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The study of potential environmental risks of some industrial pollutants factors discharged from Najibia Power Plant upon Shatt Al-Arab River

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Abstract :

A survey study was conducted upon industrial effluents of Najibia power plant comprising the annual average of thirteen physico-chemical parameters (pH, water temperature, total Suspended Solids, sulphate; chloride, oil & grease, phosphate, chemical oxygen demand, iron, copper; boron, chromium and zinc) which belongs to the period from a year of 2003 to 2012 so as to assess the physico-chemical characteristics of its effluents depending upon Iraqi and international standards and to investigate the environmental impact resulting from them. The one sample statistical test showed high significantl variation ($P < 0.001$) for all of these parameters. pH values were found to be neutral to alkaline in nature and their average value was within the Iraqi guideline (2001) and World Bank Group Standards (1998). Only the maximum value of water temperature exceeded the guidelines while all other values in addition to the average value were within the Iraqi guideline values of effluents (2001). All values of total suspended solids in addition to the average value was within the Iraqi guideline values of effluents (2001) and World Bank Group Standard (1998). All values of Sulphate in addition to the average exceeded the Iraqi guideline values of effluents (2001).The average value of chloride was within the Iraqi guideline values of effluents (2001). The maximum value of grease & oil exceeded the Iraqi guideline values of effluents (2001) and World Bank Standard (1998) while the average was within them. All values of phosphate in addition to their average was within the Iraqi guideline values of effluents (2001) while the average value was within World Bank Group Standards (1998) and most of the other values exceeded them. All values of chemical oxygen demand were within the Iraqi guideline values of effluents (2001) and World Bank Group Standards (1998). At last, the average of heavy metal values were arranged in sequence as follows: Fe > Zn > B > Cu > Cr. and all their values were within the Iraqi guideline values of effluents (2001) and World Bank Group Standards (1998).

Keywords: industrial effluents - source of effluents - environmental risk - aquatic life - human health.

1. Introduction:

Nowadays environmental pollution is a great matter of concern. This is considered as a global problem because of its adverse effect on human health, plants and animals. Industrial effluents characteristics provide basic information about the integrity of the aquatic habitat within such rivers and streams into which they are discharged and most of industries discharged their wastes directly to the river, canal or sea which are characterized by their abnormal turbidity, conductivity, chemical oxygen demand, total suspended solids and total hardness [1-3].

The main components of any thermal power plant are: furnace, boiler, turbine, generator, condenser, chimney and and other auxiliaries such as forced draft pump, air heaters, de-aerators, economiser, boiler drum as shown below in figure 1 . In its operation, the combustion of fuels (coal, gas, crude oil) in furnace supplies heat to produce steam inside the boilers, which is used to generate mechanical energy in a turbine; this energy is subsequently converted by a generator to electricity. combustion air flow is preheated via heat transfer from exhausting flue gas before flowing into the furnace. The air heaters in thermal power plants are indirect heat transfer devices that transfer energy from flue gas to entering fresh air in order to increase energy generation efficiency [4-6].

Many liquid wastes are discharged continuously as long as the plant is operating; these include waste waters from the following sources:

1) boiler blow down : boiler feed water often contains some degree of impurities, such as suspended and dissolved solids. The impurities can remain and accumulate inside the boiler as the boiler operation continues. Though to avoid boiler operational problems, water must be periodically discharged or “blown down” from the boiler to control the concentrations of suspended and total dissolved solids in it [7].

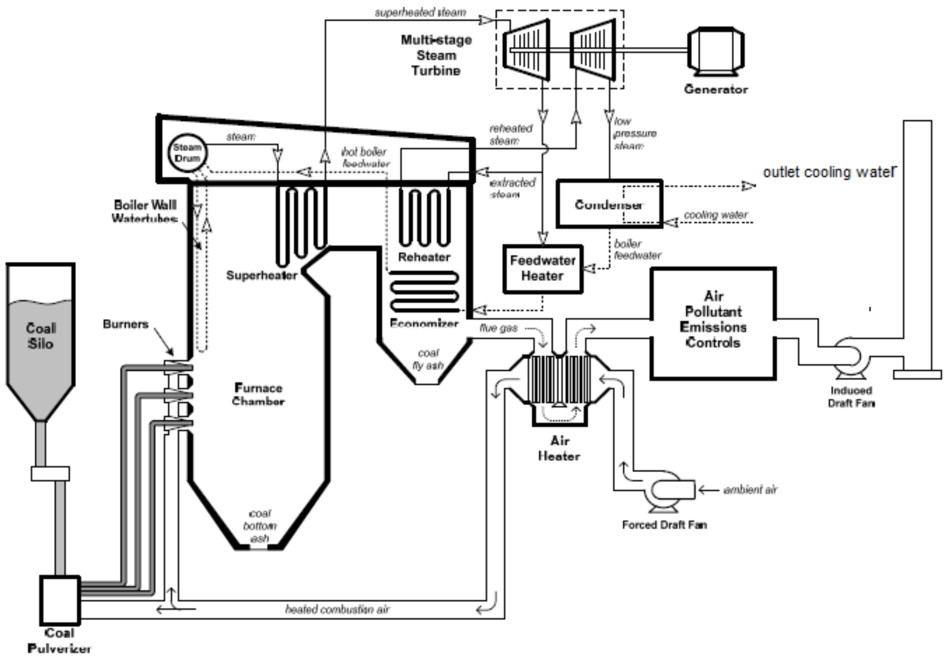

figure 1: schematic diagram illustrated steam power plant components.

2) metal cleaning wastes : result from cleaning compounds, rinse water, or any other water born residues derived from cleaning any metal process equipment including boiler tube cleaning, i.e. water-side , fire-side and air pre heater cleaning in addition to cleaning of other miscellaneous small equipments. The aim of cleaning operations is to removal of scale , corrosion and fuel combustion products [8].

3) turbine drainage: The main component of equipment used by power plants to produce electricity is the turbine; if it does not run, the plant does not produce electricity. In simple terms, a power turbine is a device that converts rotational energy into electrical energy. So, it needs lubricating oil to minimize wear by lubricating the moving parts in the steam turbine as shown below in figure 2. Besides providing wear-reducing properties, oils have secondary purposes, such as cooling, corrosion protection and transportation of contaminants (cleaning) [9], [2].

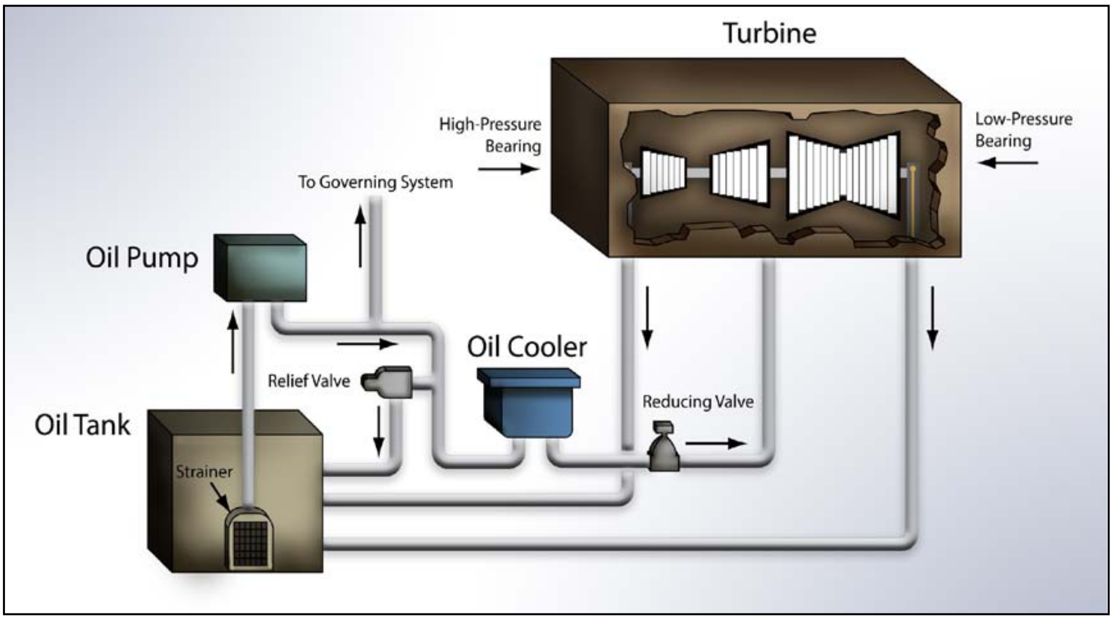

figure 2: Simple diagram illustrated turbine oil lubrication system.

The discharge frequency for these effluent sources varies from plant to plant. However, most plants do not have distinct and separate discharge points for each source of wastewater; rather, they combine certain streams prior to final discharge.

Many studies overall the world have demonstrated the influence of the power plant effluents on aquatic life [10 - 13]. In Iraq, several researchers have been studying the power plant wastes like Mahdi *et al.*, [14] who assessed the industrial wastes produced by Al-Dora and Baghdad South Electric power plants while Mohammed and Mahmoud [7] suggested re-using the boiler blow down of thermal power plants after treating it by demineralization process. At Basrah governorate, Al-Sabah [15] investigated the pollution level near Najibia and Hartha power plants. An Environmental and Social Impact Assessment Report (ESIA) has been acheived by Fichtner,a German organization , for the complete site of the Hartha Power Plant in an area approximately 5km around the power plant [16]. Hussein *et al.*, [17] investigated the impact of Hartha power plant on the abundance and distribution of algae and Hassan *et al.*, [18] demonstrated the levels of several pollutants near Najibia and Hartha power plants.

The present study was conducted on Najibia Thermal Power Plant which primarily treated by storage in pond oxidation then discharged to Garmat Ali river so as to assess the physico-chemical characteristics of its effluents depending upon Iraqi and international standards and to investigate the environmental impact resulting from them.

2. Material and Methods:

A survey study was conducted upon industrial effluents of Najibia power plant located at Basrah governorate as shown in figure 3.

figure 3: a map showing Najibia Power Plant location.

The present study comprises the annual average of thirteen physico-chemical parameter that belong to a period from a year of 2003 to 2012 which had been analyzed according to [19] by the scientific staff of Najibia Power Plant. These parameters include pH; water temperature; total Suspended Solids ; sulphate; chloride; oil & grease; phosphate; chemical oxygen demand; iron; copper; boron; chromium and zinc. Both pH and water temperature were measured at sampling sites by using Horiba model W-2030 MFG. NO.812003.Total Suspended Solids were determined by filtration with GF/F filter paper using filtration unit and vacuum apparatus. The difference between the weight of filter paper after the filtration of a known volume of sample and its initial weight resembling the total Suspended Solids. Turbidimetric method was used for determining sulphate where SO_4^{2-} is precipitated with Ba^{2+} in an acid solution. then the absorbance is measured by spectrophotometer at 420 nm.

Chloride is titrated with mercuric nitrate in the presence of bromophenol blue indicater at pH of 3.1. where mercuric chloride formed which is slightly dissociated. At the end point the excess mercuric ion (Hg^{2+}) produces violet color with diphenylcarbazone . Oil & grease were first extraction with hexane then determined gravimetrically. Phosphate was determines as orthophosphate, in a strongly acid solutions orthophosphate (PO_4-P) will form a yellow complex with molybdate ions. This can then be reduced to a highly colored blue complex. If ascorbic acid is used as a reducing agent, the formation of the blue color is stimulated by antimony and the absorbance of the blue color was determined by spectrophotometer at 885 nm. Chemical oxygen demand was estimated by oxidation with potassium permanganate $KMnO_4$ then titrated with 0.1 M sodium thiosulphate standard solution.

Soluble heavy metals were determined by colorimetric methods using spectrophotometer apparatus. Iron is determined by Phenanthroline method in which ferric state (Fe^{3+}) reduced to the ferrous state (Fe^{2+}) by boiling with acid and hydroxylamine, and treated with 1,10-phenanthroline at pH 3.2 to 3.3. Three molecules of phenanthroline chelate each atom of ferrous iron to form an orange-red complex. The absorbance of the colored solution was determined by spectrophotometer at 510 nm.

Copper has two oxidative states (i.e. Cu^+ and Cu^{+2}). Cuprous ion (Cu+) is determined by Neocuproine Method. It reacts in neutral or slightly acidic solution with 2,9-dimethyl-1,10-phenanthroline (neocuproine) to form a complex in which two moles of neocuproine are bound by one mole of Cu+ ion. The complex can be extracted by a chloroform-methanol mixture to give a yellow solution and the absorbance of the colored solution is measured at 457 nm. For determined total copper, sample is treated with hydroxylamine-hydrochloride to reduce cupric ions (Cu^{+2}) to cuprous ions (Cu+).

Boron was determined by Curcumin method as follows: When a water sample containing boron is acidified and evaporated in presence of curcumin, a red coloured product called rosocyanine is formed. This rosocyanine is extracted in organic solvent and colour is measured colorimetrically at 450 nm.

Chromium ion has two oxidative states (i.e. Cr^{+3} and Cr^{+6}). To determine total chromium all trivalent chromium must be converted to the hexavalent state by oxidation with potassium permanganate. Then the hexavalent chromium is determined colorimetrically by reaction with diphenylcarbazide in acid solution. A red-violet colour of is produced which is measured at 540 nm.

Zinc was determined by Zincon method as follows: Zinc forms a blue complex with 2-carboxy-2'-hydroxy-5-sulphoformazyl benzene (zincon) in a solution buffered to pH 9.0. The absorbance of this color is determined at 620 nm.

and the results were statistically analyzed with one sample test and spearman correlation by SPSS V.19.0

3.Results and Discussion:

The results of physico-chemical analysis for the present study and their corresponded guidelines are illustrated below in table 1, and the one sample statistical test showed high significant variation ($P < 0.001$) for all of them.

pH is an indicator of the existence of aquatic life as most of them thrive in aquatic habitats near narrow and critical pH range [2]. pH values ranged from 7.10 to 8.60 and the average value was within [20] and [21]. They were found to be neutral to alkaline in nature due to the addition of ammonium hydroxide for raising pH of boiler´s feeding water [4], [7] and they coincided with [15], [16], [18].

Water temperature values ranged from 20.00 to 45.60 ^{0}C, only the maximum value exceeded the guidelines while all other values in addition to the average value were within them [20]. Hot water leads to decrease the level of oxygen and consequently releasing of phosphate from sediments and this case will threaten the life of most aquatic organisms by reducing their diversity while permiting optimum circumferences for the proliferation of few tolerant organism [22], [10], [13], [23].

Total suspended solids (TSS) refer to the particles in the water that are larger than 0.45 µm [2] . Their prevalence in power plant effluent values ranged from 23 to 45 mg/l, all values in addition to the average value was within [20] and [21].

Table 1: the summary of physico-chemical results for Najibia Power Plant effluents.

	pH	W.T.	TSS	SO_4^{-2}	Cl^-	O.G [4]	PO_4^{2-}	COD	Fe	Zn	B	Cu	Cr
2002	7.8	27	23	730	660	4	1	4	0.8	-	-	-	0.02
2003	7.6	23	27	720	680	4.1	1.7	4.9	1	0.1	0.009	0.01	0.05
2004	7.5	28	36.5	420	350	12	1.6	2.4	1.5	0.05	0.3	0.16	0.013
2005	7.5	20	30	450	400	16.8	1.4	4.2	1.8	0.05	0.04	0.16	0.06
2006	7.6	29	28	450	360	8.4	2.8	1.5	1.9	0.15	0.04	0.02	0.03
2007	7.4	45.6	27	560	370	9.8	1.2	5.6	1	0.3	0.017	0.03	0.08
2008	7.2	23	45	650	580	8.8	2	4.6	0.4	0.2	0.05	0.2	0.06
2009	7.4	24	42.6	620	700	9	2.3	3.6	0.8	0.8	0.3	0.05	0.029
2010	7.4	24.5	42.7	696	600	9.5	2.2	6.2	1	0.03	0.1	0.04	0.03
2011	7.1	24.2	39.6	468.9	410	7.9	2.5	5.9	1	0.34	0.037	0.04	0.031
2012	8.6	23.7	34.6	486.8	483.5	7	2.3	4	1	0.425	0.037	0.04	0.089
Minimum	7.1	20	23	420	350	4	1	1.5	0.4	0.03	0.009	0.01	0.013
Maximum	8.6	45.6	45	730	700	16.8	2.8	6.2	1.9	0.8	0.3	0.2	0.089
Average	7.6	26.5	34.2	568.3	508.5	8.8	1.9	4.3	1.1	0.244	0.093	0.075	0.045
IG [1]	6-9.5	35	60	400	600	10	3	100	2	2	1	0.2	0.1
WBG [2]	6-9	≤ 3 [3]	50	-	-	10	2	250	3.5	2	-	0.5	0.5

(1) IG is a privation of Iraqi Guideline values.
(2) WBG is a privation of World Bank Group standards.
(3) The effluent should result in a temperature increase of no more than 3° C comparable with influent at the edge of the zone where initial mixing and dilution take place.

(4) O.G is oil and grease.

Water with higher solids content often has laxative and sometimes a reverse effect upon people whose bodies are not adjusted to them [23]. Unusual high TSS concentrations results on negative effects on fish due to respiratory impacts where it closed fish gills if its concentrations exceeded 200 mg/l [24].

Sulphate values ranged between 420 to 730 mg/l and all their values in addition to the average exceeded [20], and these values coincided with the results of Hartha power plant effluents [16]. High sulphate concentrations impart a bitter taste and may cause laxative effects in some individuals [25]. People who are drinking water with high level of sulphate may suffer from catharsis, dehydration and diarrhea, children are often more sensitive to sulphate than adults [26], [27], [23]. The presence of sulphate in the discharging effluents may result as deposition byproduct of SO2 which is emitted from the combustion processes of fuel [11], [16]. According to Najim and Mohammed [28], Najibia boiler furnaces have two firing system and provision to burn fuel oil, crude oil and fuel gas which were supplied from Basrah Oil Refineries, the typical analyses of fuel oil and crude oil showed a percentage of 3.5 and 1.5 by weight for sulpher content respectively.

Chloride values ranged from 350 to 700 mg/l, only the maximum value exceeded [20] while the other ones and the average one were within them where they did not threaten the life of aquatic organisms and cultured plants [24], [18], [23]. Mahdi *et al.*, [14] interpreted chloride occurrence in effluents of both Al-Dora and Baghdad South power plants due to the discharging of laboratories' wastes. Also, Wang [8] pointed to the usage of hydrochloric acid in boilers tubes (steam-side) cleaning.

The prevalence of Oil & grease in power plant effluents came from turbine oil drainage, their values ranged from 4 to 16.8 mg/l, the maximum value exceeded [20] and [21] while the average was within them. Floating oil found in effluent waste rises to the surface water and prevents sunlight from reaching the depth of the water and also affects the life of aquatic beings by inhibiting the atmospheric oxygen from dissolving in the water [24], [2], [23].

Phosphate values ranged from 1 to 2.8 mg/l and all values in addition to their average were within [20]. Also, the average value was within [21] while most of the other values exceeded the later guideline. Effluents of steam power plants were rich in phosphate due to the addition of trisodium phosphate to boiler's feeding water as anti-scaling where it reacts with dissolves solids to form substances that can be removed by blowdown [4], [7]. Also, boiler cleaning detergents contain polyphosphates. Phosphate compounds may contribute to eutrophication [22 - 23].

Chemical Oxygen Demand (COD) is defined as the amount of a specified oxidant that reacts with the organic substances under controlled conditions. The quantity of oxidant consumed is expressed in terms of its oxygen equivalence [19]. It is considered as an indicator of organics in the water, usually used in conjunction with biological oxygen demand (BOD) [2].Chemical Oxygen Demand values ranged from 1.5 to 6.2 mg/l all values were within [20] and [21]. Organic substances in power plant effluents originated from several sources where some lubricating oils contain organic compounds as an additive materials for improving oil performance such as phenolic and aromatic amines [29 - 30]. Also, microorganisms that are proliferated in the treatment ponds constituent the major source of organic substances in power plant effluents [31]. Some dissolved organic chemicals may deplete the dissolved oxygen in receiving water and some may be inert to biological oxidation, yet others have been identified as carcinogens [22 - 23].

Heavy metals are typical pollutants in urban environments. These elements are of particular concern due to their persistence in the environment and their toxicity to humans. The non biodegradability of heavy metals leads to their accumulation in the environment and thus they are also known as "chemical time bombs" [11], [3]. The present results showed that the average of heavy metal values were arranged in sequence as follows: Fe> Zn > B > Cu > Cr. The presence of heavy metals in power plant effluents is a result of several sources, such as corrosion and fuel combustion residues [32],[5]. Products of corrosion are soluble and insoluble species of iron, copper, and other metals and they are removed by cleaning operations i.e. boiler water-side , boiler fire-side and air pre heater cleaning. Another source, oil lubricating additives: they are chemical compounds added to lubricating oils to prevent turbine failure which caused as a result of oxidation, corrosion, temperature extremes, wear and deposits. So, these additives are usually known as anti-wear, extreme pressure, antioxidant, dispersant, and anti-foam additives [29], [9], [31].

Iron values ranged from 0.4 to 1.9 mg/l and all values were within [20] and [21] and the statistical analysis showed positively significant correlation ($r = 0.669$) between it and pH. Also, the statistical analysis showed negatively significant correlation ($r = - 0.640$) between it and total suspended solids. The prolonged accumulation of iron in the body may result in homochromatosis due to which tissues are damaged [33]. The primary purpose of the total boiler cleaning operation is removal of heat transfer-retarding deposits, which consist mainly of iron oxides resulting from corrosion. Hence, the present results showed a negative correlation ($r= - 0.640$) between iron and total suspended solids values. This removal of iron is evident in all total boiler cleaning operations through its presence in boiler cleaning wastes [8], [5], [6].

Zinc values ranged from 0.03 to 0.8 mg/l and all values were within [20] and [21]. Zinc is considered to be relatively non-toxic, especially if taken orally. However, excess amount can cause system dysfunctions that result in the impairment of growth and reproduction [34]. Also, it reduces immune function and the levels of high density lipoproteins [35]. According to Saeedi and Amini [6], its prevalence in power plant effluent is as a result of air heater alloys corrosion and from their contamination with residues of fuel oil combustion where zinc has been washed from air heaters during cleaning operations. Also, it may come from turbine lubricating oils where both zinc dialkyldithiophosphates and zinc diaryldithiophosphates (ZDDPs) are oil additives acting as anti-wear, anti-oxidant and corrosion inhibitors[36], [37], [38].

Boron values ranged from 0.009 to 0.3 mg/l and all values were within [20]. In the present study, in spite of its low concentrations discharged in Shatt Al-Arab River but according to [39] the ingestion of boron at concentrations usually found in natural water will be accumulated in human bones more than other parts affecting on their forms and function. The extended consumption of water containing boron can lead to a condition known as borism [26], [19]. Also, there are some investigations that give evidence of a possible toxicity of high concentrations of boron for male reproductive system [40]. From the statistical analysis, we can be determined source of boron in the discharging effluents where it showed positively significant correlation (r = 0.685) between boron and copper and positively significant correlation (r = 0.706) between boron and total suspended solids . Boron in Power Plant effluents may be originated from turbine drainage due to its usage as water inhibitor, coolant additive (borate), grease additive and limited extreme pressure additive in lubricated system of turbine as demonstrated formerly in figure 2 [36], [38]. Some extreme pressure additives, because of their reactive nature, can be corrosive to brass or copper-containing alloys [41]. Also, some detergents contain boron salts [26] where in boiler cleaning operations, cleaning mixtures have been used which include alkaline chelating rinses, proprietary rinses, organic solvents, acid cleaning mixtures, and alkaline mixtures with oxidizing agents for copper removal , the latter ones (alkaline mixtures) might include soda ash, caustic soda, phosphates, and/or detergent [8].

Copper values ranged from 0.01 to 0.2 mg/l and all values were within [20] and [21]. Copper surplus had been associated with liver damage [35]. copper may be originated from fuel oil combustion [42], brass alloy corrosion [38]. In the present study, it is found a significant correlation between copper and total suspended solids (r= 0.685) and boron (r=0.677) due to the removal of copper by detergents containing boron.

Chromium values ranged from 0.013 to 0.089 mg/l and all values were within [20] and [21]. Its alloys constituent both boiler and turbine bodies . Also, it is considered as a component of fuel oil [28]. According to Sigh [5], several high-alloy ferritic steels were developed during the last three to four decades. These include 5CrMo, 6CrMoVWTi, 7CrMoTi, 8CrMoTi, 9CrMo, 9CrMoVNb, 9CrMoWVNb, 12CrMoV and 12CrMoWVNb steels. Among these, 9Cr and 12Cr class of steels were successfully employed in several power stations. .In Power Plant effluents , chromium may be originated from cleaning operation of boiler's air heaters as a result of its alloys corrosion and fuel oil burning [6], [42] . Turbine lubricating oil can be subjected to the contamination with several contaminants like fuel combustion products which lead to deposit formation and can cause corrosion where as its contamination with water would form rusting and corrosion in addition to form sludge and acids leading to reduce the lubrication properties of oil [36], [29] . As mentioned formerly , boron acting as water inhibitor so its depletion [31] interpreted the negatively significant correlation (r = - 0.695) between it and chromium.

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دراسة المخاطر البيئية المحتملة لبعض الملوثات الصناعية المصرفة من محطة كهرباء النجيبية الى مياه شط العرب

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الخلاصة:

أجريت دراسة مسحية على المتدفقات الصناعية لمحطة كهرباء النجيبية شملت المعدل السنوي لثلاثة عشر عاملا"فيزيائيا" وكيميائيا" (الأس الهيدروجيني و درجة حرارة المياه و المواد الصلبة العالقة الكلية والكبريتات والكلوريد والزيوت والشحوم و الفوسفات والمتطلب الكيميائي للأوكسجين و الحديد والنحاس والبورون والكروم والزنك) والتي تعود للفترة الممتدة من عام 2003 الى عام 2012 لغرض تقييم الخصائص الفيزيوكيميائية لمتدفقاتها. أعتمادا" على المعايير العراقية والدولية وذللك لبيان الأثر البيئي الناجم عنها. وقد أظهر التحليل الأحصائي تغايرات معنوية ($P < 0.001$) لجميع هذه العوامل. كانت قيم الأس الهيدروجيني متعادلة الى قاعدية ومعدلها ضمن المواصفات العراقية (2001) ومعايير المجموعة المصرفية العالمية (1998) أما بالنسبة لدرجة حرارة المياه فقد تجاوزت القيمة العظمى للمواصفات بينما جميع قيمها بالأضافة الى قيمة المعدل كانت ضمن المواصفات العراقية (2001) ومعايير المجموعة المصرفية العالمية (1998). كانت جميع قيم المواد الصلبة العالقة الكلية بالأضافة الى قيمة المعدل ضمن المواصفات العراقية (2001) ومعايير المجموعة المصرفية العالمية (1998) . تجاوزت جميع قيم الكبريتات بالأضافة الى المعدل المواصفات العراقية (2001). كانت قيمة معدل الكلوريد ضمن المواصفات العراقية (2001). تجاوزت القيمة العظمى للزيوت والشحوم المواصفات العراقية (2001) ومعايير المجموعة المصرفية العالمية (1998) بينما كان المعدل ضمن تلك المواصفات . كانت جميع قيم الفوسفات بالأضافة الى معدلها ضمن المواصفات العراقية (2001) بينما كان هذا المعدل ضمن معايير المجموعة المصرفية العالمية (1998) وقد تجاوزته معظم القيم الأخرى. كانت جميع قيم المتطلب الكيميائي للأوكسجين ضمن المواصفات العراقية (2001) ومعايير المجموعة المصرفية العالمية (1998) . وأخيرا" كانت قيم معدل المعادن الثقيلة مرتبة على التعاقب كالتالي: الحديد > الخارصين > البورون > النحاس > الكروم. وقد كانت جميع القيم ضمن المواصفات العراقية (2001) ومعايير المجموعة المصرفية العالمية (1998) .

الكلمات المفتاحية: المتدفقات الصناعية – الأثر البيئي – مصدر المتدفقات – الحياة المائية – صحة الأنسان.