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Flocculation of Cu, Mn, Ni, Pb, and Zn during Estuarine Mixing (Caspian Sea)

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ABSTRACT: During estuarine mixing of fresh water with saline water and due to the flocculation process, a portion of dissolved metals come into particulate phase, and the dissolved load decreases. This process plays an important role in self-purification of heavy metals in rivers. In this study, flocculation of Cu, Mn, Ni, Pb and Zn during mixing of Cheshme-Kileh River water with Caspian Sea water has been investigated. Salinity and electrical conductivity are the governing factors for the flocculation of Mn and Cu. Zn and Ni are governed by pH. Dissolved oxygen is a governing factor for the flocculation of Pb. Rapid flocculation occurs in the earlier stages of mixing. The final flocculation rates of metals are in the following order: Mn (68.79%) > Pb (45.45%) > Ni (26.32%) > Cu (23.08%) > Zn (21.21%). In addition, electro-flocculation (EF) is investigated. The results reveal that EF had adverse effect on flocculation rates of heavy metals. General pattern of EF of metals is like the following: Mn (57.89%) > Pb (40.9%) > Cu (23.08% > Ni (22.37%) > Zn (15.15%). Furthermore, the effect of decreasing pH level on flocculation of heavy metals is studied. Except for Mn, decreasing the pH increased the flocculation rates of heavy metals. Maximum flocculation of Ni, Cu, Pb, and Zn occur at pH about 7.5. Due to the flocculation of trace metals during the estuarine mixing about 51.6, 7.8, 5.5, 3.9, and 3.6 ton/year of Mn, Ni, Zn, Pb, and Cu, respectively, are removed from the river water.

Key words: Heavy metals, Estuarine processes, Aquatic Environment, Electro- flocculation

INTRODUCTION

An estuary is the region where a free-flowing river meets the ocean or sea. It can be treated as a number of zones based on the interactions of advection, dispersion, and salinity (Chapra, 1997). Twenty-two of the world's largest cities are located on estuaries (Ross, 1995); therefore these environments are in more risk of water pollution specially due to heavy metals which are proved to be hazardous for living organisms (Pillay and Pillay, 2013; Serbaji *et al.*, 2012; Fazelzadeh *et al.*, 2012; Guinder *et al.*, 2012; Ratheesh Kumar *et al.*, 2010; Nasrabadi *et al.*, 2010a; Adjei-Boateng *et al.*, 2010; Sundararajan and Natesan, 2010; Nasrabadi *et al.*, 2010b) . Dissolved metals carried by river water are discharged into the sea through estuaries; during estuarine mixing and due to flocculation process, large amounts of dissolved metals are flocculated, and the dissolved load decreases (Eckert and Sholkovitz, 1976; Boyle, 1977; Sholkovitz *et al.*, 1977; Karbassi *et al.*, 2008a). As a result, the chemical mass balance between rivers and seas or lakes is significantly affected by the flocculation of trace metals in estuaries (Wollast and Peters, 1978; Meybeck, 1982, Zobrist and Stumm, 1981; Ahmed *et al.*, 2010; Lee and Mohamed, 2009;Mensi *et al.*, 2008; Akoto *et al.*, 2008). Many researchers reported that the flocculation of trace metals occurs in the upper part of the estuary where lower salinity regimes prevail (Gerringa *et al.*, 2001; Karbassi *et al.*, 2008b; Biati *et al.*, 2010a; Shamkhali *et al.*, 2011; Fazelzadeh *et al.*, 2011). Finding the controlling mechanisms of flocculation process has been the purpose of many investigations. In order to find the controlling factors of flocculation process during estuarine mixing, some researchers have studied the effect of salinity, pH, colloidal stability, surface properties, turbulence, ionic strength, and algal concentration on the flocculation of trace metals (Featherstone and O'Grady, 1997; Hunter, 1983; Matagi *et al.*, 1998; Shankar and Karbassi, 1992). Furthermore, other investigators has studied physico-chemical parameters of water, such as pH, dissolved oxygen, Rh, EC, dissolved organic carbon, total nitrogen, and PO_4 in order to find the controlling factors for the flocculation of dissolved heavy metals during estuarine mixing, in the north and south of Iran (Karbassi and Nadjafpour, 1996; Saeedi *et al.*, 2003; Karbassi *et al.*, 2007; Karbassi *et al.*, 2008a; Karbassi *et al.*, 2008b; Biati *et al.*, 2010a; Shamkhali *et al.*, 2011; Fazelzadeh *et al.*, 2011). Electro-flocculation (EF) has several advantages in comparison with the conventional chemical flocculation method, such as

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easy operation, no chemical usage, and avoidance of the addition anions as chloride or sulfate to the solution (Mollah *et al.,* 2001). Many researchers have reported the successful application of the electrochemical treatment for removal of metals such as boron, copper, lead and zinc, cadmium, iron, nickel, cobalt and chromium (Escobar *et al.,* 2006; Golder *et al.,* 2007; Hansen *et al.*, 2006; Fan *et al.*, 2012; Shamkhali *et al.,* 2012; Vasudevan *et al.*, 2009; Yilmaz *et al.*, 2008). EF process is dependent on the chemistry of the aqueous medium such as conductivity, pH, particle size, and chemical constituent concentration (Mollah *et al.,* 2001). During the EF process, with aluminum electrodes, the electrolytic dissolution of the aluminum anode produces Al^{3+} and $Al(OH)_2^+$. The suspended $Al(OH)_2^+$ has large surface area, which bring about a absorption of soluble organic compounds (Daneshvar *et al.,* 2004), and polymerized to $Al_n(OH)_{3n}$ as shown in the following reactions:

$$Al \rightarrow Al^{3+}(aq) + 3e^- \quad (1)$$

$$Al^{3+}(aq) + 3H_2O \rightarrow Al(OH)_3 + 3H^+(aq) \quad (2)$$

$$nAl(OH)_3 \rightarrow Al_n(OH)_{3n} \quad (3)$$

Electro-flocculation (EF) of Cd, Co, Ni, Cr, and Pb during estuarine mixing of fresh water with Caspian seawater was investigated in the north of Iran (Shamkhali *et al.,* 2011). The results revealed that EF increased the flocculation rate of Ni and Pb, and decreased the removal rates of Cr and Co. In brief, this study aims to investigate the removal of Cu, Mn, Zn, Ni, and Pb during mixing of Cheshme-Kileh River water with Caspian Sea water considering physico-chemical parameters, such as electrical conductivity (EC), dissolved oxygen (DO), pH, Eh, and salinity due to flocculation. According to the past investigations, pH is the controlling factor for the flocculation of dissolved metals, in the most estuaries in Iran (Biati and Karbassi, 2010). Therefore, in this study we investigate the flocculation rates of the studied metals when pH level was decreased, in order to find out the pH level in which the maximum flocculation occurs. Moreover, the efficiency of EF in removing studied trace metals from mixed water was investigated.

MATERIALS & METHODS

Cheshme-Kileh River is about 85 km-long and located in Tonekabon city in northern Iran. On 5 July 2012 fresh and saline water samples were collected in pre-cleaned 20-liter polyethylene bucket from the Cheshme-Kileh River upstream and Caspian Sea, at latitude of 36 N 45' 49.24" and longitude of 50 E 49' 32.35", and latitude of 36 N 50' 14.60" and longitude of 50 E 54' 18.18", respectively. On the same day, it was filtered through the 0.45-µm Millipore AP and HA filters. One liter of filtered fresh water was acidified with concentrated HNO3 to a pH of below 2 and stored in polyethylene bottles in a refrigerator prior to analysis of dissolved Cu, Zn. Mn, Pb, and Ni. This study consists of three stages.

In the first stage, filtered sea water was added to a constant level of filtered fresh water (300 mL) in five different aquaria to achieve salinities of 0.75–3.75 ppt. Samples were kept for 24 hours with occasional stirring and the resulting flocculants were collected on Millipore membrane filters (type HA, Pore size 0.45 µm). These filters were digested by adding 5 cc of extra pure nitric acid. After 6 hours, when the flocculants were solved, the liquids were transferred into 25 cc Erlenmeyer Bulb and a mixture of DI-water (482.5 mL) and 1N HCL (17.5 mL) were added. At the end, the concentrations of Cu, Mn, Ni, Zn, and Pb were determined using Atomic Absorption System (AAS, Varian model Spectra. 200). In the second stage, we investigated the electro-flocculation of studied heavy metals. 2-L reactors with two aluminum electrodes of rectangular shape (10 cm * 5 cm) were used. We installed them vertically in the middle of the aquaria, the distance between electrodes was 5 cm and their areas were 20 cm^2 (Shamkhali *et al.,* 2011). To examine the efficiency of EF process in removal of studied trace metals, electrodes were connected to a DC power providing electrical potential of 12V for ten minutes. Then, similar to previous stage, the liquid samples were filtered using Millipore membrane filters (type HA, Pore size 0.45 µm). Millipore filters were digested using 5 cc of extra pure nitric acid. The liquids were transferred into 25 cc Erlenmeyer Bulb and a mixture of DI-water (482.5 mL) and 1N HCL (17.5 mL) were added. Studied heavy metals were measured using AAS (Varian model Spectra. 200). In the third stage, the effect of pH on the flocculation of studied metals is investigated. To obtain series of different pH levels ranging from 5.5 to 7.5, appropriate volumes of HNO_3 were added to the aquaria containing mixtures of fresh and sea water. Samples were kept for 24 hours; the processes of collecting flocculants and measuring concentration of the studied heavy metals were the same as the previous stages. Then, by comparing the concentrations of heavy metals in this stage with the results of the first stage, the effect of decreasing pH on the flocculation rates of Cu, Mn, Zn, Pb, and Ni was determined. In order to determine the controlling factors for the flocculation of Cu, Mn, Zn, Pb, and Ni during estuarine mixing, physico-chemical parameters were measured. EC, DO, pH, T, and salinity of samples were measured by using WTW multichannel portable apparatus (model 340i). Eh was measured by ORP meter (Horiba D-22). Then, among the existing clustering techniques (Lance and William 1966; Anderson 1971; Davis 1973), we used the Weighted Pair Group method (Davis, 1973), in order to find the governing factors for the flocculation of studied metals.

RESULTS & DISCUSSION

The concentrations of studied heavy metals in river water, sea water, and in five aquaria with various salinities along with the physico-chemical parameters of water are illustrated in Table 1. It should be pointed out that Table 1 illustrates the results of flocculation process at the laboratory scale, which does not occur in nature. In fact, a portion of dissolved metals flocculated, due to the very first collisions of river water with sea water, and oozes out of the river water. Therefore, there are less available dissolved metals in the later stages and fewer flocculants form. To take into account this fact in our experiment, cumulative summation is used to convert the values in Table 1 to the actual metal contents that occur in nature (Karbassi *et al.,* 2007). The results are shown in Table 2.

According to Table 2, the maximum removal of all studied metals occurred between salinities 0.10 – 0.75 ppt in the first step of experiment. 17.95% of total removal of Cu (23.08%) occurred at salinity 0.75‰ and rest of it in salinities 2.25-3‰, while all 45.45% removal of Pb occurred in salinity of 0.75%. Furthermore, removal of both Ni and Zn are divided in two parts; first, 13.16% of Ni and 16.67% of Zn are removed at salinity 0.75%, then the rest of removal of both Ni and Zn took place in salinities 3 – 3.75‰, by values of 13.16% and 4.54%, respectively. For Mn about half of total removal occurred in salinity 0.75‰, and the rest (31.42%) was removed at salinities 3-3.75‰. Our findings in this study support rapid flocculation in the earlier stages (at a salinity of about- 2‰) of an estuarine mixing process (Duinker and Nolting, 1976; Bewers *et al.,* 1974). It should be pointed out that during mixing process Mn and Zn showed the highest and the lowest flocculation rates, respectively. The final percentages of flocculation of studied metals in Cheshme-Kileh River estuary are as follows: Mn

Table 1. Flocculants of metal content (laboratory scale) along with pH, redox potential (Eh), electrical conductivity (EC), temperature, salinity(S), and dissolved oxygen (DO)

Parameters	Cu(µg/l)	Mn(µg/l)	Ni(µg/l)	Pb(µg/l)	Zn(µg/l)	DO(mg/l)	Eh(mV)	pH	S‰	T	EC(µs/cm)
River water	39	190	76	22	66	9.86	91.6	8.32	0.10	14.7	291
Sea water	-	-	-	-	-	8.84	90.7	8.31	12.3	17.4	20595
Aquarium no.											
1	7	71	10	10	11	8.33	91.2	8.34	0.75	18	1264
2	7	66	10	7	9	7.9	90.8	8.38	1.5	18	2050
3	8	99	8	6	8	7.8	91.1	8.44	2.25	18	3020
4	9	129	16	4	12	7.2	90.7	8.47	3	18	3641
5	9	110	20	4	14	6.9	91.6	8.68	3.75	18	3910
Total	9	129	20	10	14						

Table 2. Flocculants of trace-metal contents (natural scale) along with pH, redox potential (Eh), electrical conductivity (EC), temperature, salinity(S), and dissolved oxygen (DO)

Parameters	Cu(µg/l)	Mn(µg/l)	Ni(µg/l)	Pb(µg/l)	Zn(µg/l)	DO(mg/l)	Eh(mV)	pH	S‰	T	EC(µs/cm)
River water	39	190	76	22	66	9.86	91.6	8.32	0.10	14.7	291
Sea water	-	-	-	-	-	8.84	90.7	8.31	12.3	17.4	20595
Aquarium no.											
1	7(17.95)	71(37.37)*	10(13.16)	10(45.45)	11(16.67)	8.33	91.2	8.34	0.75	18.9	1264
2	0	0	0	0	0	7.9	90.8	8.38	1.5	18.32	2050
3	1 (2.56)	28 (14.73)	0	0	0	7.8	91.1	8.44	2.25	18	3020
4	1 (2.56)	30 (15.79)	6 (7.89)	0	1 (1.51)	7.2	90.7	8.47	3	18	3641
5	0	0	4 (5.26)	0	2 (3.03)	6.9	91.6	8.68	3.75	17.9	3910
Total	9(23.08)	129(68.79)	20(26.32)	10(45.45)	14(21.21)						

* The values within brackets show percentile of the metal flocculation

(68.79%) > Pb (45.45%) > Ni (26.32%) > Cu (23.08%) > Zn (21.21%).

Table 3 shows the results of electro-flocculation of Cu, Mn, Ni, Pb, and Zn during mixing of Cheshme-Kileh River water with Caspian Sea water. As shown in Table 3, removal of Cu during EF process had the same pattern of natural flocculation and the total removal was about 23%. It should be noted that EF had reverse effect on the removal of other studied heavy metals. For instance, only 57.89% of Mn was removed during EF process, which is about 10% less than the natural flocculation. Moreover, removal of Ni, Pb, and Zn also decreased about 4%, 5%, and 6%, respectively. It should be pointed out that maximum removal of these metals occurred at low salinity (First stage). These findings disagree with the other research, which is done in Iran (Shamkhali *et al.*, 2011). Their result showed that the EF had the positive effect on the flocculation of dissolved metals, and as voltage was increased the more flocculants appeared. These variations during the EF process may be due to different factors such as initial metal concentration, pH, duration of electrolysis, conductivity, and metal speciation in the aqueous system (Akbal and Camci, 2008; Biati *et al.*, 2010b; Chen, 2004; Mollah *et al.*, 2001; Shafaei *et al.*, 2011). The general pattern of total flocculation of metals during passing electrical energy (12V) into the water samples is like the following: Mn (57.89%) > Pb (40.9%) > Cu (23.08% > Ni (22.37%) > Zn (15.15%).

Comparing the information on Table 2 with Table 4, it can be concluded that decreasing pH values in the first two stages, 7.5 at salinity 0.75 ppt – and 7 at salinity 1.5 ppt, has positive effect on the flocculation rates of all studied metals. The total increases in flocculation rates of heavy metals in the first two stages are as follows: 41%, 3.7%, 15.8%, 31.82%, and 34.85% for Cu, Mn, Ni, Pb, and Zn, respectively. Also, it should be pointed out that, decreasing pH values in higher salinities ranges, 2.25ppt to 3.75ppt, did not significantly affect the flocculation rates of studied

Table 3. Flocculants of trace-metal contents (natural scale) along with pH, Eh, and salinity (S) during the electro-flocculation process

Parameters	pH	S‰	Eh (mV)	Cu (μg/l)	Mn (μg/l)	Ni (μg/l)	Pb (μg/l)	Zn (μg/l)
River water	8.32	0.10	91.6	39	190	76	22	66
Sea water	8.31	12.3	90.7					
Aquarium no.								
1	8.34	0.75	91.2	6 (15.38)	69 (36.32)	10 (13.16)	9 (40.9)	10 (15.15)
2	8.38	1.5	90.8	0	0	0	0	0
3	8.44	2.25	91.1	1 (2.56)	21 (11.05)	0	0	0
4	8.47	3	90.7	1 (2.56)	20 (10.53)	4 (5.26)	0	0
5	8.68	3.75	91.6	1 (2.56)	0	3 (3.95)	0	0
Total				9 (23.08)	110(57.89)	17 (22.37)	9 (40.9)	10 (15.15)

Eh = redox potential. The values within brackets show percentile of the metal flocculation

Table 4. Flocculation of trace-metal contents (natural scale) by decreasing pH values

parameters	pH	S‰	Cu (μg/l)	Mn (μg/l)	Ni (μg/l)	Pb (μg/l)	Zn (μg/l)
River water	8.32	0.10	39	190	76	22	66
Sea water	8.31	12.3					
Aquarium no.							
1	7.5	0.75	23(58.97)*	77 (40.53)	18 (23.68)	15 (68.18)	34 (51.51)
2	7	1.5	0	1 (0.53)	4 (5.26)	2 (9.09)	0
3	6.58	2.25	0	0	0	0	1 (1.51)
4	6.1	3	1 (2.56)	12 (6.32)	1 (1.32)	0	1 (1.51)
5	5.52	3.75	0	0	2 (2.63)	0	0
Total			24 (61.54)	90 (47.37)	25 (32.89)	17 (77.27)	36 (54.54)

*The values within brackets show percentile of the metal flocculation metals, except for Mn. In fact, flocculation rate of Mn decreased about 24.21%. Moreover, by considering the whole process, the changes in flocculation rates are as follows: +38.46%, -20.53%, +6.6%, +31.8% and +33.33% for Cu, Mn, Ni, Pb, and Zn, respectively. The influence of pH on flocculation of heavy metals may be considered as a competition between H+ ion with the heavy metals for ligands such as OH-, Cl-, CO32-, HCO3-, HS-, sulfates and phosphates (Gundersen and Steinnes, 2003). According to Table 4, it can be concluded that the maximum flocculation of studied metals took place at pH level ranging from 7 to 8.5. Our finding is in agreement with the research that was take place at the University of Maryland (Ayres *et al.,* 1994). The result showed that adjusting the pH in range from 6.8 to 8.6 has effectively precipitated most of the dissolved metals from the water. It should be pointed out that, the removal of studied metals can be increased up to 30% by adjusting the pH value to about 7.5. The removal rates of studied dissolved metals during the natural estuarine flocculation, electro-flocculation and flocculation by decreasing pH values are also illustrated in Fig. 1. It should be pointed out that maximum elemental removal occurs at lower salinity (0.1–1.5‰).

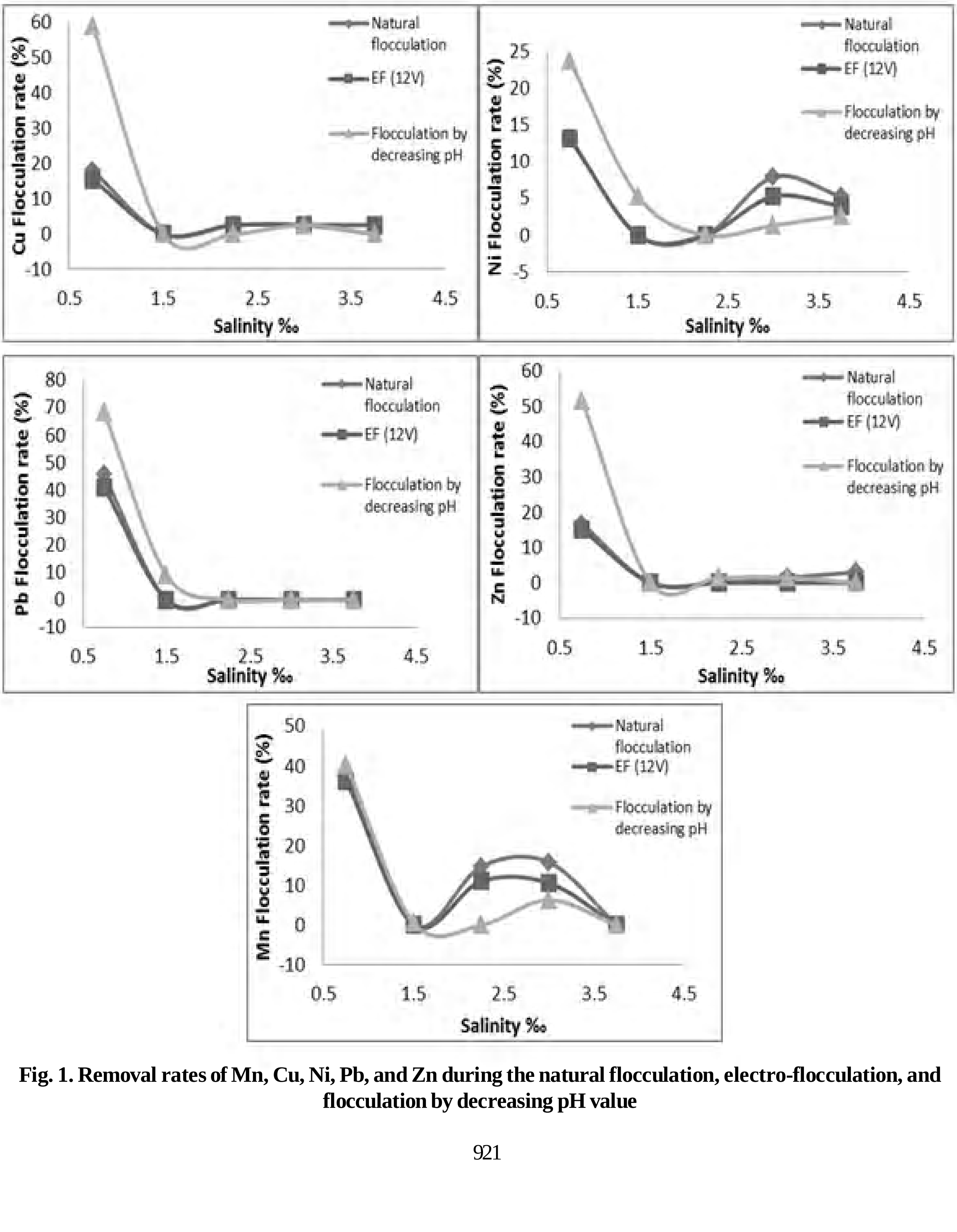

Fig. 1. Removal rates of Mn, Cu, Ni, Pb, and Zn during the natural flocculation, electro-flocculation, and flocculation by decreasing pH value

Regarding the work of other researchers, salinity is not the only governing factor for the flocculation of heavy metals during estuarine mixing (Karbassi *et al.*, 2007; Karbassi *et al.*, 2008a; Karbassi *et al.*, 2008b; Shamkhali *et al.*, 2011). Thus, cluster analysis of dissolved metal concentrations along with salinity and other physico-chemical parameters such as pH, Eh, EC, in Cheshme-kileh River water are conducted during the natural flocculation; the result of above analysis is illustrated in Fig. 2 as a dendrogram. As shown in Fig. 2, salinity and electrical conductivity are the main governing factors for the flocculation of Mn and Cu. This is contrary to other studies that have stated that salinity and EC might have reverse effect on the flocculation process (Boyle *et al.*, 1977; Duinker and Nolting, 1976; Hunter, 1983; Sholkovitz, 1976; Zhiqing *et al.*, 1987; Shamkhali *et al.*, 2011; Fazelzadeh *et al.*, 2011). Furthermore, these results revealed that the flocculation of most of the studied metals are governed by pH with Pearson coefficient of around 0.75. This finding is in agreement with the results of previous studies that are done in Iran (Saeedi *et al.*, 2003; Karbassi *et al.*, 2007; Karbassi *et al.*, 2008a; Karbassi *et al.*, 2008b; Shamkhali *et al.*, 2011; Fazelzadeh *et al.*, 2011). Also, regarding the dendrogram in Fig. 2, DO and Pb have high correlation. Therefore, it can be concluded that DO is a governing factor for the flocculation of Pb during estuarine mixing. According to Fig. 1. Eh plays no important role in flocculation of dissolved metals in comparison with other physico-chemical parameters.

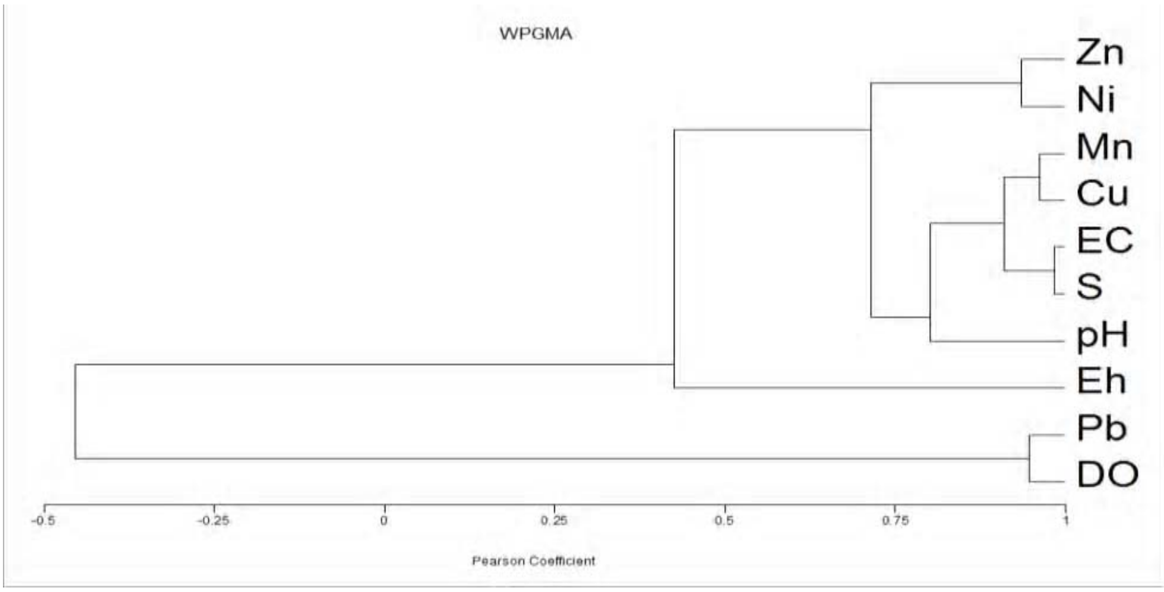

Fig. 2. Dendrogram of cluster analysis among studied parameter in the Cheshme-Kileh River

CONCLUSION

The natural flocculation, electro-flocculation, and flocculation by decreasing pH values of Zn, Pb, Cu, Ni and Mn during estuarine mixing of Cheshme- Kileh River with the Caspian Sea water were investigated. The results indicated that the maximum removal of all studied metals occurred between salinities 0.10 – 0.75‰ in the first step of experiment, and the percentages of metal element removal during the natural estuarine flocculation are: Mn (68.79%) > Pb (45.45%) > Ni (26.32%) > Cu (23.08%) > Zn (21.21%). Salinity and electrical conductivity are the main governing factors for the flocculation of Mn and Cu; results revealed that Zn, Cu, Mn, and Ni are governed by pH with correlation around 0.75. Moreover, DO is a governing factor for the flocculation of Pb during estuarine mixing. Eh plays no important role in flocculation of any studied metals. EF process had reverse effect on the flocculation of heavy metals; The general pattern of total flocculation of metals during passing electrical energy (12V) into the water samples are as follows: Mn (57.89%) > Pb (40.9%) > Cu (23.08%(> Ni (22.37%) > Zn (15.15%). Decreasing the pH in our aquaria increased the flocculation rates of heavy metals (except for Mn). The removal rates of heavy metals by decreasing pH level in the aquaria are as follows: Pb (77.27%) > Cu (61.54%) > Zn (54.54%) > Mn (47.37%) > Ni (32.89%). Results revealed that adjusting the pH value to about 7.5 lead to maximum flocculation of Ni, Cu, Pb, and Zn. Finally, it should be noted that the river's average annual discharge is about 12.75 m^3/s. Therefore, during the estuarine mixing of the Cheshme-Kileh River water with the Caspian Sea water, the amount of metal flocculation is about 51.6, 7.8, 5.5, 3.9, and 3.6 ton/year for Mn, Ni, Zn, Pb, and Cu, respectively. The flocculation rates reveal that the overall dissolved metal pollution loads may be reduced from about 20% to about more than 65% during estuarine mixing of Cheshme-Kileh River with the Caspian Sea water.

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