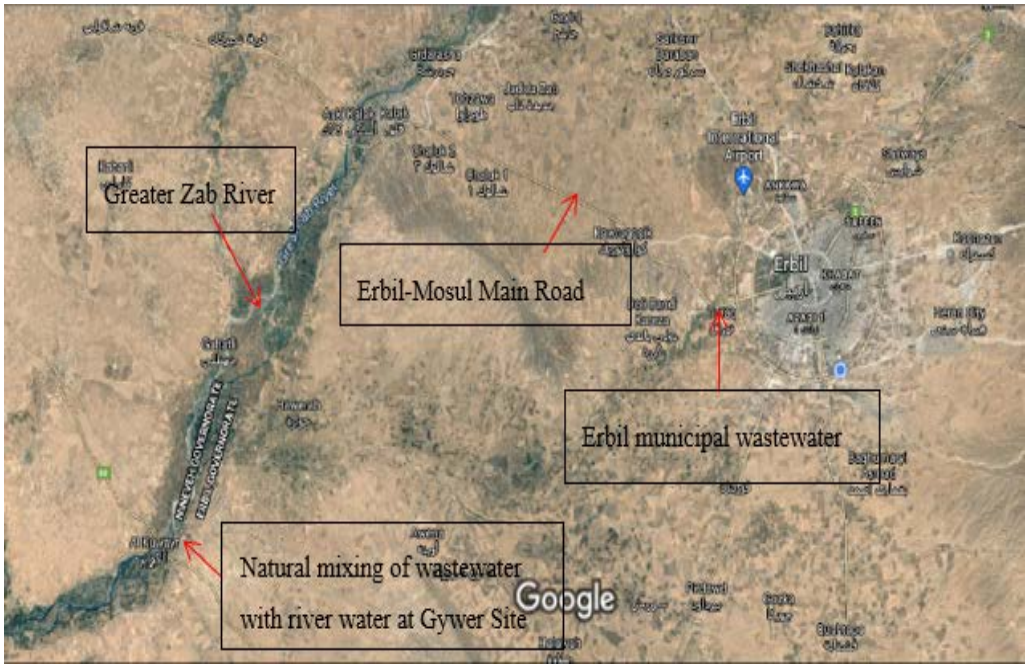

Figure 1. Different kinds of wastewater in Erbil city
Satellite image (https://www.google.iq/maps/@36.1593852,43.8110409,38506m/data=!3m1!1e3)

Table 1
Characteristics of different types of wastewater in Erbil City

No.	Types of wastewater	Q (m^3/s)	Temp. (˚C)	BOD_5 (mg/L)	k_{20} (day^{-1}) Decay Rate	References
1	Slaughterhouse	2.3	22.60	400	0.12-0.23	
2	Tannery	2.6	18.86	320	0.12-0.23	
3	Erbil Municipal	3	21.86	44	0.12-0.23	Aziz and Ali, 2018
4	Landfill leachate	4.5	12.58	273	0.12-0.23	
5	Dairy	4	21.53	650	0.12-0.23	
6	Erbil Municipal	5.5	18	62.5	0.12-0.23	Aziz, 2004; Aziz, 2020
7	Kawergosk Oil Refinery	3	32.89	155	0.12-0.23	Aziz and Fakhrey 2016

Table 2
Characteristics of Greater-Zab River water in Erbil city

References	Aziz, 2009		Aziz and Fakhrey, 2016			
River	Months / 2006	Q (m^3/s)	Months / 2015	Temp. (˚C)	BOD_5 (mg/L)	DO (mg/L)
Greater-Zab	Aug-06	165.78	Jan-15	6.3	0.2	9.11
	Sep-06	146.49	Mar-15	13.37	0.2	5.95
	Oct-06	154.85	May-15	17.11	4.2	0.17
Average	-	155.706	-	12.26	1.533	5.076

oxygen after mixing provided results in a mass of oxygen per unit time (Davis and Cornwell, 2013).

$$\textit{Mass of pollutant in wastewater} = Q_w\, C_w \quad (1)$$

$$\textit{Mass of pollutant in River} = Q_r\, C_r \quad (2)$$

$$C_m = \frac{\text{Mass of Concentraion after mixing}}{Q_w + Q_r} = \frac{Q_w\, C_w + Q_r\, C_r}{Q_w + Q_r} \quad (3)$$

Where: Cm is the concentration of pollutants after mixing (g/m^3), Q_w is the volumetric flowrate of wastewater (m^3/s), Q_r is the volumetric flowrate of river

(m^3/s), C_w is concentration in the waste water (g/m^3), and C_r is concentration in the river (g/m^3).

The conservations of pollutants (such as DO and BOD) after mixing are the respective masses per unit time divided by the total flow rate of wastewater and river flow (Davis and Cornwell, 2013).

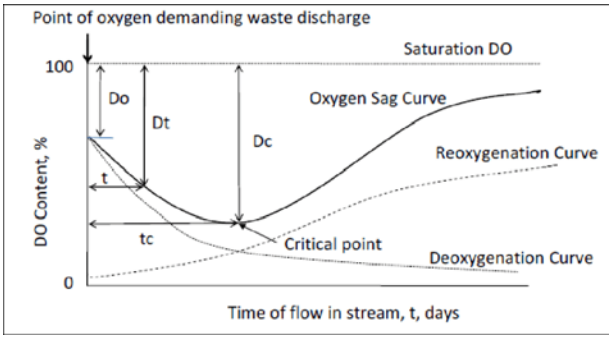

Figure 2. De-oxygenation, re-oxygenation and oxygen sag curve (Baba, 2020)

3. Results and Discussions

3.1. Characteristics of Wastewater

Commonly, the pollutants in the wastewaters exceeded the standard disposal limits. Accordingly, treatment processes are essential prior disposal to the natural environment (Bapeer, 2010; Shekha et al., 2010; Aziz and Ali, 2018; Aziz 2020). Published works revealed that different treatment techniques, such as sequencing batch reactor, adsorption, lagoons, oxidation ditch, wetland, and trickling filter, were applied for treatment of wastewaters in Erbil city (Fakhrey, 2016; Aziz et al., 2020). Of course, each treatment method has advantages and disadvantages. Additionally, initial cost, construction, operation and maintenance are other difficulties of the mentioned treatment process. Consequently, in the present work, treatment of various types of wastewaters using dilution by river water was examined. Further details are given in the future sections. Commonly, Erbil municipal wastewater is considered as weak wastewater; While, landfill leachate is regarded as strong type wastewater (Metcalf and Eddy, 2014; Aziz and Ali, 2018; Aziz, 2020).

3.2. Greater-Zab River Water

The characteristics of Greater-Zab River water was aforementioned earlier from the published works (Aziz, 2004; Aziz, 2009; Shareef et al., 2009; Toma, 2013; Aziz and Fakhrey, 2016; Shekha, 2016; Aziz and Mustafa, 2019). In addition, the discharge of Greater-Zab River water was reported as well. It is clear that Greater-Zab river water needs treatment, if used for water Supply system (Aziz and Mustafa, 2019). Regarding BOD and NH_3-N values, Greater-Zab river water is considered as non-polluted water (Table 3). The minimum value of Greater-Zab River water flow was 57 m^3/s which was informed in September 2001. While, the maximum flow of 1,182 m^3/s was described in February 2006.

3.3. Treatment by Dilution Method

Ratios (Dilution factor) of Greater-Zab River water to wastewaters were calculated as given in Table 4. Values of dilution factors for different types of wastewaters varied from 10.36 to 513.91. Standards of dilution are shown in Table 5. If minimum flow of Greater-Zab river water was used, the wastewater should be treated thoroughly so that the effluent did not contain more than 30 mg/L of suspended solids and its BOD_5 at 18.3 °C did not exceed 20 mg/L. While, if maximum discharge was applied easier treatments were required. For maximum discharge of Greater-Zab River, commonly sedimentation was suggested prior dilution of wastewater with the Greater-Zab river water.

Table 3
Water quality standard for rivers (Aziz and Fakhrey, 2016)

No.	Water Quality/Item	Non (Slightly) polluted	Lightly-polluted	Moderately-polluted	Severely-polluted
1	DO (mg/L)	DO ≥ 6.5	6.5 > DO ≥ 4.6	4.5≥ DO ≥ 2	DO < 2
2	BOD_5 (mg/L)	$BOD_5 \leq 3$	3 < $BOD_5 \leq 4.9$	5.0 ≤ $BOD_5 \leq 15$	$BOD_5 > 15$
3	TSS (mg/L)	TSS ≤ 20	20 < TSS ≤ 49.9	50 ≤ TSS ≤ 100	TSS > 100
4	NH_3-N (mg/L)	NH_3-N ≤ 0.5	0.5 < NH_3-N ≤ 0.99	1 ≤ NH_3-N ≤ 3	NH_3-N > 3
5	Point sources	1	3	6	10
6	Pollution Index Integral Value	S ≤ 2	2 < S ≤ 3	3.1≤ S ≤ 6	S > 6

Table 4
Ratio (Dilution factor) of Greater-Zab river water to wastewaters amount

No.	Types of wastewater	Q (m^3/s)	References	Amount of Greater-Zab River/Wastewater	
				For Min. Q (57 m^3/s)	For Max. Q (1,182 m^3/s)
1	Slaughterhouse	2.3		24.78	513.91
2	Tannery	2.6		21.92	454.62
3	Erbil Municipal	3	Aziz and Ali, 2018	19	394
4	Landfill leachate	4.5		12.67	262.67
5	Dairy	4		14.25	295.5
6	Erbil Municipal	5.5	Aziz, 2020	10.36	214.91
7	Kawergosk Oil Refinery	3	Aziz and Fakhrey, 2016	19	394

Table 5
Standards of dilution (Punmia et al., 1998)

Dilution factor	Standards of purification required
Above 500	No treatment required. The raw sewage or wastewater can be discharged directly in the receiving water.
Between 300 to 500	Primary treatment consisting of plain sedimentation is required so that effluent does not contain more than 150 mg/L of suspended solids.
Between 150 to 300	Treatment such as sedimentation, screening and chemical precipitation are required, so that the effluent does not contain more than 50 mg/L of suspended solids.
Less than 150	The wastewater/sewage should be treated thoroughly so that the effluent does not contain more than 30 mg/L of suspended solids and its 5-day BOD at 18.3 °C does not exceed 20 mg/L.

3.4. Application of Mass Balance Approach

To obtain the required amount of Greater-Zab water for dilution of different types of wastewaters, the following equation was derived and applied.

$$Q_r = \frac{Q_w\, C_w - Q_w\, C_m}{C_m - C_r} \quad (4)$$

The items of the equation were previously defined. Table 6 illustrates the calculated discharges of Greater-Zab river water for mixing of wastewaters with the river water. BOD of 3 mg/L was decided, because river water with this value of BOD was regarded as non-polluted river water, while, BOD of 15 mg/L was considered as moderately polluted river water (Table 3).

It was suggested to not change the quality of Greater-Zab River as non-polluted after disposal of the wastewaters to the river water. Minimum Greater-Zab water flow of 57 m^3/s was suitable for treatment of Erbil municipal and treated Kawergosk oil refinery wastewaters. On the other hand, maximum discharge of 1,182 m^3/s was sufficient for the treatment of all mentioned types of wastewaters in Erbil City.

Table 6
Required amount of Greater-Zab River water after mixing wastewaters

Raw Wastewater	Raw Wastewater			Raw River Water		Wastewater plus River water		Discharge Required
Type	BOD (mg/L)	Q (m^3/s)	References	BOD (mg/L)	Q (m^3/s)	BOD (mg/L)	Q (m^3/s)	Q (m^3/s)
Slaughterhouse	400	2.3	Aziz and Ali, 2018	3	57	15	59.3	73.79
Tannery	320	2.6		3	57	15	59.6	66.08
Erbil Municipal	44	3		3	57	15	60	7.25
Landfill leachate	273	4.5		3	57	15	61.5	96.75
Dairy	650	4		3	57	15	61	211.67
Erbil Municipal	62.5*	5.5**	Aziz, 2004*; Aziz, 2020**	3	57	15	62.5	21.77
Kawergosk Oil Refinery	155	3	Aziz and Fakhrey, 2016	3	57	15	60	35.00

Mixing of wastewaters with river water caused depletion of DO in the river (Davis and Cornwell, 2013; Slewa et al., 2018). Percentage depletion of DO is given in Table 7. Furthermore, one of the main factors that influenced the decreasing of DO levels in the rivers was the ultimate BOD (La) and BOD rate constant (k). The numerical value of rate constant was dependent on the type of the wastewater that was discharged into the river, capability of organisms to operate the waste in the system, and the temperature of the water. Therefore, monthly temperature was measured and BOD_5 was experimentally tested behind the DO of the Greater-Zab River. For more simplification and implementation of the mass balance concept, the average value of DO was estimated to be 5.076 mg/L during the year of 2016.

The BOD rate constants k per day (d^{-1}) for compound wastewaters was to be supported by the proportionate of the various components. As explained in the references, the typical BOD rate constant at standard (20 °C) mixture temperature ranged between from 0.35 to 0.7 d^{-1} for raw sewage water, while for well-treated sewage and polluted river water was between 0.12 to 0.23 d^{-1} (Davis and Cornwell, 2013). These values showed that there was a lower rate constant for treated sewage compared to raw sewage result from the more quickly reducible of organism compound completely removed than less readily degradable organic compounds during wastewater treatment. Hence, the laboratory testing was done at a standard temperature of 20 °C, the BOD rate constant (k_{20}) was modified to the accommodate water temperature constant rate (k_T) by using the following equation:

$$k_T = k_{20}\ \theta^{(T-20)} \quad (5)$$

where: T is the temperature of the mixture in °C and θ is the temperature coefficient which was 1.135 for temperature range from 4 to 20 °C and equals to 1.056 for temperature range (20 to 30) °C.

In this investigation, the average typical value of BOD rate constant for Greater-Zab River polluted with different kinds of wastewaters was taken as average value of 0.175 d^{-1} then the ultimate BOD values for wastewater (L_w) were determined by equation:

$$L_w = \frac{BOD_5}{1 - e^{(-k\,T)}} \quad (6)$$

Greater-Zab River may contain large deposits of organic matter within the sediments at their bed. These may be natural deposits of leaves and dead aquatic plants or may be sludge deposits from different types of wastewaters that are not treated and discharged into the system of this river. In either case, decomposition of this organic matter places an extra capacity on the stream's oxygen resource since the oxygen demand must be supplied from the excessively water.

Aquatic plants may have a considerable effect on the DO levels. During the mid-day, their photosynthesis has a specific act to generate the oxygen that abundance the reaeration and may even cause oxygen supersaturation. However, plants consume oxygen for respiration processes. Although there's a net overall production of oxygen, plants respiration can severely lower DO levels during the night.

For these purposes, the contaminants inside the wastewaters or sewage should be transported by well treatment processes then convert it into an effluent that can be returned to the water cycle with acceptable impact on the environment, or reused for various purposes.

Table 7
Variation of BOD and DO in Greater-Zab River after mixing

No.	Wastewater Type	k_T (day^{-1})	Lw (mg/L)	After Mixing (wastewaters + Greater Zab River)	La (mg/L)	DO (mg/L)	% DO depletion in river
1	Slaughterhouse	0.2016	404.2422		7.3953	5.0029	1.4742
2	Tannery	0.1515	339.5047		7.0841	4.9935	1.6665
3	Municipal*	0.1937	44.6474		2.3483	4.9809	1.9228
4	Landfill Leachate	0.0684	473.1661		14.7809	4.9344	2.8842
5	Dairy	0.1902	661.0060		18.0504	4.9498	2.5637
6	Municipal **	0.1358	68.43		6.8978	4.9038	3.5251
7	Kawergosk Oil Refinery	0.8952	155		2.9221	4.9809	1.9228

* Aziz and Ali (2018)
** Aziz, 2004
L_w is ultimate BOD of the waste water (mg/L).
La is the initial ultimate BOD after mixing.

4. Conclusions

Treatment of different types of wastewaters (such as slaughterhouse, tannery, municipal, landfill leachate, dairy, and oil refinery) using dilution by Greater-Zab River water was studied. Wastewaters need treatment before disposal to the water sources. The following conclusions were outlined:

- Types of wastewaters varied from weak (municipal wastewater) to strong wastewaters (landfill leachate).
- Greater-Zab River was considered as non-polluted river according to BOD_5, NH_3-N, and DO values.
- Dilution factor for Erbil wastewaters varied from 10.36 to 513.91. Mixing the wastewaters with Greater-Zab river water led to decreasing of DO in the river water by 3.525 %.
- Commonly sedimentation was suggested as a step taken prior to the dilution of wastewater with the Greater-Zab River water.
- Maximum discharge of 1,182 m^3/s was sufficient for treatment all mentioned types of wastewaters in Erbil City.
- Dilution using various quantities of raw river water via applying mass balance approach resulted in decreasing the pollutants in the wastewaters to an acceptable level and it was regarded as treatment process.
- Further, each type of wastewater needs a definite quantity of raw water for the treatment.

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Primena tehnike smanjenja masenog bilansa za odlaganje otpadnih voda u reku Gornji Zab u Erbilu u regiji Irački Kurdistan

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INFORMACIJE O RADU

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I Z V O D

Prečišćavanje otpadnih voda pre njivog puštanja u životnu sredinu ili izvore vode predstavlja neophodan korak. Za prečišćavanje različitih vrsta otpadnih voda primenjuju se brojne tehnike. Do sada nije zabeležena primena postupka smanjenja masenog bilansa za prečišćavanje različitih vrsta otpadnih voda u gradu Erbilu koji se nalazi u regiji Irački Kurdistan. Shodno tome, cilj ovog rada je ispitivanje primene metode smanjenja masenog bilansa dodavanjem rečne vode za prečišćavanje različitih vrsta otpadnih voda. Ispitivane su osobine različitih vrsta otpadnih voda, kao i osobine vode u reci Gornji Zab koja protiče kroz Erbil. Ispitivane su osobine otpadnih voda iz klanica, pogona za štavljenje, komunalni otpad, procedne vode, kao i otpadne vode iz mlekara i rafinerija koje se nalaze u Erbilu. Postupak koji uključuje maseni bilans je primenjen da bi se potvrdilo smanjenje različitih vrsta otpadnih voda u prisustvu vode iz reke Gornji Zab. Izračunat je faktor smanjenja i potrebna količina rečne vode. Temperatura, biohemijska potrošnja kiseonika (BPK) i rastvoreni kiseonik su takođe ispitani. Rezultati su pokazali da je faktor smanjenja kod ovih otpadnih voda varirao između 10,36 i 513,91. Mešanje otpadnih voda i vode iz reke Gornji Zab je dovelo do smanjenja količine rastvorenog kiseonika u rečnoj vodi za 3,525 %, kao i do povećanja biohemijske potrošnje kiseonika u vodi Gornjeg Zaba. Smanjnje masenog bilansa koristeći različite količine neobrađene rečne vode je dovelo do smanjenja zagađivača u otpadnim vodama na prihvatljiv nivo i voda se smatrala prečišćenom. Za prečišćavanje različitih vrsta otpadnih voda potrebna je određena količina neobrađene vode. Sedimentacija je postupak koji se obično preporučuje pre primene postupka smanjenja masenog bilansa vodom iz Gornjeg Zaba. Maksimalni protok od 1.182 m^3/s smatra se dovoljnim za tretman svih pomenutih vrsta otpadnih voda na teritoriji grada Erbil.

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Assessment of sustainability and management for groundwater source in Erbil city

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ABSTRACT

The issue of rationalizing water consumption and preserving it for future generations is one of the most important indicators of sustainable development referred to in the Agenda 21. This study aims to assess the sustainability of water resources for the city of Erbil in terms of quantity and quality. In this study, the amount of water available in the existing water sources was evaluated and compared with the volume of water demand. The reliability of water sources, especially groundwater, in the selected area was evaluated and confirmed. The study also focused on the management of groundwater by the concerned authorities and the identification of factors that help to develop the sustainability of these sources. The problems facing the management of groundwater and the proposed solutions to solve these problems were also identified. Due to the rapid growth of the populations and lack of both water demand and water supply system, Erbil City required a fundamental evaluation of water supply systems and good planning for future. However, in this study, the assessment was conducted based on the existing data and the accurate archived documents as well. As a result, the study concluded that there have been a lot of problems that should be taken into consideration in order to provide good managing of the groundwater system. It was also observed that there was slightly higher depletion in groundwater table due to poor supplying. This study can be used as a fundamental reference for future investigations especially for those areas having the same problems in sustainable management of the subsurface basins.

1. Introduction

Generally, groundwater has a crucial role in water supply system worldwide due to its large percentage as Earth's water. Recently, Erbil City, which is in the northern part of the Kurdistan Region of Iraq and it is rapidly expanding area due to increasing the population growth, has faced economic problems. However, it is necessary to monitor and better manage the sources of water and provide for water in the following years. It can be pointed out that the impact of climate change and sustainability on both groundwater and surface water

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resources is important. The requirement for groundwater studies are necessary for providing sustainable management of water resources and its variability for a long period in order to better manage the system (Nanekely et al., 2017). However, in most of the countries, groundwater is a vital source for agricultural, domestic, and industrial purposes. The requirement is to increase water demand due to high population growth, therefore, the problems that the groundwater sources face should be taken into account (Hawez et al., 2020).

Moreover, in Erbil City, due to rapid population growth, the demand for water has increased and the percentage of domestic wells represents 40 % of water supply system in the city. Erbil City mostly uses surface water from Ifraz water treatment plant, which is directly located on the Greater-Zab River. The second source for groundwater is in the area which is used for the irrigation, industrial, and other daily activities as well (Wali and Alwan, 2016). In addition, the groundwater quality depends on the composition of the aquifer recharge and the interactions between both material and the groundwater. It is obvious that clean water is applied for many activities based on World Health Organization (WHO) which states that about 80 % of all the diseases in human beings are caused by water (Toma et al., 2013).

Similarly, there are numerous researchers that work on the sustainability of the water resources. The study of Menon (2007) focused on managing of the groundwater, and Halim et al. (2010) studied the causes of spreading disease through water. Later, Vishwajit et al. (2012) investigated sustainability, and the study of Toma et al. (2013) conducted an investigation into groundwater quality in Erbil City. Jadoon et al. (2015) studied water quality in Erbil City. Miran and Ahmed (2016) explained the sustainability for water sources in their study area.

Moreover, Bapper et al. (2016) evaluated the water quality in Erbil City as well. However, the investigation of Nanekely et al. (2017) was also on sustainability of groundwater management in Erbil City. In addition, there is also the study of Dizayee (2018), which was on groundwater level in Erbil Basin. However, Qurtas (2018) determined the recharge of Erbil groundwater. In spite of this, Mawlood and Omer (2019) used a method to estimate the depth of the Erbil Groundwater. Later, Mawlood (2019) did the investigation on groundwater sustainability for the studied area, and then the study of Mahmood and Omar (2019) investigated the amount of water supplied for population of the selected area.

Hawez et al. (2020) studied quality of the groundwater in Kurdistan Region Provinces. Sustainable water management in Iraq is becoming an urgent matter, despite the political instability in the region with special attention to the Kurdistan Region, and also presents to offer possible changes to the legislative framework (Yousuf et al., 2018). The current research aimed to evaluate the sustainability of water resources in Erbil City in terms of amount and characteristics. In this research, the quantity of water available in the existing water sources was assessed and compared with the volume of demand. The reliability of water sources, especially groundwater, in the selected area was evaluated and confirmed as well. Additionally, the research focused on the groundwater management by the concerned authorities and the identification of issues that assist the development of sustainability of these sources.

2. Study Area Location and Data Collection

Erbil Province is the capital of Kurdistan Region of Iraq, and it is located in the north-east of Iraq, and it covers area of about 197 km^2 with the elevation of the 414 m above sea level (Mahmood and Omar, 2019). It is surrounded by the Greater-Zab River at the north-west and by the Lesser-Zab River at the south-east. However, the sources of water supply depend on both surface water and the groundwater that supply water in the form of wells, Figure 1. Ifraz 1, Ifraz 2, and Ifraz 3 water treatment plants are constructed on the Greater-Zab River and supply drinking water to a big part of Erbil City (Aziz and Mustafa, 2019).

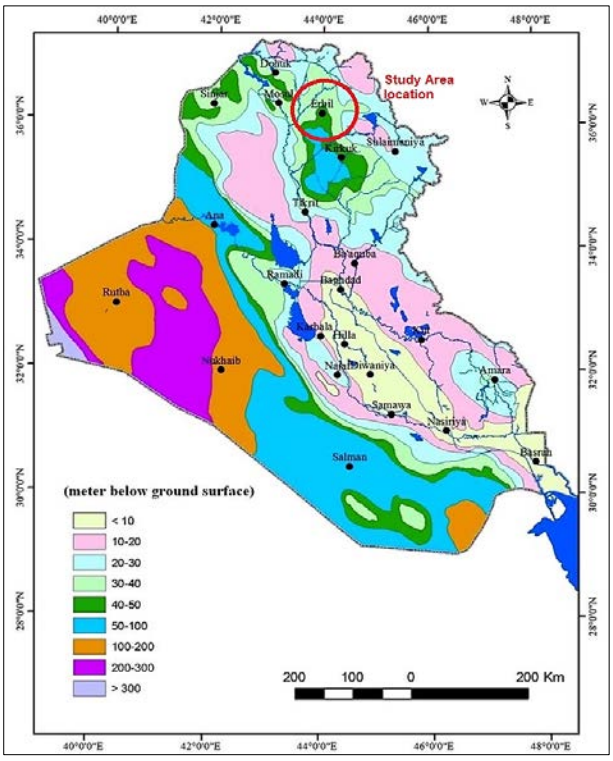

Figure 1. Location of Erbil City

Erbil groundwater basin is divided into three sub-basins, Kapran in the northern part with the area of about 915 km^2, central part is about 1,400 km^2, and Bashtepa area is about 885 km^2, Figure 2. Based on the data on Erbil groundwater, the depletion in Erbil basin is about 100 m. The lowering groundwater in the area refers to

drilling uncontrolled wells in the area. However, the increase in groundwater level mainly depends on the amount of Recharge of the aquifer storage in the recharge area and the velocity of the porous media in the region.

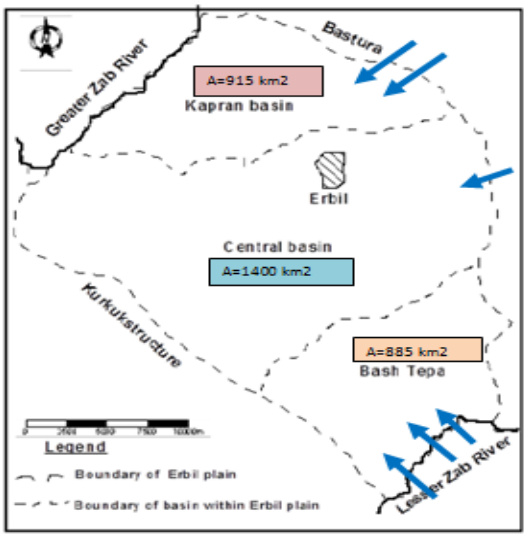

Figure 2. Map of groundwater basins in Erbil City (Abdulnasir, 2011)

During the study the data was collected from the following directorates:

- The data on water quantity were obtained from General Directorate of Water and Sewerage in Kurdistan Region of Iraq (2021);
- The water quality Data were obtained from Erbil Health Laboratory Center (EHLC);
- General Directorate of Health-Erbil, Ministry of Health, Kurdistan Region, Iraq, 2021; and
- Wells data and Monitoring levels were obtained from Directorate of groundwater of Erbil, Kurdistan Region of Iraq (2021).

3. Estimation of Water Quantity

Generally, estimating the quantities of the groundwater mainly depend on production wells. Meanwhile, the collected data of surface water, which include the diverted water form Greater-Zab River, form existing water treatment plants (i.e. Ifraz 1, Ifraz 2, and Ifraz 3) for Erbil City during 2014 up to 2018, Table 1. Table 2 illustrates the details of Ifraz 1, Ifraz 2, and Ifraz 3 Water Treatment Plants.

On the other hand, the estimated amount of groundwater is presented based on the number of populations with wells number and operation time. The current study estimates the approximate quantity of waters based on the data available, number of wells are about 1,200 based on data taken form General Directorate of Water and Sewerage in Kurdistan Region of Iraq (2021).

The estimated rate of well drainage for each well = 25 m^3/hr.

The average number of operating hours for each well = 15 hours.

The produced water from wells = 1200 wells · 25 m^3/hr · 15 hr = 450,000 m^3/day.

The total quantity of water (i.e. Water treatment plants, Table 2, plus groundwater wells) = 34,000 + 44,000 + 216,000 + 450,000 = 744,000 m^3/day.

The rate of losses is about (15 %) (General Directorate of water and Sewerage in Kurdistan Region of Iraq, 2021).

Thus, the remaining net quantity = 744,000 · 85 % = 632,400 m^3/day.

Average daily water consumption in Erbil City is about 380 liters/Capita/day based on the obtained data form Directorate of Water and Sewerage in Kurdistan region of Iraq (2021), Erbil city for water supply depending on 45 % of the groundwater through wells and 55 % of Surface water through water treatment plant units which are three Ifraz projects.

Table 1
The estimated amount of water per year (Mahmood and Omar, 2019)

Year	2014	2015	2016	2017	2018
m^3/year	139,036,720	143,472,095	158,069,446	164,331,177	172,687,525

Table 2
Detail of the Water Treatment Plants on Greater-Zab River (Omar, 2020)

No.	Water treatment plant	Constructed year	Location of Water treatment plant	discharge (m^3/day)	Location of distributions
1	Ifraz 1	1968	Ifraz village	34,000	Erbil city
2	Ifraz 2	1983	Erbil city	44,000	Erbil city
3	Ifraz 3	2007	Ifraz village	216,000	Erbil city

4. Groundwater Water Quality

Physical and chemical characteristics of 265 groundwater wells in Erbil City for the period of January to June of 2021 is given in Table 3, and the Data were obtained from Erbil Health Laboratory Center (EHLC, 2021). It can be noticed from the table that commonly all parameters are within the allowable limits according to Iraqi specification NO. 1974/417. Only, turbidity and nitrate have surpassed the standards. Nitrate value of one well in Ashti location were out of standard range, probably due to seepage of sewerage system into groundwater that caused the increase of the nitrate concentration.

There are a numerous well inside the area, Figure 3. Practically, groundwater is used for water supply in different locations. Groundwater disinfected via chlorine and it is used by consumers for domestic uses. In the past two decades, some groundwater wells were closed in some quarters in Erbil City due to nitrate problems. On the other hand, termination of some groundwater wells in Erbil City and its replacement by Ifraz water treatment plants is regarded as application of sustainable approach and management towards groundwater sources in the city.

Table 3
Characteristics of some wells of Erbil groundwater (EHLC, 2021)

Parameter	Min.	Max.	Standard
pH	7.0	8.2	6.5-8.5
Turbidity (NTU)	0.2	35	0-5
EC (ms/cm)	0.124	0.977	0.5-1.5
Total dissolved solids (mg/L)	27	625	0-1000
Total alkalinity (mg/L)	66	167	0-200
Total hardness (mg/L)	80	376	0-500
Chloride (mg/L)	9.4	21	0-250
Calcium (mg/L)	11	124	0-200
Magnesium (mg/L)	5	62.5	0-150
Sodium (mg/L)	2.8	192	0-200
Potassium (mg/L)	0.14	24	0-250
Nitrate (mg/L)	3	138	0-50
Salphate (mg/L)	41	148	0-500

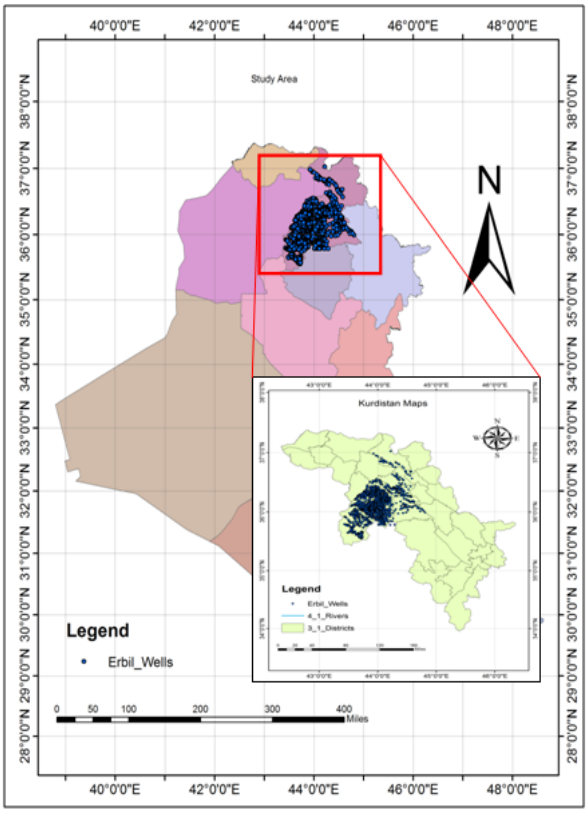

Figure 3. Distribution of the wells in the study area

In addition, for determination of the quality of water in Erbil City is based on the previous study performed by Aziz (2004), who studied the seasonal variation of water and wastewater for the study area. The author collected the samples from well No.3 in Iskan Quarter. Toma et al. (2013) investigated water qualities for the six-wells in various quarters of Erbil City (Ronaky 1, Tayrawa 1, Badawa 13, Azadi 8, Rizgari 1, and Ankawa 9). Their results explained that the quality of water was suitable for drinking purposes. Moreover, the water quality for fifty wells within Erbil city were tested by Daham et al. (1998). In addition, the study observed a high pH, turbidity, total hardness, and alkalinity of water in Erbil City. Similarly, in both Bakhtiari and Ainkawa quarters, five wells were tested by Jadoon et al. (2015). The authors found that the water quality from the wells was also subjected to significant contaminants such as high concentration nitrates and pathogens (Hawez et al., 2020), Figure 4. Aziz and Mawlood (2015) conducted a study on the effect of Erbil Landfill Site on the groundwater contamination by formed landfill leachate.

They found that produced leachate polluted the groundwater close to the landfill area. In another research carried out by Aziz and Fkhrey (2016), the impact of Kawer Gosk Oil Refinery wastewater on the groundwater in the surrounded area was studied. The researchers reported that there was no impact of Kawer Gosk Oil Refinery wastewater on the groundwater in Aghulan village near the refinery in 2016.

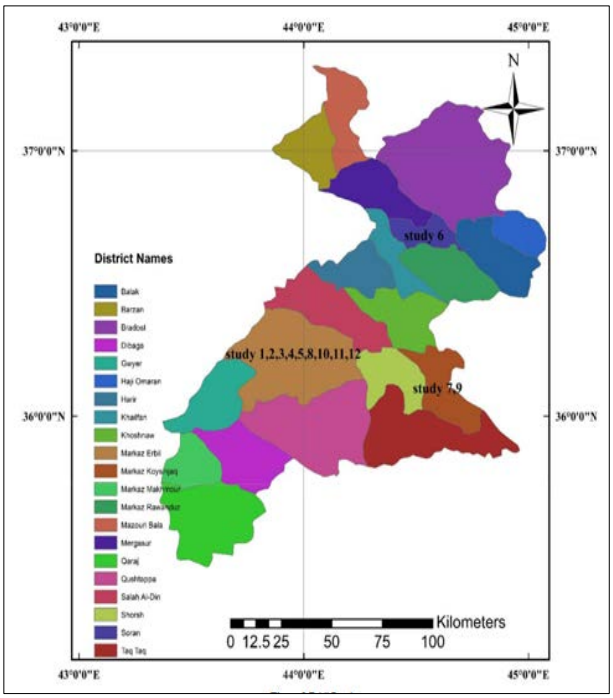

Figure 4. Groundwater quality investigation locations (Hawez et al., 2020)

According to Al Sudani (2019), the groundwater quality was increasingly threatened due to industrial wastes and urban and agricultural wastes that were leaked or injected into the underlying aquifers. However, groundwater was exposed to pollution when pollutants entered from landfills and locations that used to store waste. In addition, the chemical spills and the subsurface storage tanks leakage were also seen as a threat, as well as the sites of the hazardous waste that were improperly managed. Groundwater pollution can also be a result of using fertilizers and pesticides, the disposal of human, animal and the agricultural waste, and the use of chemicals. Additionally, most of the serious effects on water pollution is human infectious disease, especially when sanitation facilities are rarely found. Meanwhile, the safety measures are simpler and fewer costly than remedial measures for groundwater pollution.

5. Evaluation of Erbil Groundwater Sustainability

According to Agenda 21, which addresses the critical issues faced by the global community, this problem will require not only the leadership and funding of governments and business, but also the vision, cooperation and work of every citizen. Sustainable development cannot be achieved without all sectors of society working together. One of the most important points is about protecting and managing water resources and to keep safe drinking water and sanitation, which are the basic requirements for public health and dignity. A cleanup of the most obvious sources of pollution is also needed in order to provide suitable water and sanitation for all in the future. However, according to Vélez et al., (2020) "The concept of sustainability was brought to the forefront by the World Commission on Environment and Development (WCED) held in 1987, and, since then, it has been commonly applied to the whole variety of resources exploited by human society, including groundwater. In fact, the European Water Framework Directive, enacted in December 2000, establishes that it is necessary to promote a sustainable water use". Raouf (2011) stated that the rapid population growth, increase in the number of residential, housing projects, old ways, and methods to manage the resources of water also cause the shortage of water in some areas in Erbil. It also represents one of the reasons that has led to the decrease of Erbil groundwater level. Accordingly, the Kurdistan Region Government should formulate long term strategic policies to develop the water resources management.

The current study states that Erbil groundwater requires the development of sustainability to keep the safe drinking water for future challenges. The detail of the sustainability development of groundwater is explained in Figure 5.

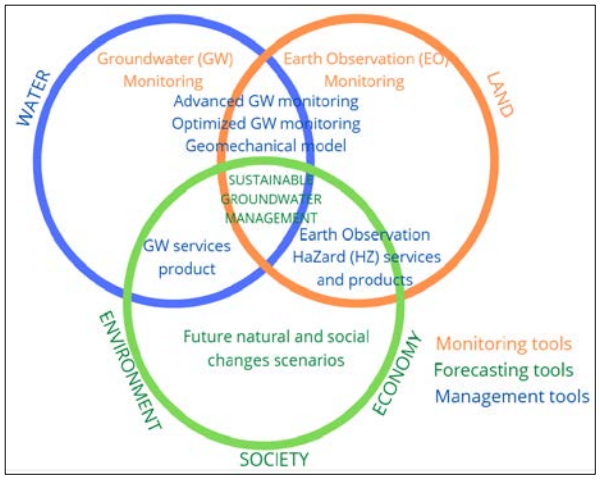

Figure 5. Diagram of Sustainability of Groundwater Management (https://reservoir-prima.org/about-us)

5.1. Sustainability Management of Groundwater in Erbil City

The actual number of drilled wells in Erbil basin is higher than the number of recorded wells which legally drilled, and for these reasons, it is noticed from the previous studies that the ground water table has depleted, and people in this area are facing many problems due to water shortage because several wells have dried in the area as well. This is all due to the increasing number of illegal drilled wells which are located within the selected area and poor water supply and management. The current study highly depends on the available data on the drilling of wells that can be provided from Ministry of Agriculture and Water Resources. Another researcher described that the number of wells in the Central sub-

basin is much higher than the number of wells provided in the data. However, most of the illegal wells are not recorded in the documents. Based on this, other study stated that out of the 650 wells that the author used to conduct the research, 46.6 % (303 wells) were found to be illegal according to Dizayee (2018). Although, the study of Nanekely et al. (2017) determined the conditions of the groundwater levels in area and it was highly declined in the period 2006-2009. However, lots of studies presented that the groundwater pumping intensified during the previous years. It was the same as that the total pumping rates exceeded the recharge rates over large areas, as groundwater tables were declining a negative residual term was found of about 10 mm per year. Moreover, sustainable groundwater should be implemented by management related organizations especially by the regional stakeholders, and also the hydrologists, environmental and political constraints as well. Securing water for future involves many considerations, from those minimizing the net groundwater losses from the aquifer storage, managing groundwater as an integrated part of the hydrologic cycle, developing infrastructure based on an understanding of the natural hydrologic system, and using water based on the required amount and efficiency. In spite of this, Figure 6 shows that there is a large number of wells that exist in the selected area, which caused the depletion in efficiency and the capacity of the production wells, and also caused the production wells to dry in the short period of time and cause drought problems.

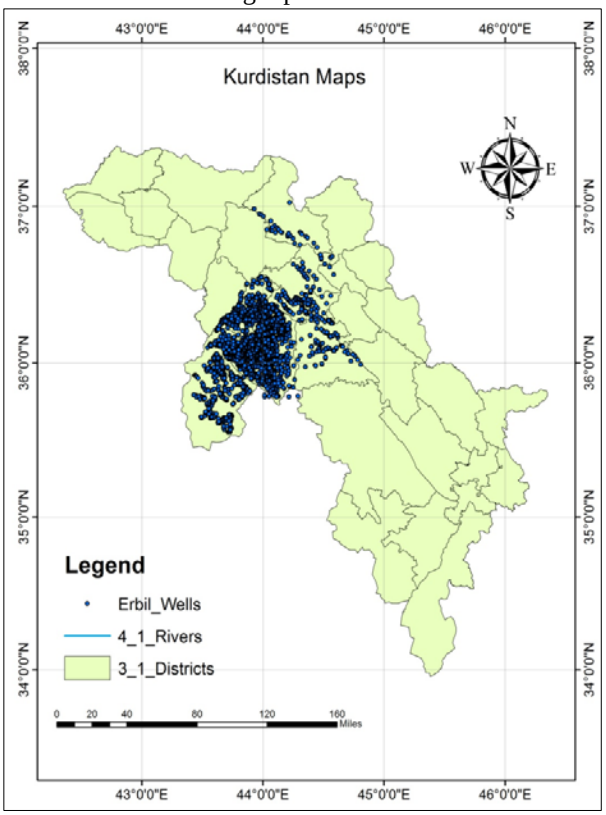

Figure 6. Wells in the study area Created by ArcGIS (Arc Map 10.4)

5.2. Groundwater conditions in Erbil Area

The current study presented the groundwater deletion in the area. The data collected during the study was based on the information obtained from the General directorate of Groundwater in Erbil. There is a number of production wells used for monitoring groundwater fluctuations in the region. Depending on the data available, a large depletion of groundwater reserves has been recorded, which is the worst case of the aquifer system in Erbil basin. However, the paper tried to assess the problems in water resources management in the Erbil Area, as well as, determine the best solutions for water sector problems. For instance, the main problem is groundwater depletion due to the uncontrolled drilling of illegal wells. Consequently, it is required to develop the scientific plan for better management of the groundwater resources in the area. In general, there are a several production wells used for monitoring of the groundwater fluctuations inside all Erbil regions, Figure 7:

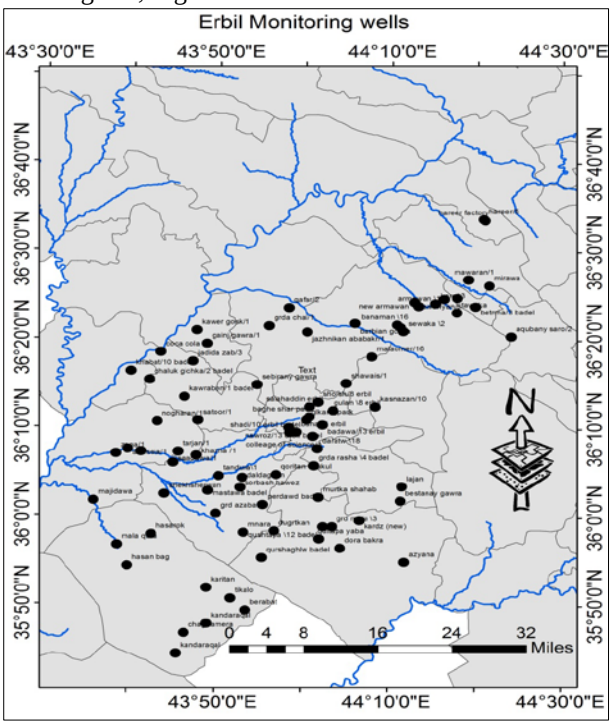

Figure 7. Production wells used for monitoring Groundwater level in the area (ArcGIS 10.4)

Depending on the obtained data from the directorate of Erbil Groundwater, there is a slight depletion in water level, and the details are shown in Figure 8. It is impossible to use production wells for monitoring purposes and it is not allowed within the standard limitations, because inside the production wells there are great losses due to casing. In addition, the sounder may take the error data and spiral with the well pumps. Therefore, it is important to install new observation wells (Unconfined) or piezometric wells (for confined) aquifer

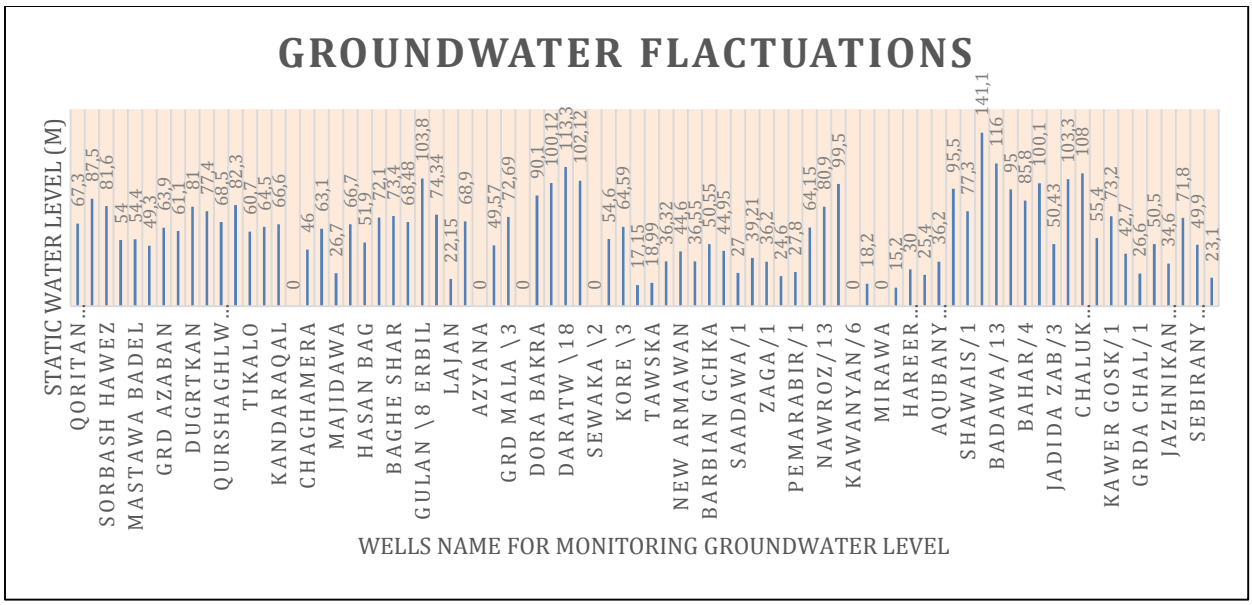

Figure 8. Groundwater Fluctuation in the Erbil Area

for monitoring purpose instead of taking data on the production wells. This is in case if the authority decides to manage water resources in an appropriate way.

6. Proposed Plans for Groundwater in Erbil City

The current study verified that the Erbil City directly provided its required source of water of which about 55 % depends on the Greater-Zab River and 45 % on Groundwater. This water is provided by the water treatment plants, which is responsible for the determining the required amount of supply for each capita. Some of the groundwater pumped out from the wells is subjected to pollutants, such as a high concentration nitrates and pathogens. This water source also has a higher nitrate and E.coli level than the water that comes from the Ifraz. However, when the pathogen (coliform, E.coli) amounts increase, the potential for creating higher levels of disinfection by-products also exist which is also a water quality concern. Meanwhile, Erbil continually imports this treated water by Ifraz water treatment plants. The treated water from water treatment plants is normally disinfected by chlorine gas. Jadoon et al. (2015) stated that chlorine has the effect on the human health. Based on the report of Japan company for the Ministry of Municipalities and Public Works, Iraq, in 2015, the water supply and water demand for Erbil central and surrounding parts are shown in Table 4.

For sustainable management and future plans of the water sources in Erbil City, it is recommended to minimize usage of the groundwater and increase usage of the Greater-Zab River by constructing a new water treatment plant. Additionally, reusing of Erbil municipal wastewater for the irrigation purpose, instead of using groundwater for irrigation, on the other hand, finding other sources for car washing, watering gardens, fish production etc. can be seen as a solution as well. Treated wastewater can be used for recharging groundwater as well. Construction of a proper sewerage system for collection of black water and grey water for avoiding groundwater pollution and treatment purpose is also important. Currently, black water in Erbil City is discharged directly to cesspools which cause groundwater pollution in some old areas in the city.

Table 4
Data of water demand based on (Japan ICA NJS, 2015)

Location	Water supply (m^3/day)	Service population (person)	Water supply per capita (L.pcd)	Service coverage (%)	Water demand (m^3/day)
Erbil/Central	320,680	695,958	461	95 %	338,000
Erbil/periphery	223,675	570,400	392	54 %	414,000

Municipal wastewater is discharged directly to the environment or is used for irrigation without treatment.

Based on the study of Al-Ansari et al. (2015), Iraq is suffering from water shortage problems, due to several factors, which include global warming. However, based on the study, the water supply and the demand are predicted to be 17.61 and 77 Billion m^3 in 2025 respectively. Correspondingly, based on the future prediction, the Tigris and Euphrates Rivers will be completely dry in 2040.

Consequently, in order to avoid this big problem, an appropriate water management policy should be planned, which involve the strategic water management, irrigation techniques development, water losses reduction, use of scientific water resources, research and water development planning. Whereas, the study of Costa et al. (2019) stated that the water management may involve the seasonal storage of surface water in region of low recharge potential or modification of the irrigation methods, protection of the vegetation is also recommended because these locations were considered as the groundwater recharge.

7. Conclusion

The current study concluded that the sustainability of the groundwater management can play a major role to control managing of water for Erbil City future, which partially depends on drilling wells. The rapid growth of the population and their additional exploitation of wells causes the depletion in the aquifer storage and decrease the capacity of the wells within the selected site. The groundwater source faces the pollution in some areas. In spite of this, there is a number of illegal wells that are drilled inside the study region and this should be avoided. It was also observed that most of the consumers spent large quantities of water without any control, which was far from water conservation rules, due to the lack of awareness among people. Using raw river water or treated wastewater for car washing, irrigation, construction etc. is recommended, instead of using groundwater source. At the end of the study it should be noted that if this irresponsible behavior continues, the groundwater will face high depletion and drought in the near future.

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Procena održivosti i upravljanja izvorima podzemne vode u gradu Erbilu

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INFORMACIJE O RADU

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Ključne reči:
Podzemne vode
Erbil
Upravljanje
Održivost

I Z V O D

Pitanje racionalizacije potrošnje vode i njenog očuvanja za buduće generacije je jedan od najvažnijih pokazatelja održivog razvoja koji se pominje u Agendi 21. Ovaj rad ima za cilj da proceni održivost resursa vode u Erbilu sa fokusom na količinu i kvalitet. Procenjena je količina vode koja je dostupna u postojećim izvorima, a zatim je upoređena sa količinom koja se potražuje. Ocenjena je i potvrđena i pouzdanost izvora vode, posebno izvora podzemnih voda na ispitanom području. Rad je takođe ispitao i upravljanje izvorima podzemnih voda koje sprovode nadležne vlasti, kao i identifikaciju faktora koji pomažu u razvoju održivosti ovih izvora. Identifikovani su i problemi sa kojima se suočavaju prilikom upravljanja podzemnim vodama i predložena su rešenja za ove probleme. Zbog brzog rasta broja stanovnika i lošeg odnosa između potražnje i potrošnje vode, potrebno je uraditi temeljnu procenu sistema vodosnabdevanja u Erbilu i isplanirati pouzdan sistem za ubuduće. U ovom radu je sprovedena procena na osnovu postojećih podataka i dostupne arhivirane dokumentacije. Rezultati ispitivanje su pokazali da postoji mnogo problema koje treba uzeti u obzir kako bi se obezbedilo dobro upravljanje sistemom podzemnih voda. Takođe je uočeno da postoji nešto veće iscrpljivanje podzemnih voda zbog lošeg snabdevanja. Ovaj rad se može koristiti kao osnova za buduća istraživanja, posebno za područja koja imaju probleme u održivom upravljanju podzemnim slivovima.

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