ISSN: 0975-8585

Research Journal of Pharmaceutical, Biological and Chemical Sciences

Assessment of Heavy Metals Pollution in Wastewater of Petrochemical Industries

Rahman Moradi[1]*, Gevorg Pirumyan[2], and Farhang Farahmand[3]

[1]Department of chemistry,Islamic Azad university,varamin-pishva branch,Varamin, Iran
[2]Department of chemistry,Yerevan state university,Yerevan, Armenia
[3]Department of chemistry,Islamic Azad university,Varamin-Pishva branch,varamin, Iran

ABSTRACT

The heavy metals concentration in wastewater of petrochemical industries were determined at different sampling stations of Abadan Petrochemical industries in Khozestan. The research was done in autumn 2009. The level of residual concentration of heavy metals was determined by Icp technique. The reason for this research was that wastewater of these industries, after treatment, pours into Arvand River, and the end destination is Persian gulf. Sampling from the sewerage outlets in different units of this complex were done on the working days in 9 station during 9 weeks. The heavy metals of Hg^{2+}, Cd^{2+}, Cr^{2+}, Pb^{2+}, Zn^{2+}, Cu^{2+} and Cr^{3+} were identified in these samples.

Keywords: Pollutant, Heavy metals, Icp, Sampling, Station

Corresponding author

ISSN: 0975-8585

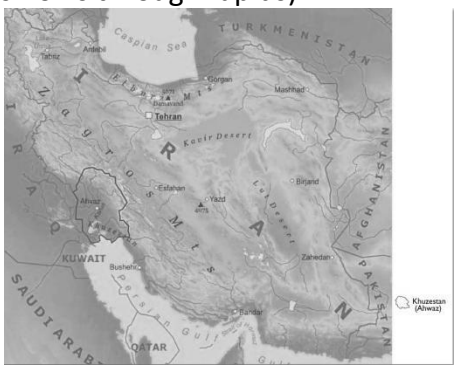
INTRODUCTION

The increasing development of the chemical production and their use in different processes is a sign of an industrial society.[1] The most important and dangerous effect of pollution is produced because of the entry of disease causing factors into the water.[2] The pollution from the sewerage is into ground and influence in underground water sources threatens these vital water.[3] Probably the most important part of the water pollution is because of waste disposal and the entering of a huge amount of nutrition like nitrogen and phosphate in them, especially if nitrogen compounds are in maximum oxidation from in nitrate enters in it.[4] All societies produce waste materials both in the form of solid and liquid.[5] The liquid part of this waste material or sewerage basically is the water used in that society and has become polluted because of different uses.[6] From the view point of production, sewerage was classified into a mixture of liquid which has been carried from domestic, administrative, industrial and commercial by water and has been mixed with underground, surface and flood waters.[7] Moreover the untreated wastewater contains diseases causing microorganisms which live in human digestive system or they maybe found in some industrial sewerage.[8] The wastewater also contains some nutrition materials which may cause the growth of aquatic plants.[9] The industrial sewerage contains some low concentration of heavy metals which cause intoxication.[10] They diminish the possibility of the existence of microorganisms in such wastewater.[11] Unfortunately the entry of industrial sewerage into water causes the increase of the concentration of pollutant in them.[12]

MATERIALS AND METHODS

The Areas under study

The Abadan petrochemical industry situated in the city of Abadan and its geographical coordinate is 30˚, 20́, 21́ North and 48˚, 18́, 15́ East. Abadan is a city of Khuzestan province, in Iran. Khuzestan province is one of the 31 provinces of Iran. It's southwest of the country, bordering Iraq's Basra. Province and the Persian Gulf. It's capital is Ahwaz and covers an area of 63.238 $Km^{2.}$ It lies on Abadan island (68 km / 42 miles long, 3-19 Km or 2-12 miles wide). The island is bounded in the west by the Arvand water way and to the east by the bahmanshir out let of the Karun river, 53 Km(33 miles) from the Persian Gulf. The river Karun is navigable all the way to Ahwaz (above which, its flows through rapids).



ISSN: 0975-8585

Fig.1 Iran and Khuzestan province map

Sampling Technique

For preparing the samples, 200ml of samples were transferred to beakers. 4ml of HNo_3 1:1 (V/V) were added in each sample. Watch glasses were used to cover the containers to prevent them from contamination. Then samples were heated to 80-85˚c using hotplates to obtain the final volume of about 10-20ml before metal precipitation Barkacs et al (2002). The above procedure was repeated twice. The beaker walls and the covers were washed carefully with ultrapure deionized water and then the rinse water was filtered. The filtered was transferred to a 100ml volumetric flask with the addition of about 10ml of water. All samples were prepared in duplicate.

Table 1: Name and number of the station

Number	Names
1	Biological Treatment unit
2	Administration wastewater
3	Domestic wastewater
4	Alkaly chlorine unit
5	Ethylen & Propylen unit
6	EDC
7	Vinil chloride
8	Pvc unit
9	Dodecyl benzene

Table 2: The order of sampling at the determined stations

Day	Number	No	No	No	No	No	No	No	No
Saturday	1	8	6	4	2	9	7	5	3
Sunday	2	9	7	5	3	1	8	6	4
Monday	3	1	8	6	4	2	9	7	5

Tuesday	**4**	**2**	**9**	**7**	**5**	**3**	**1**	**8**	**6**
Wednesday	**5**	**3**	**1**	**8**	**6**	**4**	**2**	**9**	**7**
Thursday	**6**	**4**	**2**	**9**	**7**	**5**	**3**	**1**	**8**
Friday	**7**	**5**	**3**	**1**	**8**	**6**	**4**	**2**	**9**
Number of week	**1^{st}**	**2^{nd}**	**3^{rd}**	**4^{th}**	**5^{th}**	**6^{th}**	**7^{th}**	**8^{th}**	**9^{th}**

Analytical methods

First essential information of the petrochemical industry was obtained and heavy metals pollutants were identified.[13] For the determination of heavy metals, the samples of wastewater were collected from 9 stations prior to sample collection, the flasks were rinsed with top water and then kept overnight with 1:1 HNo_3-H_2o and finally rinsed with duble-distilled water.[14] collected samples were stored in pure polyethylene vials for analysis. The samples were acidified with (0.2 Vol%) nitric acid ultrapure (Merck, Germany) for obtaining PH less than 2.[15] Acidification minimizes the adsorption of metals on to the walls of the container. The samples were stored at approximately 3-4°c in refrigerator before analysis.[16] Sampling was done on the working days from different wastewater of determined Stations in autumn 2009. The samples were taken to the laboratory for the chemical analysis every day.[17] During each day instant sampling was done every two hours since 8am till 8pm. In this way 7 samples were taken daily and during and week 49 samples, and during 9 weeks 441 samples were taken.[18] Element concentration were determined by an instrument of inductively coupled plasma atomic emission spectrometry (Icp-AES jobin-Yvon-138 ultrace, France) equipped with VGA (Vapor generation accessory).[19] The operating parameters were as follows : Forward power : 800w, RF frequency : 16 MHz, plasma gas (Ar) : 12 L/min, aerosol gas (Ar) : 0.29 L/min, flow rate of sheath gas (Ar) : 0.18 L/min, nebulizer type : mein hard. The procedure's method was followed by standard method EPA 2007 for concentration determinations of pb, Cr, cd, Hg, Zn, Cu in wastewaters and waters (Determination 2007).[20] All standard and sample solutions were prepared with deionized triplet distilled water obtained by Aquamax ultra 370, young lin Instrument co. Korea vapor generation accessory was applied for determination of Pb, Cd and Cr.[21] Determination of Hg were performed by a shimadzu graphite furnace absorption spectroscopy (AA680,japan) according to water and wastewater standard methods of 3113B.[22] All glassware were previously soaked in 15% HNo_3 solution for at least 48 hr and after wards rinsed with deionized water (Kanicky et al.1999).[23] Calibration curves for Icp-AES were determined using different sets of standard solutions. The sets consisted of standards containing 0, 25, 50, 100, 200, 500 and 1000 µg/L of metals in ultrapure HNo_3.[24]

Table 3.Concentration levels of Heavy metals in station no 6

Pollutant	Concentration (mg/L)	Concentration (µg/L)
Hg^{2+}	0.024	24

Cd^{2+}	0.009	9
Cr^{2+}	0.021	21
Pb^{2+}	0.059	59
Zn^{2+}	0.054	54
Cu^{2+}	0.121	121
Cr^{3+}	0.239	239

RESULTS AND DISCUSSION

As shown in table 1, there are 9 stations allocated for this study. These stations are located in the petrochemical industries. The sampling from unites was carried out every alternate week according to table 2 for autumn 2009, therefore the sampling was performed for 9 weeks on a rotational schedule according to which most of the stations would be sampled at least once every alternate week. [25] It implies that in every consecutive week of sampling all stations are tested in different days from the last sampling for a proper random sampling of every station. The concentrations of heavy metals in the wastewater collected in autumn from specified stations are given in table 3. Heavy metals are the cause of more environmental pollution than organic chemicals. [26] Although some of the metals such as Cu and Zn are essential nutrients to human, plants and animals but when present at high concentrations they can be toxic. The concentration of different trace metals such as : Hg, Cd, Pb and Cr were measured in the wastewater of petrochemical industries under investigation. The national standard guideline have recommendation limits in concentration values for different metals as depicated in table 4.[27] The data of the measured amounts of the pollutant of the wastewater show that Hg^{2+} was observed in the stations number 1,4,5,6,7. The highest amount of Hg^{2+} was observed in station number 7. And the lowest that was in station No 1. Hg^{2+} was not observed in the stations No 2,3,8,9. The Cd^{2+} was observed in all stations. The highest amount of Cd^{2+} was observed in station No 8. And the lowest amount that was in station No 3. The Cr^{2+} was observed in all stations. The highest amount of Cr^{2+} was observed in station No 6. Also the lowest amount that was in stations No 1, 3. The Pb^{2+} was observed in all stations. The highest concentration of Pb^{2+} was observed in station No 7.Also the lowest concentration that was in station No 3. The Zn^{2+} was observed in all stations. The highest concentration of Zn^{2+} was observed in station No 8. And the lowest concentration that was in stations No 2, 3. The Cu^{2+} was observed in all stations. The highest amount of Cu^{2+} was observed in station No 5.Also the lowest amount that was in station No 2. The Cr^{3+} was observed in all stations. The highest concentration of Cr^{3+} was observed in station No 6. And the lowest concentration that was in station No 3. [28] Heavy metals enter the living environment by natural and anthropogenic routes. Increased anthropogenic input of toxic metals in soils and wastewater may result in the transport of an increased content of metals in the groundwater or surface water. Hazardous metals input include those from commercial fertilizers, phosphate industry waste and mining and water processing. In these regions industrials wastewaters, specially petro chemistry is the

ISSN: 0975-8585

major source of pollution. Also chemical fertilizers containing heavy metals such as Cd, Pb and Cr used in agriculture related industries. The chemical fertilizers and industrial wastewaters are major sources of heavy metals in soil, groundwater and surface water and transfer in soil-plant systems. The increase in solution of such metals could be due to desorption of heavy metals from the soil. [29]

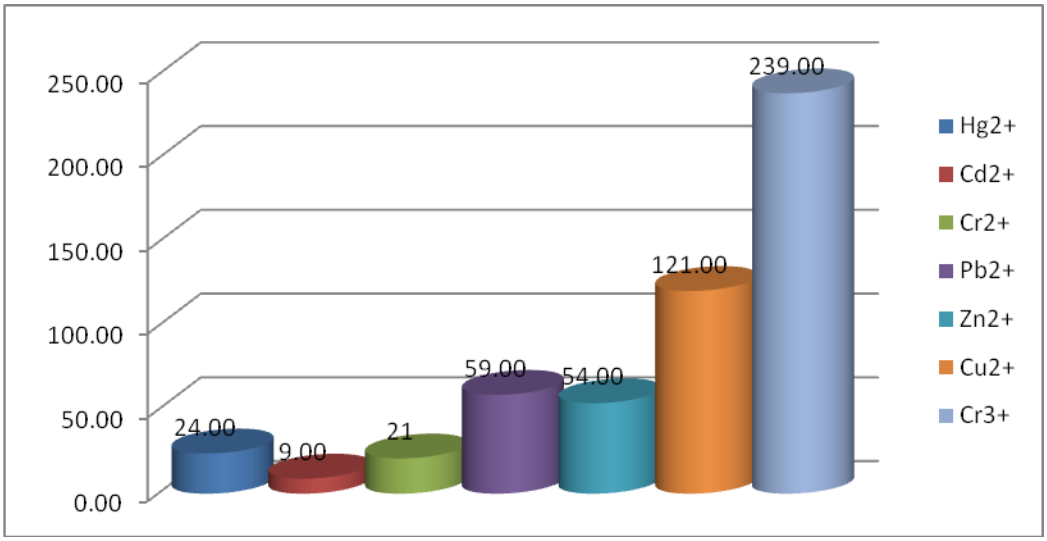


Fig 2: The diagrams of heavy metals concentration in selected station no.6 (µg/L)

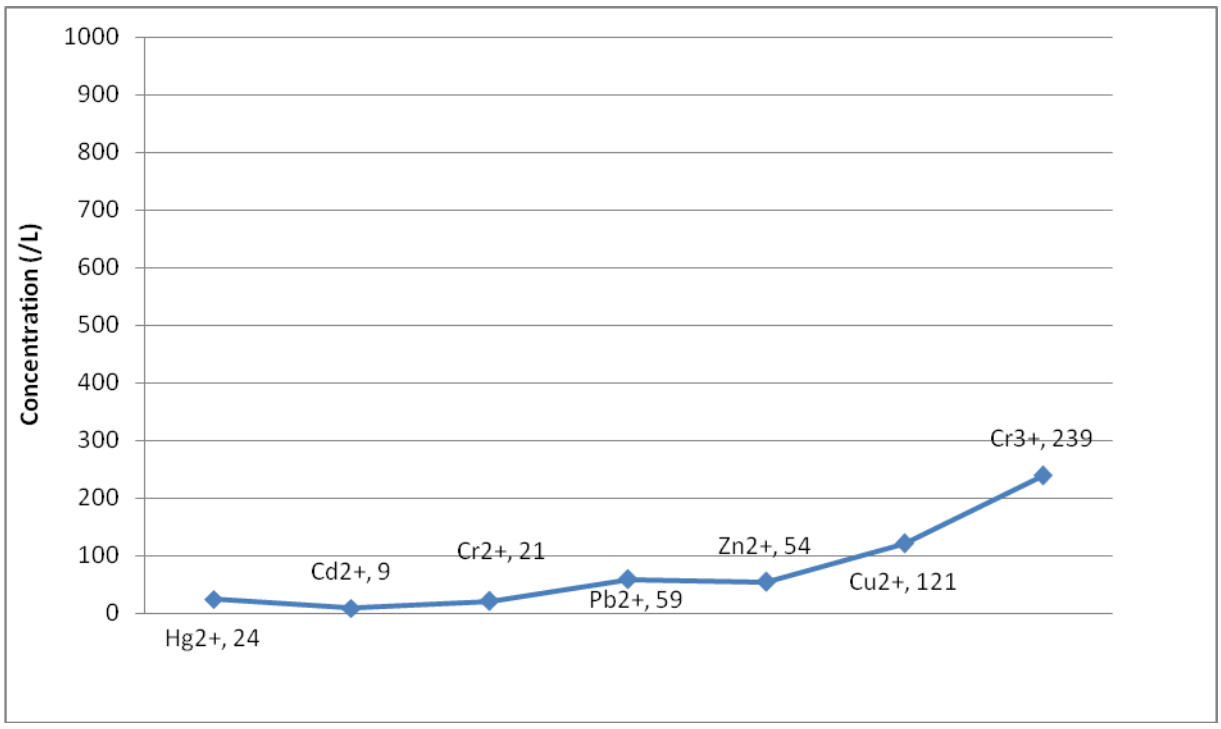


Fig 3: The diagrams of heavy metals concentration in selected station no.6 (µg/L)

ISSN: 0975-8585

Table 4.the international standard amounts of Heavy metals concentration based on EPA (Environmental Protection Agency)

Type of pollutant	Hg^{2+}	Cd^{2+}	Cr^{2+}	Pb^{2+}	Zn^{2+}	Cu^{2+}	Cr^{2+}
Maximum allowed level(mg/L) PPM	0.01	0.1	2	1	2	1	2
Maximum allowed level(µg/L) PPb	10	100	2000	1000	2000	1000	2000

CONCLUSION

In this study7 heavy metals and their concentrations were detected and measured in the wastewater of 9 stations in the petrochemical industry of Abadan the city of khozestan province from Iran. Cr^{3+} is reported as the highest concentration with Cu^{2+}, Pb^{2+} and Zn^{2+} standing next in 9 stations. Then Cd^{2+} concentration is higher than from other metals. And in the end of, Cr^{2+} and Hg^{2+} standing. The lowest concentration was observed in all stations, it was Hg^{2+}. The concentrations of Hg^{2+}, Cd^{2+} and Cr^{3+} are higher than the official safe Recommended values in table 4. And the concentrations of Cr^{2+}, Pb^{2+}, Zn^{2+} , and Cu^{2+} are below than guideline values. In this region wastewaters of petrochemical industries are the major sources of water and soil pollution by heavy metals. Therefore the discharge such wastewaters in the water, soil and agricultural lands should be of serious concern. In order to delete the heavy metals pollutant we can use from Ion exchange, chemical oxidation, reduction and aeration oxidation treatments.

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