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Role of Saline Water in Removal of Heavy Elements from Industrial Wastewaters

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ABSTRACT: Flocculation processes during estuarine mixing can reduce the elemental concentrations of river water. In the present investigation, natural flocculation processes concept is used to reduce the elemental contents of industrial wastewater. For this purpose, various amounts of saline water were added to an artificial industrial wastewater with known concentrations of heavy metals. The results of investigation show that in the salinity of 0.9‰, percentage of elemental flocculation occurs in the order of: Ni (95.4%) > Pb (87.6%) > Zn (85%) > Mn (56.25%) > Cu (14.4%). Flocculation of Cu is insignificant at lower salinities. Though higher removal of heavy metals is obtained at greater salinities but due to the environmental limitations, we propose salinity of 0.9‰. Use of seawater to flocculate heavy metals can greatly reduce the costs associated with the purification of wastewater treatment.

Key words: Flocculation, Metal, Wastewater, Purification, Pollution

INTRODUCTION

Dissolved and particulate matters find their ways into lakes and seas through rivers (Meybeck, 1988). Due to flocculation processes, considerable amount of dissolved metals come into particulate phase (Boyle *et al.*, 1977; Eckert and Sholkovitz, 1976). Therefore, flocculation of dissolved metals during estuarine mixing can significantly influence the chemical mass balance between rivers and Seas or lakes. Many investigations have been carried out on flocculation of dissolved substances to know about the controlling mechanisms. In wetlands, flocculation is enhanced by increased pH, turbulence, concentration of suspended matters, ionic strength and high algal concentration (Matagi *et al.,* 1998). Flocculation mechanisms and mainly due to colloidal stability, Surface properties, humic acids, salinity and pH (Hunter, 1983; Zhiging *et al.*, 1987; Feather stone and O' Grady, 1997; Karbassi *et al.*, 2007; Karbassi *et al.*, 2008a,b; Karbassi and Nadjapour, 1996). Some investigations showed DOC as the main governing Factor in flocculation of trace elements (Sholkovits, 1978; Mantoura and Wood word, 1993; Meyer, 1983; Karbassi *et al.*, 2008a, b). Adverse effects of heavy metals and their compounds (such as toxicity and biomagnifications) on human and aquatic ecosystems have been a growing concern for researchers of the world, in recent years. (Viesman and Hammer, 1993; Gardea-Torresday *et al.*, 1996; Karvelas *et al.*, 2003). Environmental impact by heavy metals was earlier noticed to be mostly connected to industrial sources (Karvelas *et al.*, 2003). A significant part of anthropogenic emissions of heavy metals resulting from the production of chemical pharmaceutical, steel, cardboard, paper and glass industries and etc ends up in wastewaters (Osibanjo, 1989; Foess and Ericson, 1980). Major

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industrial sources include surface treatment processes with elements such as Cu, Zn, Pb, Ni and etc. that at the and of their life, and discharged in wastes (Sun and Shi, 1998; Osibanjo, 1989; Foes and Ericson, 1980). Flocculation-coagulation process has been employed by several researchers (Sletten *et al.*, 1995; Rossini *et al.*, 1999; Tatsi *et al.*, 2003; Amuda *et al.*, 2006) in the treatment of wastewater for removal of organic matter and trace metals.

In the present study, effective parameters in natural flocculation process are used in heavy metals clean up of a synthetic wastewater. In others words removal of Cu, Zn, Mn, Ni and Pb during mixing of wastewater with saline water in relation to parameters such as EC, pH, Eh, Salinity, DO, DOC, COD, Cl and Temperature due to flocculation process is investigated.

MATERIALS & METHODS

A Synthetic wastewater was prepared by dissolving nitrates of Zn, Ni, Pb, Cu and Sulfate of Mn in distilled water. About one liter of filtered wastewater was acidified with concentrated HNO_3 to a pH of approximately 1.8 and stored in polyethylene bottles in a refrigerator prior to the analysis of dissolved metals. The rest of filtered waters were also kept in refrigerator. Saline water sample was collected from Persian Gulf approximately 16 km away from coast (on 6th Jul. 2009) to ensure that the sample was not diluted by river water (salinity 37.5‰). In Order to prevent the contamination of samples, all equipment was acid washed with a mixture of HNO_3 and HCl. Rinsing was done with running Mili-Q water. The samples were filtered through 0.45 µm Millipore AP and HA filter. Filtered wastewater and sea water were mixed at room temperature in various proportions yielding salinities 0.9‰ to 3.46‰. They were kept for 24 hours with occasional stirring. The resulting flocculants were collected on 0.45 µm diameter Millipore membrane filters (type HA). Millipore filters were digested by 5 mL concentrated HNO_3 overnight. The concentrations of Cu, Zn, Ni, Pb and Mn were determined by ICP (JOBINYVON model JY138 ULTRCE). Procedural blanks and duplicates were run with the samples in a similar way. Calibration of ICP was done by dilution of single concentrated standards purchased from $\text{SPEX}_{\text{CerPrep}}$ Company.

The accuracy of the analysis was about 5% for all elements in the dissolved and flocculent phases. Table 1 shows summary of methods used in the present Study. Of the existing clustering techniques (Lance and William, 1966; Anderson 1971; Davis, 1973) the Weighted Pair Group (WPG) method (Davis, 1973) was used in this study.

RESULTS & DISCUSSION

The base metal (Cu, Mn, Pb, Zn and Ni) concentrations at various salinities, as well as other physical-chemical characteristics of the synthetic wastewater are presented in Table 2. Flocculation of elements and the percentage of removal in different salinity regimes are presented in Table 3. The values given in Table 3 are actually derived from Table 2 by subtracting concentration of elements at each salinity from the initial concentration of element in wastewater. It should be noted that the term "salinity" does not necessarily imply salty water. There are many other constituents in saline water that can lead to the flocculation of heavy metals. It is reported that NaClO is an effective flocculants as well (Robinson and Ronek, 1986).

Table 1. Methods and apparatus used for measurement of various parameters

Parameter	Method/apparatus of measurement	
Mn, Cu, Pb, Zn, Ni	ICP (JOBINYVON model JY138 ULTRCE	
pH/Eh	pH meter (Metrohm 744)	
EC	Conductimeter (CRISON GLP32)	
DO	DO meter (Inolab WTW)	
DOC	Photo Cathalitical Oxidation method (ANATOC™ SERIES II)	
Chloride	Argentometric method (4500-Cl^-)	(APHA, 2005)
COD	Open Reflux method (5220 B)	(APHA, 2005)
Salinity[1]	Titration method	(APHA, 2005)
Temperature of water	Thermometer (accuracy of 1C°)	

1Salinity in sampling locations was measured by portable apparatus (ATAGO S/Mill-E)

The Flocculation of Pb, Ni, and Cu raises in salinities of 0.9 ‰ (and 2.7‰ as well) and decreases in higher salinities. In contrast, more than 55% of total Mn contents and more than 77% of total Zn contents flocculate in salinity of 2.9 ‰ to 3.46‰.According to the data shown in Table 3 the maximal removal of studied metals in different salinity regimes are as follows: Zn and Mn in salinity of 3.46 ‰, Pb in salinity of 2 to 2.2 ‰. Ni in salinity of 2 to 2.7 ‰ and Cu in salinity of 2.2 ‰. Many researchers have reported rapid flocculation in the lower salinities (about 2‰) (Bewers *et al.*, 1974; Burton, 1976; Duinker and Nolting, 1976). The general pattern of flocculation of the studied metals in mentioned salinities is Ni (83%) >Zn (78%) >Pb (76.4%) > Mn (56%) >Cu (16.7%). The highest flocculation of Zn (383 and 386 mg/L) is found at salinities of 2.9 ‰ and 3.46 ‰. The other salinities have lesser role in flocculation of Zn (328 and 352mg/L). Amongst studied metals the highest flocculation belongs to Ni (83%). The initial concentration of Cu in wastewater is 126 mg/L and only 3 to 17 mg/L of Cu flocculates in different salinity regimes (about 2.4% to 13. 6% of total Cu contents).

Contrary to data showing almost rapid flocculation in the lowest salinity (0.9 ‰) for Zn, Pb and Ni, the flocculation rates in the higher salinities are more considerable for Mn. Flocculation of Cu in comparison with other studied elements are not significant in various salinity regimes. Although it seems that flocculation of heavy metals increases in higher salinities, heavy metals clean up from wastewaters must be carried out by environmentally justifiable methods that dose not result in more undesirable consequences. Therefore, amongst studied salinities, salinity of 0.9 ‰ is preferable for removal of heavy metals from wastewater. The percentage of flocculation taking into consideration the initial metal contents in the wastewater in salinity of 0.9 ‰ is Ni (79.2%)>Pb (72.7%)>Zn (66.3%)>Mn (31.5%)>Cu (2.4%). Karbassi *et al.*, (2008a) have reported that flocculation of elements increases with an increase in the initial contents of elements. Though such trend holds good in the present study but the metals in dissolved form follow a nonlinear behavior in terms of physical-chemical parameters variations during mixing of the wastewater with the saline water. It can be concluded from dendogram (Fig.1) that flocculation of Zn and Mn is controlled by EC, pH, salinity and Cl as they join each other at a high similarity coefficient. Copper is clustered with temperature. Nickel and Pb join Eh and DOC under high similarity coefficient. These clusters join dissolved oxygen at a lower similarity coefficient. Chemical Oxygen Demand (COD) does not show any relation with the studied metals and parameters.

CONCLUSION

The flocculation process of Cu, Ni, Pb, Mn and Zn during mixing of a synthetic wastewater with saline water was investigated. Metals in dissolved form seem to follow nonlinear behavior. The removal of dissolved metals is not influenced by COD and this statement is supported by the results of cluster analysis. Electrical conductivity, pH, salinity and Cl show significant role in

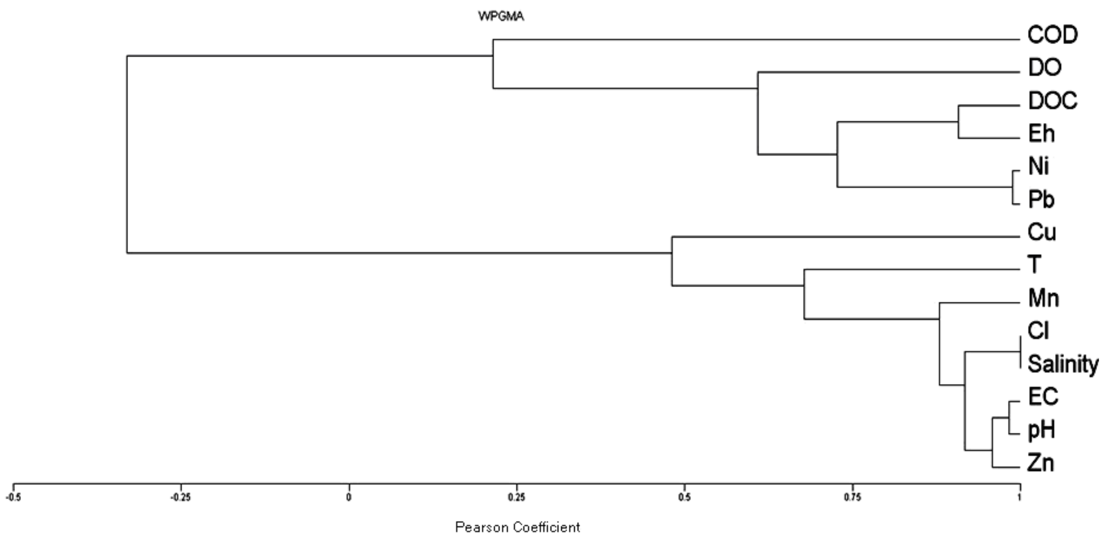

Fig. 1. Dendogram of cluster analysis showing flocculation of metals and their governing factors

Table 2. Trace metal contents along with physical-chemical characteristics of synthetic wastewater

Cl (mg/L)	COD (mg/L)	DOC (mg/L)	DO (mg/L)	S ‰	T (C)	EC (µs/cm)	Eh (mV)	pH	Mn (mg/L)	Cu (mg/L)	Ni (mg/L)	Pb (mg/L)	Zn (mg/L)	Parameters Aquarium No.
-	820.8	273.5	8.9	0.03	21.1	8880	91	4.74	200	126	53	330	495	**Wastewater**
22.75	883.2	**-	-	37.5	23.2	56700	-84	8.14	44*	14*	13*	200*	34*	**Saline water**
0.48	844.8	270	8.8	0.9	21.6	9120	82	5.05	137	123	11	90	167	**1**
0.91	835.2	257	9	1.67	20.6	9240	85	5	136	122	11	88	166	**2**
0.96	796.8	249	9	1.76	20.5	9350	85	5.02	138	119	11	87	165	**3**
1.01	806.4	242	8.8	1.85	21.6	9540	84	5.03	139	119	10	83	161	**4**
1.1	859.2	227	8.8	2	21.4	9850	81	5.1	138	115	9	78	144	**5**
1.2	859.2	214	8.9	2.2	21.2	10210	78	5.13	139	105	9	78	142	**6**
1.5	825.6	206	8.8	2.7	21.7	10890	75	5.2	113	109	9	86	143	**7**
1.6	811.2	198	8.4	2.9	23.7	11400	72	5.25	90	112	37	254	112	**8**
1.9	811.2	188	8.8	3.46	21.9	12100	70	5.31	88	109	43	244	109	**9**

***Concentration of Elements in Saline water: µ g/L**
****Not Determined**

Table 3. Trace metal flocculation along with their percentage of removal in various salinities

Cl (mg/L)	COD (mg/L)	DOC (mg/L)	DO (mg/L)	‰ S	T (C)	EC (µs/cm)	Eh (mV)	pH	Mn (mg/L)	Cu (mg/L)	Ni (mg/L)	Pb (mg/L)	Zn (mg/L)	Parameters Aquarium No.
-	820.8	273.5	8.9	0.03	21.1	8880	91	4.74	-	-	-	-	-	**wastewater**
22.75	883.2	**-	-	37.5	23.2	56700	-84	8.14	-	-	-	-	-	**Saline water**
0.48	844.8	270	8.8	0.9	21.6	9120	82	5.05	63 (31.5)	3 (2.4)	42 (79.2)	240 (72.7)	328 (66.3)	**1**
0.91	835.2	257	9	1.67	20.6	9240	85	5	64 (32)	4 (3.2)	42 (79.2)	242 (73.3)	329 (66.5)	**2**
0.96	796.8	249	9	1.76	20.5	9350	85	5.02	62 (31)	7 (5.6)	42 (79.2)	243 (73.6)	330 (66.7)	**3**
1.01	806.4	242	8.8	1.85	21.6	9540	84	5.03	61 (30.5)	7 (5.6)	43 (81.1)	247 (74.8)	334 (67.5)	**4**
1.1	859.2	227	8.8	2	21.4	9850	81	5.1	62 (31)	11 (8.7)	44 (83)	252 (76.4)	351 (70.9)	**5**
1.2	859.2	214	8.9	2.2	21.2	10210	78	5.13	61(30.5)	21 (16.7)	44 (83)	252 (76.4)	353 (71.3)	**6**
1.5	825.6	206	8.8	2.7	21.7	10890	75	5.2	87 (43.5)	17 (13.5)	44 (83)	244 (73.9)	352 (71.1)	**7**
1.6	811.2	198	8.4	2.9	23.7	11400	72	5.25	110 (55)	14 (11.1)	16 (30.2)	76 (23)	383 (77.4)	**8**
1.9	811.2	188	8.8	3.46	21.9	12100	70	5.31	112 (56)	17 (13.5)	10(18.9)	86 (26.1)	386 (78)	**9**

***Concentration of Elements in Saline water: µ g/L**
****Not Determined**
( ) Percentage of removal

flocculation process. Although temperature is directly joined Cu, it plays less important role in flocculation. Dissolved Oxygen (DO), DOC and Eh control flocculation of Ni and Pb. Despite the fact that flocculation rates is more dominant at higher ranges of salinities but we propose salinity of 0.9 ‰ to prevent environmental adverse effects of saline water discharge. In general percentage of elemental flocculation is in the following order: Ni (95.4%) > Pb (87.6%) > Zn (85%) > Mn (56.25%) > Cu (14.4%). It can also be inferred that flocculation of Cu is insignificant at lower salinities.

REFERENCES

Amuda, O.S., Amoo, I.A., Ipinmoroti,K.O. and Ajaya, O.O (2006). Coagulation/ flocculation process in the removal of trace metals present in industrial wastewater. J. Appl. Sci. Environ. Mgt., **10(3)**, 159-165.

Anderson, A.J.B. (1971). Numerical examination of multivariate of samples. Math. Geol., **3**, 1-14.

Boyle, E.A., Edmond, J.M. and Sholkovitz, E.R. (1977). The mechanism of Fe removed in estuaries. Geochim. Cosmochim. Acta, **41**, 1313-1324.

Davis, J. B. (1973). Statistic and data analysis in geology. New York: Wiley International, 456-473.

Eckert, J.M. and Sholkovitz, E.R. (1976). The flocculation of Fe, Al and humates from River water by electrolytes. Geochim. Cosmochim. Acta, **40**, 847-856.

Featherstone, A.M. and Oågrady, B.V. (1997). Removal of dissolved Cu and Fe at the freshwater - seawater interface of an acid mine stream. Mar. Poll., **34**, 332-337.

Foess, G. W. and Ericson ,W.A. (1980). Toxic control:- The trend of the future. Water Wastes Eng., 21-27.

Gardea- Torresday, J. L., Tang, L. and Salvador, J.M. (1996). Copper adsorption by esterifies and unesterified fractions of Sphagnum peat moss and its different humic substances. J. Hazard. Mater, **48**, 191-206.

Hunter, K.A. (1983). On the estuarine mixing of dissolved substances in relation to colloidal stability and surface properties. Geochim. Cosmochim. Acta, **47**, 467-473.

Karbassi, A. R., Nouri, J., Mehrdadi, N. and Ayaz, G. O. (2008a). Flocculation of heavy metals during mixing of freshwater with Caspian Sea water. Environ. Geol., **53,** 1811–1816.

Karbassi, A. R., Nouri, J., Gh.R. Nabi Bidhendi, Gh. R. and Ayaz, G. O. (2008b). Behavior of Cu, Zn, Pb, Ni and Mn during mixing of freshwater with the Caspian Sea water. Desalination, **229(1-3),** 118-124.

Karbassi, A.R. Nouri. J.and Ayaz, G.O. (2007). Flocculation of Trace Metals During Mixing of Talar River Water with Caspian Seawater. Int. J. Environ. Res., **1 (1)**, 66-73.

Karbassi, A. R and Nadjafpour Sh (1996). Flocculation of dissolved Pb, Cu, Zn and Mn during estuarine mixing of river water with the Caspian Sea. Environ. Poll., **93,** 257–260.

Karvelas, M, Katsoyiannis, A. and Samara, C. (2003). Occurrence and Fate of Heavy Metals in the Wastewater Treatment Process. Chemosphere**, 53 (10)**, 1201-1210.

Lance, G.N.and William, W.T. (1966). A generalized sorting for computer classification. Nature, 212-218.

Martoura, R. F. C. and Woodward, E. M. S. (1983). Conservative behavior of riverine dissolved organic carbon in the Severn estuary: Chemical and geochemical implications. Geochim. Cosmochim. Acta, **47**, 1293-1309.

Matagi, S.V., Swai, D. and Mugabe, R. (1998). A review of heavy metal removal mechanisms in wetlands. Afr. J. Trop. Hydrobiol. Fish, **8**, 23-25.

Meybeck, M. (1988). How to Establish and use world budgets of riverine materials.In A. Lerman, and M. Meybeck (Eds.), Physical and chemical weathering in geochemical cycles. Kluwer, Dordrecht, 247-272.

Meyer, J.L. and Tate, C.M. (1983). The effects of watershed disturbance on dissolved organic carbon dynamics of a stream. Ecology, **4**, 33-44.

Osibanjo, O. (1989). Present water quality in Nigeria. Federal Environmental Protection Agency, Lagos.

Rossini, M., Garrido, J.G.and Galluzzo, M. (1999). Optimization of the coagulation- flocculation treatment: Influence of rapid mix parameters. Water Res., **33 (8),** 1817-1826.

Shokovitz, E. R. (1976). Flocculation of dissolved organic and inorganic matter during the mixing river water and seawater. Geochim Cosmochim Acta, **40**, 831-845.

Sletten, R. S., Benjamin, M. M., Horng, J. J. and Ferguson, J. F. (1995). Physical-chemical treatment of Landfill leachates for metal removal. Water Res., **29 (10),** 2376-2386.

Sun, G.and Shi, W. (1998). Sunflower stalks as adsorbent for the removal of metal ions from wastewater. Ind. Eng. Chem. Res., **37**, 1324-1328.

Tatsi, A.A., Zouboulis, A. L., Matis, K. A. and Samara, P. (2003). Coagulation-flocculation pretreatment of sanitary land fill leachates. Chemosphere, **53**, 737-744.

Viesman, W. and Hammer, M.J. (1993). Water Supply and pollution control. 5th (Ed.), New York: Harper Collins College Publisher.

Zhiqing, L.E., Jianhu, Z. and Jinsi, C. (1987). Flocculation of dissolved Fe, Al, Mn, Si, Cu, Pb and Zn during estuarine mixing. Acta Oceanol. Sin., **6**, 567-576.