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An Investigation on the Role of Flocculation Processes in Geo-Chemical and Biological Cycle of Estuary (Case Study: Gorganrood River)

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ABSTRACT: The present investigation provides a thorough study of eliminating soluble and colloidal elements of copper, iron, magnesium and zinc during estuarine mixing of Gorganrood River water with Caspian Sea water in Iran. The processes of flocculation were carried out in 10 aquariums in order to furnish the salinity in an interval of 0.3 - 4.4 ppt. The obtained result is indicative of non- conservative behavior of studied metals. Higher flocculation resulted in a lower salinity and vice-versa. The obtained results indicated that most metal were eliminated during the initial mixing of fresh water with sea water at 0.6 - 1.0 ppt salinity interval. The trend of flocculation rates of elements in the river were obtained as follows: Fe (97.33%)> Mn (91.66%) >Zn (72.72%) > Cu (52.63%).The annual average elimination of soluble elements of iron(Fe), manganese(Mn), zinc(Zn) and copper(Cu) from Gorganrood river to Caspian Sea decreases from 1040.68, 59.1498, 302.26, 263.64 tons per year to 27.75, 124.88, 83.255, 124.88 tons per year, respectively. According to the cluster analysis, parameters such as salinity, temperature, electrical conductivity, Eh and suspended solid materials do not have any impact on flocculation of elements. The only parameter that influences the flocculation of elements is the pH. This research illustrates that estuarine processes are effective mechanisms in self- purification of heavy metals from water resources. Metal speciation studies that are carried out by Eh-pH software show that studied metals are present as solid (in case of Cu), free ions (Fe and Mn) and finally hydroxides (Zn).

Key words: Caspian sea, Estuarine, Flocculation, Gorgaanrood river, Heavy elements

INTRODUCTION

"An estuary is a semi- enclosed coastal body of water which has a free connection with the open sea and within which sea water is measurably diluted with fresh water derived from land drainage"(Pritchard, 1967). Estuaries had drawn the attention of scientists due to having important ecological and environmental impacts. The estuary has a special ecological environment that provides a suitable habitat for phytoplanktons, zooplanktons, benthos, native and migrant fishes. On the other hand, the estuary is a transporting corridor for exchanging materials (e.g. heavy metals) from rivers or streams to sea. Many significant physical, chemical, biochemical, geochemical and bio-geochemical reactions also occur at this region, which has an impact on aquatic ecosystem. Flocculation is a crucial physio-chemical process that occurs in estuaries. Flocculation occur due to the mixture of river's fresh water and sea's saline water especially in the upper part of the estuary where lower salinity regimes are found (Gerringa *et al.*, 2001; Karbassi *et al.*, 2008; Biati *et al.*, 2010). Dissolved metals come into the particulate phase due to flocculation processes during estuarine mixing(Eckert and Sholkovitz, 1976; Sholkovitz, *et al.*,1977 and Boyle, *et al.*, 1977). The variability information of micro-elements in estuarine water would help one to understand the behavior of geochemical barrier and estuarine ecology(Anikiev and Goryachev, 1991; Achterberg *et al.*, 2003;Savchenko, 2009). By reducing the concentration of dissolved pollutant metals and transforming them into micro-nutrients, the flocculation process provides a valuable nutrient resource for aquatic organisms. Hence, flocculation of dissolved metals can significantly affect the chemical mass balance between rivers and seas or lakes as well as the nutrient and organic matter in coastal zones (Wollast and Peters, 1978; Meybeck, 1982, Zobrist and Stumm, 1981). Not much information

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is available on recognition of dissolved metals flocculation processes during estuarine mixing of river waters with brackish lake waters such as the Caspian Sea water (Karbassi and Nadjafpour, 1996 and Saeedi, *et al.*, 2003). Due to growing concern over the diverse effects of heavy metals and their compounds on aquatic ecosystems, studies have been conducted on concentration of elements controlling mechanisms in some rivers flowing into Caspian Sea and Persian Gulf in the North and South of Iran (Karbassi and Nadjafpour, 1996; Saeedi *et al.*, 2003; Karbassi *et al.*, 2007, Karbassi *et al.*, 2008). The present study, for the first time, investigates the effect of flocculation on self-treatment of metal pollutants in the estuary of Gorganrood river, which is one of the important rivers in Northern of Iran that flows into Caspian Sea. It is worth noting that other researchers mainly focused on salinity, pH, humic acids, colloidal stability and surface properties (Zhiqing, *et al.*, 1987; Hunter, 1983, Featherstone and O'Grady, 1997; Shankar and Karbassi, 1992); however, this researcher focuses on flocculation of Cu, Fe, Mn, and Zn during the esturine mixing in relation to important sea water parameters such as pH, salinity, Electric conductivity (Ec), temperature, total-dissolved-solids(TDS), and voltage(Eh).

MATERIALS & METHODS

The main branch of Gorgaanrood River, shown in fig. 1. is 350 Km long expanded from East to West in Northern Iran and its average annual discharge is 44 m^3/s. Due to its significant status, Goorganrood river is protected by the Environmental Protection Organization of Iran for about 12 Km from its estuary towards East. Freshwater sample was collected from the surface of the Gorganrood river, where no saline water can penetrate the freshwater, 16Km East of the estuary at latitude of 37 N 00' 8.7" and longitude of 54E 15' 6.4" .The sample was collected in a 20-L clean polyethylene bucket and was taken to the lab. Similarly, Caspian sea water was collected in 20-L polyethylene bucket, 16 Km away from the shore with latitude of 37N 02' 26.8" and longitude of 53E 52' 33.6". The places were river water and sea water sample were collected are shown in fig. 1. The two samples of fresh and saline water were kept stationary for 24 hours to ensure precipitation of undesired impurities. The samples were then transferred to two new containers. To prevent the samples from being contaminated, the new containers as well as all the test equipments were cleaned thoroughly with 5cc concentrated nitric acid (HNO_3). The two samples were then separately filtered through 0.22ìm Millipore filters, changing the dirty filters occasionally. Following the filtration, the two samples were mixed with predefined proportion of fresh and saline water and transferred to 10 different acid-clean 25cm×30cm×35cm aquariums. The mixture proportionality of the saline water and freshwater are shown in Table 1. The mixture of the two waters are stirred occasionally during the first hour while the flocculates start forming. The aquariums are left for 24 hours to ensure complete flocculation. 50cc of the liquids from each aquarium are taken to measure the parameters such as temperature, salinity, acidity, Eh, Ec and TDS of flocculants. Meanwhile, a sample of 1000cc filtered freshwater was concentrated to bellow 50cc over a temperature of 50°C. It is then diluted to 50cc with hydrochloric acid (HCl). This concentration of heavy elements in the sample serves as the control to be compared with the mixed waters in the aquariums. After 24 hrs, the aquariums are stirred once more and filtered with 0.22µm Millipore filters to collect the flocculants on the filter. These filters containing the flocculants are transported into small beakers and 5cc of extra pure nitric acid is added. After 6 hours, when the flocculants are solved, the liquids in beakers are transferred into 25cc Erlenmeyer Bulb and a mixture of DI-water (482.5mL) and 1N HCL (17.5mL) are added. The samples are now ready for analysis with atomic absorb system (AAS).

Table 1. Predefined mixture proportionality of saline and fresh waters in 10 different aquariums

No. of aquarium	Vol. of river water(L)	Vol. of sea water(L)
1	0.50	0.00
2	0.50	0.250
3	0.50	0.375
4	0.50	0.50
5	0.50	1.00
6	0.50	1.50
7	0.50	2.50
8	0.50	3.50
9	0.50	4.00
10	0.50	5.50

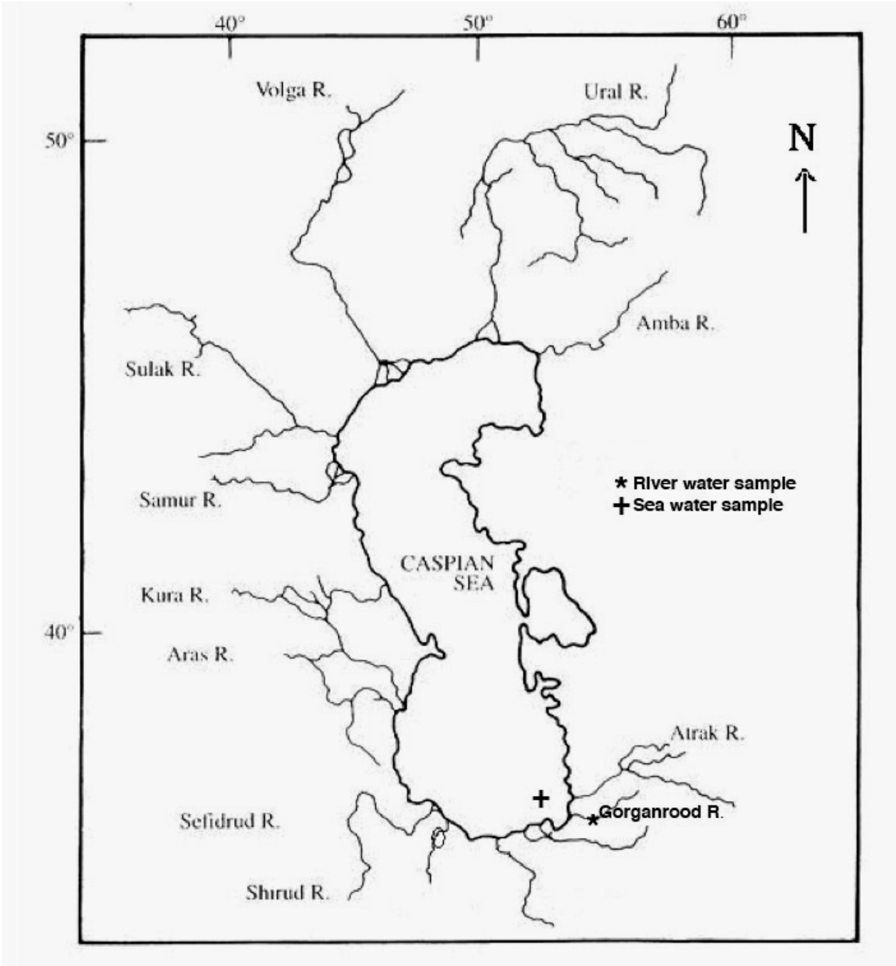

Fig. 1. Locations of water samples from Gorganrood River and Caspian Sea

RESULTS & DISCUSSION

As it was discussed in previous section, the sample of freshwater was taken from Goorganrood river and the saline water was taken from Caspian Sea The physico-chemical parameters at the location where the samples were taken are summarized bellow in Table 2. Following the mixing of freshwater and saline water in the lab, as mentioned in previous section, the concentration of heavy metals and physico-chemical parameters were measured and recorded as shown in table 3.Note that the salinity of samples from aquariums 1 through 10 varies from 0.3ppt (Gorganrood river) to 4.4ppt.

Furthermore, Table 4 indicates the concentration of heavy metals in flocculants as the occur in the nature. The concentration values in table 4 are obtained by subtracting the concentration values from its previous values respecting their corresponding salinity. According to Table 3 and 4, the maximum elimination of heavy metals occurred between a salinity of 0.6 ppt to 1.0 ppt (i.e. in aquarium 2 and 3). The total 52.63% elimination of Cu element was during 0.6ppt-1ppt. This

Table 2. Fresh and saline water important physico-chemical parameters at the location of sampling

Location of sample taken	S (ppt)	Temp (°C)	pH	Ec (µS)	TDS (mg/L)	Eh (mV)
16km before Gorgaanrood river estuary	0.14	15.7	8.31	10.60	700	-112.3
16km toward the sea	11.7	19.6	8.40	19.6	1370	-110.7

percentage corresponds to 100 µg/L of Cu removal. From a total of 97.33% Iron (Fe) removal, 94.66% were removed at salinity of 0.6 ppt (i.e. aquarium no. 2) and the rest of 2.6% was during the salinity of 1.4 ppt (i.e. aquarium no. 4). The Manganese element was entirely flocculated (91.66%) during the salinity of 0.6 ppt (i.e. aquarium 2). Furthermore, the total removal of zinc (72.72%) occurred during a salinity of 0.6ppt-1ppt (i.e. 45.45% in aquarium 2 and 27.3% in aquarium 3). Note that all the heavy elements were mostly flocculated during the first steps of mixing during a salinity interval of 0.6 ppt -1.4 ppt. This indicates that as the salinity is increased the flocculation decreases. This agrees with previous studies that reported a high rate of flocculation during the first steps of mixing with low salinity (Burton, 1976, Duinker *et al.*, 1980). The Fe and Cu elements had the most and least flocculation during the mixing process, respectively. The final percentages of flocculation of metals in Gorgaanrood river estuary are as following: Fe (97.33%) > Mn (91.66%) > Zn (72.72%) > Cu (52.63%).

To observe the hierarchical effect of each physico-chemical parameter on flocculation, cluster analysis was performed. Among all existing cluster analyses (Lance and William, 1966; Anderson, 1971; Davis,1973), the Weighted Pair Group (WPG) technique (Davis, 1973) was used. Fig. 2 illustrates the *dendrogram* plot of this cluster analysis. As shown in the figure, the only parameter that effectively plays a role in flocculation process is the pH, for its correlation coefficient being greater than 0.45. On the other hand, temperature and voltage parameters do not have a meaningful effect on the flocculation process. Note that electric conductivity, t*otal-dissolved-solids* and salinity entirely correlated with each other. This is caused by the fact that Ec and TDS are controlled by the salinity of the water. However, due to their negative correlations with the four studied elements, these parameters impede the process of flocculation. Other studies have shown that besides pH, the salinity of water also plays a role in flocculation process (Scholkovitz, 1976; Duinker *et al.*, 1983; Hunter, 1983; Zhiqing *et al.*, 1987; Day *et al.*, 1989; Karbassi & Nadjafpour, 1996) but in this study salinity is an impedance parameter.

To observe the state of the metal species, the Eh-pH diagram for each aquarium was plotted. Fig. 3 illustrates Eh-pH diagrams for Cu, Fe, Mn and Zn species. The state of these species are in good agreement with results in Atlas of Eh-pH diagrams with corresponding Eh and pH (Takeno, 2005). According to the results obtained, the Cu metal appeared as solid Cu(s), Fe as Fe^{2+} ion, Mn as Mn^{2+} ion and Zn as Zn(OH) flocculants in the water in all the aquariums. Note that the *star* on the figure indicates the state of each flocculant in the aquarium.

Table 3. Concentration of heavy elements in flocculants with important physico-chemical parameters in Gorgaanrood River (with no flocculation)

No. of Aquarium	Cu (µg/L)	Fe (µg/L)	Mn (µg/L)	Zn (µg/L)	S (ppt)	Temp (°C)	pH	Ec (µS)	TDS (mg/L)	Eh (mV)
1 (Gorgaandrood River)	190	750	1080	220	0.3	21.8	8.31	10.66	746	-66
2	90	710	990	100	0.6	22.2	8.32	11.20	768	-71
3	100	690	960	160	1.0	22.6	8.31	11.70	819	-70
4	100	730	960	70	1.4	21.8	8.31	12.40	868	-71
5	90	680	890	60	2.2	21.8	8.32	13.60	956	-76
6	70	710	940	40	3.1	22.4	8.31	15.10	1057	-75
7	68	660	890	60	3.6	21.9	8.30	16.00	1120	-73
8	70	700	900	80	4.0	21.8	8.30	16.50	1155	-72
9	71	730	940	100	4.2	22.0	8.30	17.00	1190	-69
10	70	660	900	90	4.4	22.8	8.28	17.20	1206	-72

Table 4. Actual concentration of heavy elements in flocculants with important physico-chemical parameters in Gorgaanrood River (with flocculation)

No. of Aquarium	Cu (µg/L)	Fe (µg/L)	Mn (µg/L)	Zn (µg/L)	S (ppt)	Temp (°C)	pH	Ec (µS)	TDS (mg/L)	Eh(mV)
1 (Gorgaandrood River)	190	750	1080	220	0.3	21.8	8.31	10.66	746	-66
2	90(47.36)*	710 (94.66)	990 (91.66)	100 (45.45)	0.6	22.2	8.32	11.20	768	-71
3	10 (5.26)	0(0)	0(0)	60 (27.3)	1.0	22.6	8.31	11.70	819	-70
4	0(0)	20(2.6)	0(0)	0(0)	1.4	21.8	8.31	12.40	868	-71
5	0	0	0	0	2.2	21.8	8.32	13.60	956	-76
6	0	0	0	0	3.1	22.4	8.31	15.10	1057	-75
7	0	0	0	0	3.6	21.9	8.30	16.00	1120	-73
8	0	0	0	0	4.0	21.8	8.30	16.50	1155	-72
9	0	0	0	0	4.2	22.0	8.30	17.00	1190	-69
10	0	0	0	0	4.4	22.8	8.28	17.20	1206	-72
Total	100 (52.63)	730 (97.33)	990 (91.66)	160 (72.72)						

* The amounts in parentheses are indicated as percentage of removal

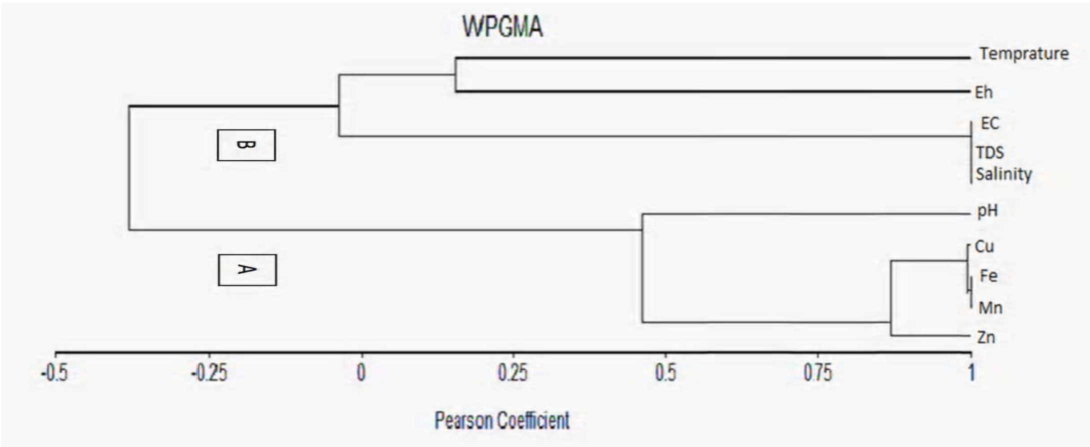

Fig. 2. Dendrogram of cluster analysis for physico-chemical parameters and concentration of heavy metal elements during flocculation in Gorgaanrood River estuary

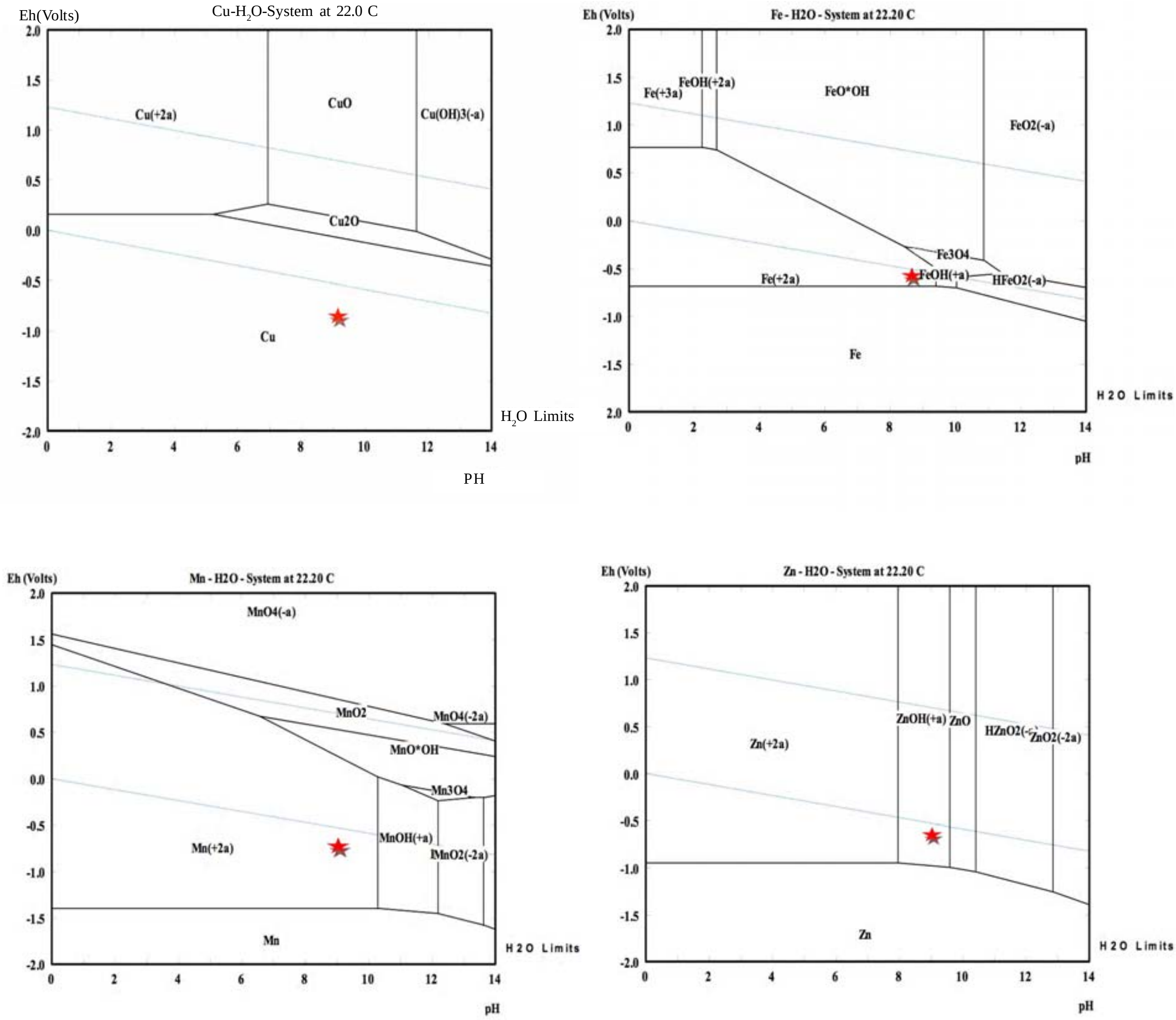

Fig. 3. Eh-pH diagrams of and the state of (a) Cu, (b) Fe, (c) Mn and (d) Zn flocculants

CONCLUSION

Flocculation process on dissolved heavy metals Cu, Zn, Mn and Zn was investigated during the estuarine mixing of Gorgaanrood River flowing into Caspian Sea in Northern Iran. The results indicated that without flocculation, the amount of dissolved elements flowing into the Caspian Sea are: Cu (263.64 ton/yr), Fe (1040.68 ton/yr), Mn (1498.59 ton/yr) and Zn(305.268 ton/yr). However, after the flocculation process, the amount of these dissolved elements are dramatically reduced to Cu (124.882 ton/yr), Fe (27.751 ton/yr), Mn (124.882 ton/yr) and Zn(83.255 ton/yr). The corresponding percentages of metal element removal during the flocculation are: Fe (97.33%) > Mn (91.66%) > Zn (72.72%) >Cu(52.63%). It was shown that the main factor in flocculation process was the pH and other factors such as salinity, temperature, voltage, electric conductivity and total-dissolved-solids did not positively contribute in this process. During the flocculation process copper appeared as solids, iron and manganese as ions, and zinc as zinc-hydroxide according to Eh-pH plots. Further investigation is required to observe the role of other constituents of seawater in flocculation of trace metals.

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