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Article

Assessment and heavy metal behaviors of industrial waste water: A case study of Riyadh city, Saudi Arabia

Abdullah S. Al-Farraj[1], **Mohammad Al-Sewailem**[1], **Anwar Aly**[1,2], **Mohamed Al-Wabel**[1], **Sallem El-Maghraby**[1]

[1]Department of Soil Sciences, Food Sciences and Agriculture, King Saud University, P.O. Box 2460, Riyadh 11451, Saudi Arabia

[2]Soil and Water Science Dept., Alexandria University, Egypt

E-mail: sfarraj@ksu.edu.sa,aaaly@ksu.edu.sa

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Abstract

This study focuses on the temporal monitoring and chemical analysis of two pathways, unpadded and open drain canal, of the surface industrials effluent on industrial city of Riyadh city, Saudi Arabia. The distribution of the chemical constituents (Major, Minor, and Heavy metals) is determined and compared with Saudi Arabia and USEPA standards. The obtained results indicated that most collected water samples exceeded the acceptable limits set by standards used for most parameters determined. The concentrations of total suspended solids, Fe, Mn, Zn, Cd, Ni, Pb, Mo, As, B, NO_3^-, and NH_4^+ in industrial effluents decreases away from the point source of pollutions. On the other hand, the SAR , RSC, total hardness, and soluble ions (Ca^{2+}, Mg^{2+}, Na^+, K^+, Cl^-, CO_3^{2-}, HCO_3^-, and SO_4^{2-}), remained constant. Most heavy metals on wastewater effulent were above permissible limits. On the other hand, the filtration of wastewater decreases the heavy metal concentrations to permissible levels. The highest average metals concentration in digested effluents for deferent locations and sampling periods were Fe (17.1 mg L^{-1}) followed by Mo (11.6 mg L^{-1}), then Co (0.03 mg L^{-1}). However the Mo recorded the highest value in filtrated effluents (23.2 µg L^{-1}) followed by Fe (21.6 µg L^{-1}), and then Cd (8.02 µg L^{-1}). The monitoring of wastewater heavy metals concentrations (determined on filtrate for both pathway) recorded that the concentration of Fe, Mo, Zn, Cd, Pb, As, Ni, and Mn decreased from (60-100 µg L^{-1}) at point sources to be (5-10 µg L^{-1}) at 1000 m from point sources, however no clear behavior was recorded for Cu and Co. Moreover the concentrations of all heavy metals by the last sampling point on downstream were remained at 10 µg L^{-1} or less. The study emphasis that continuous application of industrial wastewater on Riyadh environment will lead to more accumulation of heavy metals in the soil and natural plants, and also high possibilities of groundwater contamination by nitrate.

Keywords industrial effluents; heavy metals; chemical constituent; Riyadh city.

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1 Introduction

Pollution is defined as the release of undesirable substances to the environment by human in quantities that damage the health and/or the natural resource (Tripathi et al., 2007). Pollution caused by heavy metals is increasing with the increase usage of chemicals in industry and agriculture. The heavy metals has usually been used to describe metals have atomic weight greater than iron and/or have density greater than 5 g mL^{-1} (Velaiappan et al., 2002). The Environmental contamination by trace and heavy metals through industrial wastes is one of the main health problems in industrial countries. Metal contaminants can easily enter to food chain if contaminated water, soils and/ or plants are used for food production. The industrial effluents generally consist of organic compounds, inorganic complexes and other non-biodegradable substances (Huguet et al., 2009). Pollution of the environment by toxic metals has accelerated dramatically in recent years due to increasing industrialization, leading to highly contaminated biosphere and atmosphere (Tiwari et al., 2008). The rational use of natural resources and environmental protection of industrial raw materials has become an important scope of mankind’s development in the 20th century. Mankind’s demand for resources and raw materials treatments has intensified the ecological and economic contradictions in the industries (Sen and Chakrabati, 2009). This wide spread industrial development in urban areas has radically reduced land area for waste disposal. The untreated industrial and domestic wastes disposal into environment affects quality of soil and ground water and considered as undesirable soil use (Quazilbash et al., 2006). Therefore, the mankind’s growing concern for the damage caused to the environment is emphasized. The main concern is linked with the protection of living being on our environment (Kolomaznik et al., 2008). These pollutants not only alter the quality of soil and ground water but also pose serious problems (Karthikeyan et al., 2010). There is a rising sense of global urgency concerning the environmental pollution by chemicals arrangement used in various activities (Palaniappan et al., 2009). Soil, water and biodiversity are essential elements of ecosystem and are the subject of many agricultural, ecological, biological and hydrological studies, since large amounts of chemical enter animal and human food chain through cultivated contaminated soils (Nolten et al., 2005). Rapid industrial development plays an important role in polluting environment and causes severe degradation in ecosystem. Water used in industries carry a potential hazard waste such as heavy metals into soil and our environment (Azumi and Bichi, 2010). The accumulation of metals in an aquatic environment has direct impact to man and ecosystem (Alam and Mahbub, 2007). The release of pollutants differs from industry to others. The waste from the pulp industry mainly contain carbohydrates, textile industry contain dyes, plating industry contain nickel and leather tanning wastes contain mainly chromium, zinc, copper, sulfides, carbonates, sodium and many other toxic organic compounds and inorganic compounds (Nouri et al., 2009).

The heavy metal contents of wastewaters can be effectively removed by precipitating in an insoluble form. The heavy metals are typically precipitated from wastewater as: hydroxides, sulfides or sometime sulfates, and carbonates. Metal co-precipitation during flocculation with iron or aluminum salts is also possible for some metals (e.g., arsenic) (Wentz, 1995). Carbonate precipitation takes place only if Carbonate ions (CO_3^{-2}) are present. Free carbonate ions are present only if the pH is high (Lindsay, 1979).

The main objectives of this study were to; evaluate physical and chemical characteristics of Riyadh industrial wastewater using Saudi Arabia (KSA) (2003), and USEPA (2004) standards; and study the wastewater movement effect on heavy metals precipitation and behaviors.

2 Material and Methods

2.1 Sampling sites and dates

Wastewater samples were collected from two locations in the third industrial zone of Riyadh, Saudi Arabia. The georeferenced coordination for the first location was (24° 32' 025" N & 46° 55' 377" E) and for the second one was (24^o 32' 874" N & 46^o 55' 377" E). Water samples were collected at four different dates from each site (Box.1) in attempt to capture the seasonal variations and temporal changes in the wastewater chemistry. Once it was collected, water samples were transported immediately to the laboratory in iceboxes and chemical analyses were carried out to assess the wastewater characteristics.

Box 1 Sampling Dates.

Samples number	Sampling dates
1st sample	29/9/2004
2nd sample	28/3/2005
3rd sample	22/9/2005
4th sample	13/4/2008

2.2 Analytical methods

2.2.1 Field measurements

The field measurements included measuring the wastewater temperature, odour, and color.

2.2.2 Laboratory measurements

Characterization of wastewater in laboratory included measuring chemical properties as described by STM (1998) and Sparks (1996). The pH was determined by pH-meter and the electrical conductivity, in decisiemens per meter (EC, dSm^{-1}), was measured by conductivity Meter. Compleximetric EDTA titration was employed for determining calcium and magnesium simultaneously and individually (Sparks, 1996). Sodium and potassium were determined using flame photometer (Corning 400). Carbonate and bicarbonate were determined by titration with sulphuric acid while silver nitrate was used to determine chloride (Sparks, 1996). Sulfate was determined by turbidity method as described by Tabatabai (1996), boron was determined coloremetically by Sparks (1996) method, and COD was determined by STM (1998) method. The wastewater samples were prepared for heavy metals determination using two methods; i) The studied samples were filtered and preserved by acidity with concentrated nitric acid to pH<2, ii) the studied samples were digested by nitric and birchloric acid. Then ICP Perkin Elmer, Model 4300 DV was used for measuring Fe, Mn, Zn, Cu, Cd, Mo, Co, Ni, and As in both filtrated and digested wastewater samples.

3 Results and Discussion

3.1 Physical properties of wastewater

The field measurements of wastewater recorded that: i) a bad smell of wastewater, particularly at the beginning of effluents source, the smell was gradually disappear away from the source of the effluents (Table 1). This smell refer to emissions of sulphur gases and the rule of reduction and anaerobic conditions in the environment (UNIDO, 2011); ii) the average temperatures of wastewater was higher than the permissible limits (35^{o}C) set by Saudi Arabia (KSA) (2003) standard (Table 1). The high wastewater temperature may be the result of the compounds chemical reactions that have received by wastewater from deferent factories in the area and/or the decomposition of organic compounds that included in wastewater; iii) the colour of studied wastewater in both streams was grey, coloured black in some areas and dark green in other areas and have varied according to distance from sources, for instance, the water was dark brown at the beginning of the first stream converted to gray and then yellow in the last sampling point (1000 m from source) this is due to coagulation and deposition during water movement (Wang and Howard, 2004; Rahbar et al., 2006); iv) the turbidity increases at the wastewater sources beginning in both streams and decrease gradually moving away from the sources, the turbidity values ranged between (6,5 to 8,8 NTU) in the first stream however they ranged between (8 to 11.5 NTU) in the second stream, these values are high and cause waters restriction in uses for agricultural, especially when use modern irrigation methods, because of turbidity may cause blockages in drippers of irrigation networks; v) the total suspended solids (TSS) were two to three fold more than the maximum limits allowed by KSA and USEPA standards, the concentration was high at the beginning and decrease gradually moving away from the point sources of wastewater, this is due to the gradually decrease in wastewater speed and thus the opportunity is suitable for suspended solids deposition (Mouedhena et al., 2008).

In general, results in Table (1) indicate that the average wastewater temperature, TDS, and turbidity were all exceeded the acceptable limits permitted by KSA and USEPA standards. Moreover the wastewater smell and odour were unacceptable.

Table 1 Comparison of physical properties of industrial wastewater for the third industrial zone in Riyadh with recommended maximum limits of USEPA and KSA standards.

Property	Distance from the downstream (m)	First stream	Second stream	KSA standards*	USEPA standards**
Odour	0	+++++	+++++	-	-
	50	+++++	+++++		
	100	+++++	+++++		
	200	+++	+++		
	500	+++	+++		
	1000	++	++		
Temperature oC	0	41.5	42.5	35	-
	50	41.5	41.5		
	100	39.5	40.5		
	200	38.5	40.5		
	500	38.5	39.5		
	1000	38.5	39.5		
Color	0	brown	black	-	-
	50	gray	brown		
	100	gray	gray		
	200	gray	gray		
	500	gray	gray		
	1000	yellow	gray		
Turbidity NTU	0	8.8	11.5	5	5
	50	8.5	10.5		
	100	7.5	10.5		
	200	7.0	9.5		
	500	6.5	8.0		
	1000	6.5	8.0		
Total solids mg L^{-1}	0	1650	1960	500	500
	50	1600	1900		
	100	1600	1900		
	200	1600	1860		
	500	1500	1800		
	1000	1300	1600		

* USEPA standards (2004)

** Kingdom of Saudi Arabia standards (2003)

3.2 Chemical properties of wastewater

Results in Table 2 indicated that the pH of wastewater ranged between 8.3 and 10.6 with an average value of 9.3. Most wastewater samples recorded high values of pH and Alkalinity and exceeded the permissible limits allowable by KSA and USEPA standards. The wastewater is considered as saline water with an average salinity of 7.4 dSm^{-1}, and ranged between 5.1 and 9.6 dSm^{-1}. The results also indicated that salinity in the second stream was higher than first one. The values of sodium adsorption ratio (SAR), alkalinity, total hardness, and residual sodium carbonate (RSC) were higher than the permissible limits set by standards used (Table 2), and causes problem in soil permeability if discharge to it. Moreover the presence of salts in carbonates forms may cause impermeable soil surface layer (Al-Matroud et al., 2003). The nitrate, phosphate, and Boron concentrations were recorded higher than the acceptable limits, however the amonium and sulphate were within the acceptable safe limits according to the used standards (Table 2).

Table 2 Descriptive statistics of wastewater chemical composition in Riyadh, third industrial zone, (n = 48).

	Max.	**Min.**	**Ave.**	**St. deviation**	**Variance**	**Var. of mean**	**St. error**	**Median**	**Skew**
pH	10.6	8.3	9.3	0.61	0.78	0.02	0.13	9.31	0.26
Alkalinity	1176	500	834	156	12.5	0.26	0.5	837	0.05
Osmotic Pressure	3.5	1.8	2.7	0.4	0.6	0.01	0.11	2.6	0.16
EC (dS/m)	9.6	5.1	7.4	1.10	1.05	0.02	0.15	7.3	0.16
SAR[1]	18.9	7.1	12.8	2.6	1.6	0.03	0.18	12.6	-0.01
Ca^{2+} (meq L^{-1})	22.4	6.8	13.9	3.95	1.99	0.04	0.20	13. 8	0.27
Mg^{2+} (meq L^{-1})	17.3	6.3	11.9	2.5	1.59	0.03	0.18	12.1	-0.20
Na+ (meq L^{-1})	54.5	25.4	40.3	6.9	2.6	0.05	0.2	39.8	0.12
K^+ (meq L^{-1})	1.3	0.6	0.9	0.17	0.4	0.01	0.09	0.9	0.25
NH_4^+ (mg L^{-1})	15.9	2.8	7.7	3.7	1.9	0.04	0.2	6.6	0.59
NO_3^- (mg L^{-1})	144	11	41	36.3	6.0	0.13	0.4	25.0	1.63
CO_3^{2-} (meq L^{-1})	19	8	13	2.7	1.7	0.03	0.2	12.4	0.37
HCO_3^- (meq L^{-1})	6.3	2.0	4.0	1.3	1.1	0.02	0.2	4.1	0.04
Cl^- (meq L^{-1})	49	25	37	5.7	2.4	0.05	0.2	36.3	0.16
SO_4^{2-} (meq L^{-1})	22.9	6.6	14.4	4.3	2.1	0.04	0.2	15.0	-0.10
RSC[2]	17.7	1.4	10.1	4.9	2.2	0.05	0.2	11.4	-0.52
B (mg L^{-1})	10.4	3.0	4.9	1.7	1.3	0.03	0.2	4.3	1.69
Total Hardens	2000	780	1300	290	17	0.36	0.6	1280	0.37
PO_4 (mg L^{-1})	94	22	44	18	4.3	0.09	0.3	37.7	1.04
TDS (mg L^{-1})	6125	3238	4743	707	27	0.55	0.7	4688	0.16
COD [3] **(mg L^{-1})**	76	47	62	13	3.6	0.08	0.3	62.5	-0.03

[1]SAR and [2]RSC are Sodium Adsorption Ratio and Residual Sodium Carbonate, calculated as described in Nishanthiny et al (2010). [3] COD is Chemical Oxygen Demand.

Most heavy metals on wastewater effulent were above permissible limits for agriculture reuse, using KSA and USEPA standards (Table 3). Saad and Omar (2010) concluded a same finding using FAO standards. Making filtration for wastewater samples decrease the heavy metals concentration to be within the permissible limits sets by standards used (Table 3).

The highest average metal concentration in digested effluents for deferent locations and sampling periods were Fe (17.1 mg L^{-1}) followed by Mo (11.6 mg L^{-1}), then Co (0.03 mg L^{-1}) (Fig. 3 and 4). However the Mo recorded the highest value in filtrated effluents (23.2 µg L^{-1}) followed by Fe (21.6 µg L^{-1}), and then Cd (8.02 µg L^{-1}) (Fig. 1 and 2).

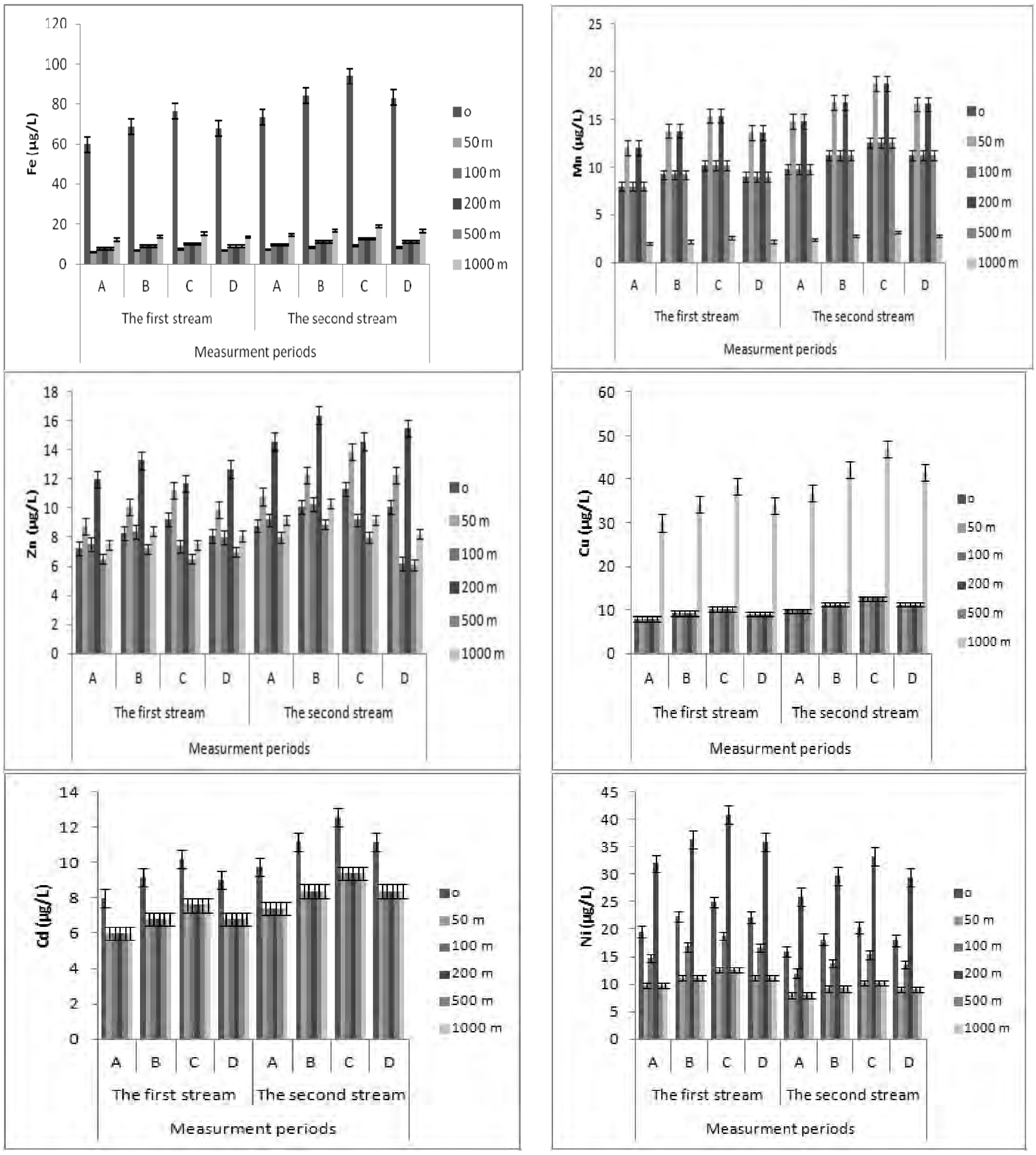

Fig. 1 Concentrations of heavy metals in filtrate of industrial wastewater for the third industrial zone in Riyadh City. The letters:" A = first sampling period (29/9/2004), B = second sampling period (28/3/2005), C = third sampling period (22/9/2005), and D = fourth sampling period (13/4/2008)". The numbers: "0, 50, 100, 200, 500, 1000 m are the sampling distance from point source "

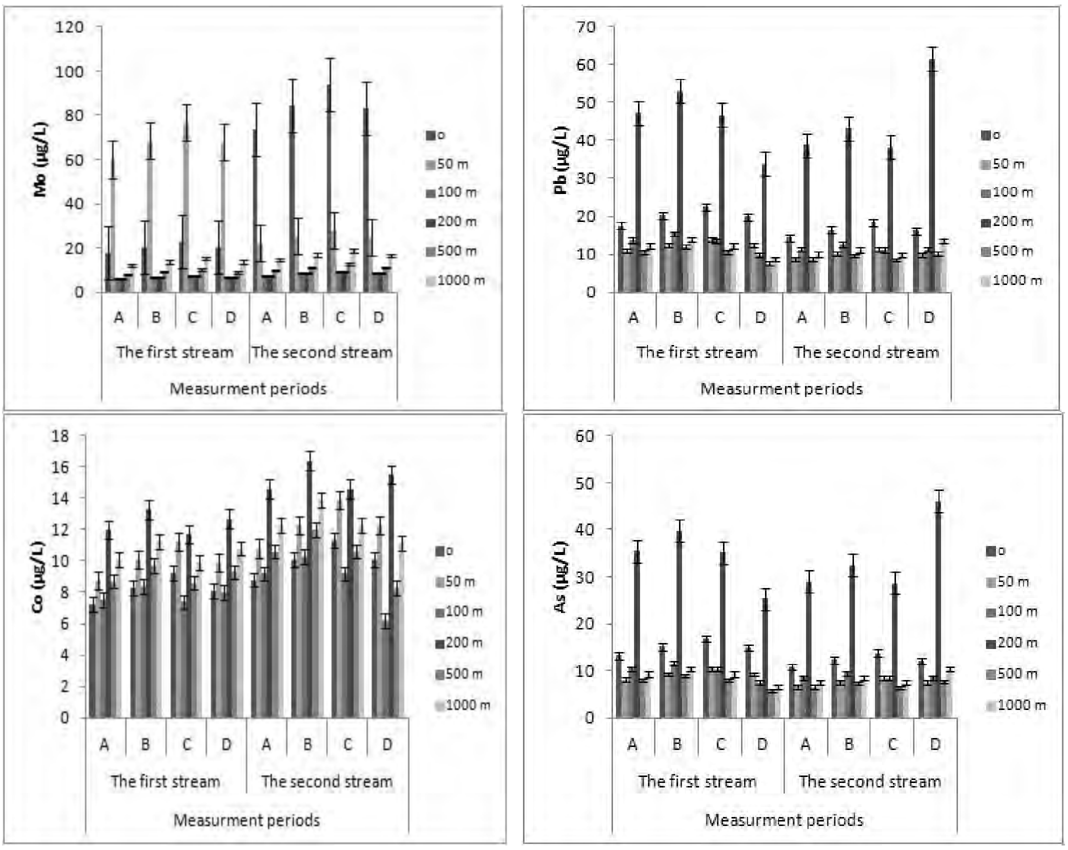

Fig. 2 Concentrations of heavy metals in filtrate of industrial wastewater for the third industrial zone in Riyadh City. The letters:" A = first sampling period (29/9/2004), B = second sampling period (28/3/2005), C = third sampling period (22/9/2005), and D = fourth sampling period (13/4/2008)". The numbers: "0, 50, 100, 200, 500, 1000 m are the sampling distance from point source "

Table 3 Comparison of heavy metals concentration determined on digested and filtrated wastewater samples with recommended maximum concentration of USEPA, and KSA standards for agriculture reuse.

Elements	Average of concentration				KSA guidelines	USEPA guidelines (long term use)
	filtrated wastewater	digested wastewater	digested wastewater at point source	digested wastewater at 1000 m from point source		
	µg L-1	mg L-1				
Fe	21.6	17	25	5.6	-	5.0
Cd	8	4.8	6.4	0.7	0.02	0.01
As	13.5	6.0	3.3	6.4	0.01	0.10
Cu	14.7	2.8	3.3	0.1	0.20	0.20
Pb	18	0.4	0.1	0.5	2.0	5.0
Zn	9.7	7.9	3.3	2.0	1.00	2.00
Co	10.6	0.03	0.02	0.02	-	0.05

Finally the study results emphasis that the continuous application of Riyadh industrial wastewater for local environment without treatments will lead to more accumulation of heavy metals in soil and natural plants, and also high possibilities of groundwater contamination by nitrate. Regular monitoring of heavy metals in an environment subject to industrial effluents is also necessary. Adoption of adequate measures to remove the heavy metal load from the industrial wastewater and renovation of sewage treatment plants are suggested to avoid further deterioration of Riyadh ecosystem.

3.3 Heavy metals behaviors of wastewater

Concentration of heavy metals on Riyadh wastewater generally decreased towards the downstream. The monitoring of wastewater heavy metals (determined on filtrate for both streams) recorded that the concentration of Fe, Mo, Zn, Cd, Pb, As, Ni, and Mn decreased from (60-100 µg L^{-1}) at point sources to be between (5-10 µg L^{-1}) at 1000 m from point sources, however no clear behavior was recorded for Cu and Co. Moreover the concentrations of all heavy metals by the last sampling point on downstream were remained at 10 µg L^{-1} or less (Fig. 1 and 2). The results on Fig. 1 through Fig. 4 concluded that the Mn, Zn, Ni, Pb, As, and Co concentration were re-increased on 200 m from point source of pollution, this is due to wastewater velocity decreasing with small lakes formation at this point. Undoubtedly this is the main cause for heavy metals concentration increase especially in the conditions of high temperature and evaporation as in Riyadh conditions. It is also a matter of saying that no increases were observed for Fe, Cd, Cu, and Mo. Furthermore the concentrations of heavy metals were rapidly re-decreased in the next sampling point (500 m from source point). Science the pH of Riyadh wastewater is high; the heavy metals precipitation in the form of carbonate is possible. High wastewater pH also promotes the precipitation of the metals as oxides and hydroxides (Corbitt, 1990). Fig. 1 showed that Fe concentration in Riyadh wastewater filtrate was rapidly decreased, this is due to iron precipitation by oxidation as follows (Anwar 2009): $4Fe^{2+}$ (soluble) + $3O_2 \rightarrow 2\ Fe_2O_3$ (precipitate). A same finding was observed for Ni and Mo (Fig. 1 and 2), the nickel can be removed from wastewater in both streams by precipitation as hydroxide, sulfate or carbonate (solubility: 0.12 ppm at pH ranging from 10 to 11). However Mo can be removed due to presence of insoluble ferric salts, this ferric salts (ex. Ferric sulfate) are react with Mo to form molybdenum complexes of ferric salts (molybdates), which subsequently removed from wastewater (Ramirez and Far Hills, 1980). Cadmium can also be removed by precipitation as hydroxide (solubility between: 1 to 0.05 ppm at pH ranging from 8 to 11) (Haas and Vamos, 1995), on the other hand, lead can be removed by precipitation as hydroxide and lime at pH 11.5 (Eckenfelder, 1989; Wentz, 1995; Haas and Vamos, 1995). The Arsenic can also be removed by co-precipitation with $FeCl_3$ when a $Fe(OH)_3$ flocculation is formed. The effluent as concentration is then 5 µg L^{-1} or less (Fig. 2) (Haas and Vamos, 1995).

For sake of brevity, most soluble heavy metals were removed from industrial wastewater at the last sampling point for both stream (table 3); this mean that leaving high pH industrial wastewater moves short distance in open air and lined channel will help in contaminants removal, therefore it is recommended to use this stage as a first step for industrial wastewater treatments for agriculture reuse.

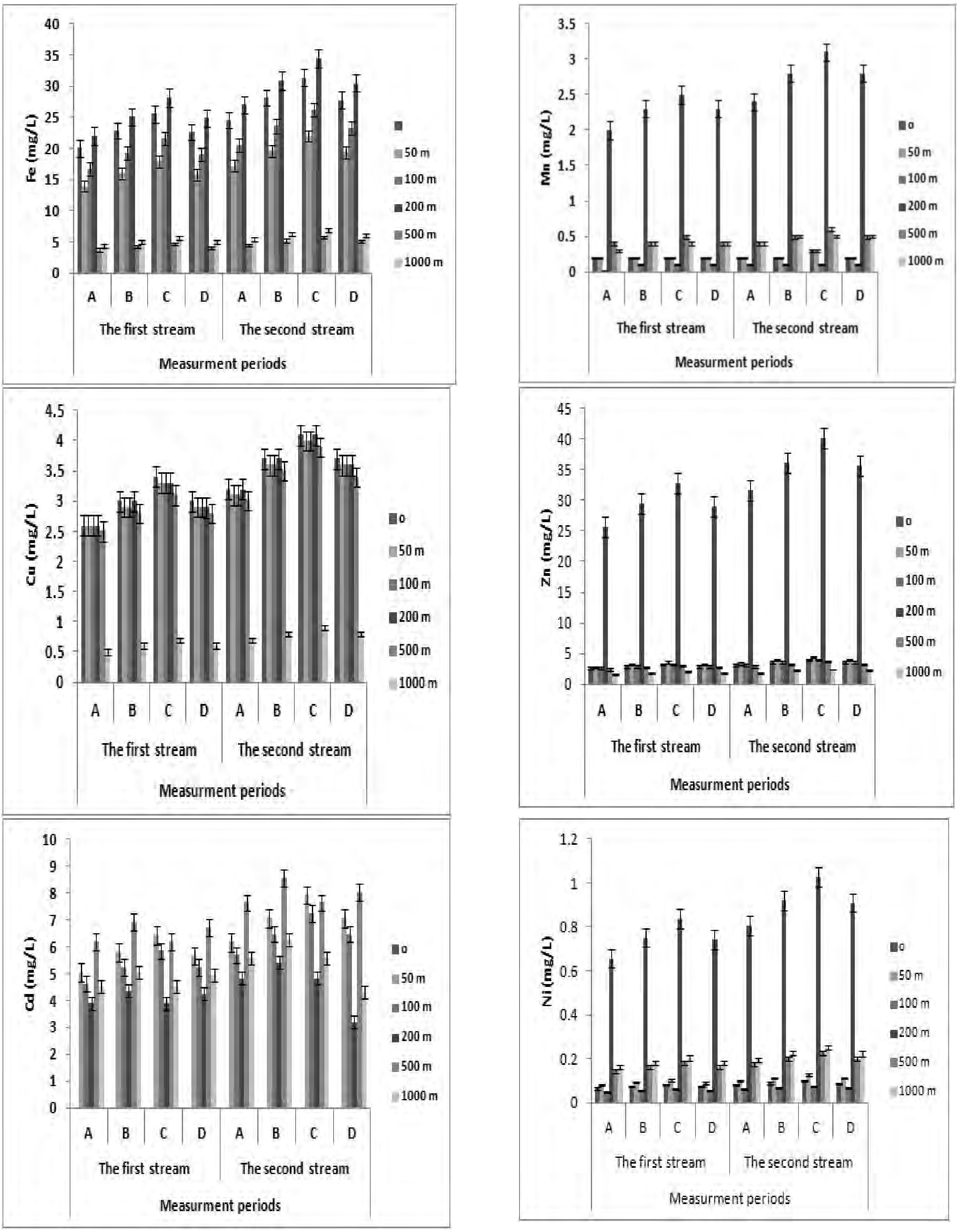

Fig. 3 Concentrations of heavy metals in digested industrial wastewater for the third industrial zone in Riyadh City. The letters:" A = first sampling period (29/9/2004), B = second sampling period (28/3/2005), C = third sampling period (22/9/2005), and D = fourth sampling period (13/4/2008)". The numbers: "0, 50, 100, 200, 500, 1000 m are the sampling distance from point source "

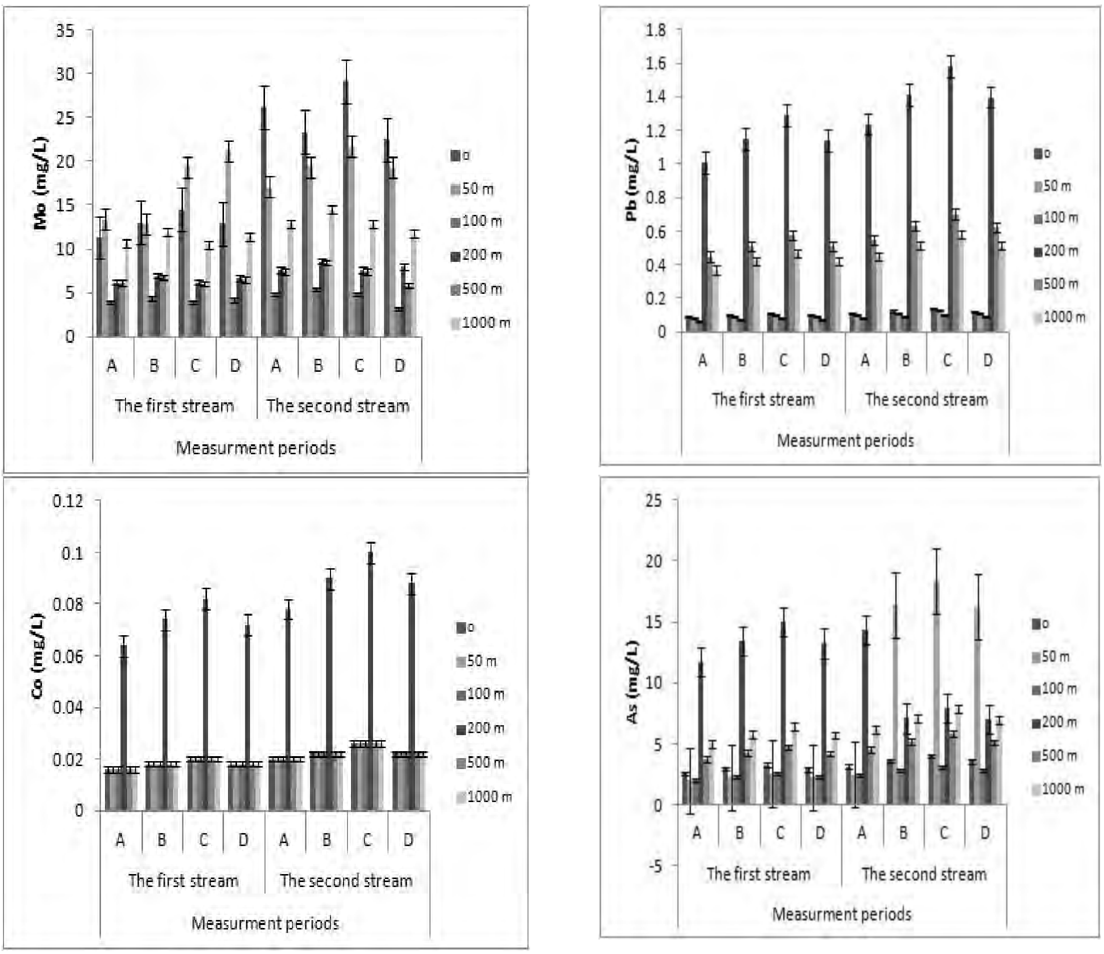

Fig. 4 Concentrations of heavy metals in digested industrial wastewater for the third industrial zone in Riyadh City. The letters:" A = first sampling period (29/9/2004), B = second sampling period (28/3/2005), C = third sampling period (22/9/2005), and D = fourth sampling period (13/4/2008)". The numbers: "0, 50, 100, 200, 500, 1000 m are the sampling distance from point source "

4 Conclusion

The results showed that the wastewater of industrial zone in Riyadh city is characterized by gray color, bad smell, high temperatures, and high pH at point source. Also, it contains high concentrations of soluble ions (Ca^{2+} , Mg^{2+}, Na^{+} , K^{+} ,Cl^{-}, CO_3^{2-}, HCO_3^{-} ,SO_4^{2-}), heavy metals (Fe, Mn, Zn, Cd, Ni, Pb, Mo, and As), and (B, NO_3^{-}, and NH_4^{+}). The color, smell, temperatures, heavy metals, B, NO_3^{-}, and NH_4^{+}concentrations varied according to sampling distance from the effluents sources and decreasing away from the point source. However the SAR, RSC, total hardness, and soluble ions remained constant. The results also concluded that the concentration of total soluble salts, soluble ions and also most of heavy metals have exceeded the allowable limit set by KSA and USEPA standards. On the other hand, filtrating, the industrial wastewater decreases the heavy metals concentration to reach the permissible limits. The monitoring of wastewater heavy metals concluded that the concentration of most heavy metals decreased toward downstream, moreover the other wastewater physical characteristics improved by last sampling point (1000 m from source point). Consequently, leaving high pH industrial wastewater moves short distance on open lined channel can recommend as a first step for heavy metals removal, and/or first step for industrial wastewater treatment. Finally the study recommended adoption of adequate measures to remove or lower heavy metals load from industrial wastewater and renovation of sewage treatment plants are suggested to avoid further deterioration of Riyadh ecosystem.

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