

## ORIGINAL RESEARCH PAPER

# Role of estuarine natural flocculation process in removal of Cu, Mn, Ni, Pb and Zn

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**ABSTRACT:** The flocculation of dissolved heavy metals is a process which has an important effect on decreasing the concentration of the colloidal elements during estuarine mixing of river water and sea or ocean water. During this important process, a large amount of colloidal elements change into particles in the form of flock and the dissolved loads decline. This study is performed to evaluate the mechanism of self-purification of heavy metals in Sardabroud's estuary. For this purpose, the effect of salinity (varying from 1 to 8.5‰) on the removal efficiency of colloidal metals (copper, zinc, lead, nickel and magnesium) by flocculation process during mixing of Sardabroud River water and the Caspian Sea water was explored. The flocculation rate of Ni (25%) > Zn (18.59%) > Cu (16.67%) > Mn(5.83%) > Pb(4.86%) indicates that lead and manganese have relatively conservative behavior but nickel, zinc and copper have non-conservative behavior during Sardabroud River's estuarine mixing. The highest removal efficiencies were obtained between salinities of 1 to 2.5‰. Due to flocculation process, annual discharge of dissolved zinc, copper, lead, manganese and nickel release into the Caspian Sea via Sardabroud River would reduce from 44.30 to 36.06 ton/yr, 3.41 to 2.84 ton/yr, 10.22 to 9.7 ton/yr, 8.52 to 7.8 ton/yr and 3.41 to 2.56 ton/yr, respectively. Statistical analysis shows that the flocculation rate of Nickel is highly controlled by redox potential and dissolved oxygen. Moreover, it is found that total dissolved solid, salinity, electrical conductivity and potential of hydrogen do not have a significant influence in flocculation of studied metals.

**KEYWORDS:** *Caspian Sea; Efficiency removal; Estuarine mixing; Flocculation; Heavy metals; Sardabroud River*

## INTRODUCTION

Estuaries are one of the coastal points where a free-flowing river meets the ocean or sea. Estuaries are very important aquatic systems that act as a connection between fresh water and saline water (Levin *et al.*, 2001; Currie and Small, 2005; Dobson and Frid, 2009). Heavy metals which carried by rivers are discharged into the sea through estuaries (Brayan *et al.*, 1971; Meybeck, 1988; Chen *et al.*, 2004; Karbassi and Heidari, 2015). Therefore, these environments

are in risk of water pollution specially due to heavy elements which have long lasting detrimental effects on environment and are dangerous for living organisms (Adjei-Boateng *et al.*, 2010; Ratheesh Kumar *et al.*, 2010; Sundararajan and Natesan, 2010; Bainbridge *et al.*, 2012; Brodie *et al.*, 2012; Fazelzadeh *et al.*, 2012; Guinder *et al.*, 2012; Serbaji *et al.*, 2012; Pillay and Pillay, 2013; Janadeleh *et al.*, 2016). Some heavy metals have various harmful effects on organisms living in water such as fish species, their population and long life cycle. Use of polluted water and fishes living in contaminated water may also have serious consequences for human health. Many significant

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reactions, such as adsorption, desorption and flocculation also occurs in the current region (Li *et al.*, 1984; Edmond *et al.*, 1985; Renault *et al.*, 2009).

When the flocculation process occurs in an estuary, a considerable amount of dissolved elements are flocculated, leave the soluble phase and the dissolved loads decrease (Eckert and Sholkovitz, 1976; Boyle *et al.*, 1977; Dobias 1993; Bratby 2006). Hence, estuarine processes can significantly affect chemical composition of the saline water (Troup and Bricker, 1975). The flocculation process provides a valuable nutrient resource for aquatic organisms by transforming dissolved pollutant metals into micro-nutrients (Bainbridge *et al.*, 2012). To achieve optimum removal efficiency and identify effective parameters in flocculation process, many studies have been performed widely. Many investigation all around the world have focused on various variables such as colloidal stability, salinity, pH (potential of hydrogen), (Charerntanyarak, 1999; Guibal and Russy, 2007), electrical conductivity (EC), Eh (redox potential) and dissolved oxygen (DO) (Eckert and Sholkovitz, 1976; Fox and Wofsy, 1983; Hunter, 1983; Featherstone and O'Grady, 1997; Matagi *et al.*, 1998; Saeedi *et al.*, 2003; Abdel-Ghani *et al.*, 2016). However, it is believed that due to the hazards of heavy metals and the ecological importance of estuary, further investigations are necessary. In the present work, a laboratory experiment on specimens taking from the Sardabroud River and the southern coasts of the Caspian Sea was conducted. The Caspian Sea is the largest lake in the world which is located between the east of the Caucasus Mountains of southwestern Russia and northern Iran. This landlocked sea has a surface area of about 371000 km<sup>2</sup> and a volume of 78,200 km<sup>3</sup>. Its salinity is approximately 4‰ in the northern parts and about 13‰ in the southern parts (Chenar *et al.*, 2013). The Caspian Sea has a mean depth of about 200 m and its depth increases from north to south (about 5 m in the north and 1020 m in the south). The temperature of water in this lake changes from 13°C at the surface to about 55 °C at the deep parts. Over 130 rivers flow into the Caspian among which the Volga is the largest river in Europe in terms of length, discharge, and watershed (Pourkazemi, 2006; Kroonenberg, *et al.*, 1997). The next large rivers are Ural River and Kura River which flow into the sea from the north and the west, respectively. These rivers convey a substantial

amount of chemical and biological pollutants to the Caspian Sea and have a negative impact on the sea's water quality (De Mora, *et al.*, 2004).

This study aims to investigate the removal of Cu, Mn, Zn, Ni, and Pb during mixing of Sardabroud River as well as Caspian Sea water considering physicochemical variables, such as pH, salinity, EC, Eh, DO and TDS (total dissolved solid) due to flocculation. The study has been carried out in the Caspian Sea region of Iran in 2016.

## MATERIALS AND METHODS

Sardabroud River is one of the approximately long rivers in Mazandaran province (North of Iran) which is important due to drinking, agricultural and aquaculture purposes. In the current region, the important sources of pollution are mostly agricultural activities. Sardabroud River lies between longitude of 51°8' and 51°23' and latitude of 36°29' and 36°41'. The mean annual discharge of Sardabroud is 4.5m<sup>3</sup>/s and its length is approximately 100 km. River water and lake water samples were taken from the Sardabroud River (salinity= 0.07‰) and the Caspian Sea (salinity=11.5‰) on 13 April 2016. Sampling of saline water was from a place far enough from the estuary to ensure that the sea water and fresh water were not blended. After transferring to the laboratory and before using for the subsequent experiments, the specimens kept steady for 24 h in order to deposit of suspended particles. Then, they were filtered using 0.45 screen filters (type CA) and a vacuum pump. To analyze the concentration of considered heavy metals in Sardabroud River by ICP, 1000 cc of filtered fresh water with a pH of about 2 was prepared (the pH was adjusted by adding concentrated HNO<sub>3</sub> solution). The locations of Sardabroud River, Caspian Sea, freshwater and seawater specimens are shown in Fig. 1.

In the laboratory, appropriate volumes of lake water and fresh water were mixed together at room temperature in six proportions yielding salinities of 1–8.5‰. The volume of the freshwater was constant in all samples (500 cc), (Table 1). Blended water was conveyed to the aquariums which were constructed from plexiglas and their volume is about 2 L as shown schematically in Fig. 2.

These samples were stored for 24 h and stirred slowly throughout the first h. For each sample, a 2.5 centimeter diameter screen filters (type CA, Pore

size 0.45  $\mu\text{m}$ ) was used to collect the flocculants of the samples. Then, the membrane filters were transferred into beakers and digested by adding 5 mL concentrated nitric acid in each beaker. The concentrations of considered elements (zinc, copper, nickel, manganese and lead) were measured by ICP-OES (Varian, Vista MPX model). Three steps of experiment including sampling, conducting the experiment and analysis of the samples are shown in Fig. 3. Methods and apparatus used in this experimental work are presented in Table 2.

Obtained experimental data were analyzed using cluster analysis to illustrate correlation coefficient between physicochemical parameters and the flocculation process of considered metals using the Weighted pair group (WPG) method which is one

of the existing clustering techniques (Karbassi *et al.*, 2010; Karbassi *et al.*, 2013). Also, for cluster analysis, the multivariate statistical package (MVSP) was used.

**RESULTS AND DISCUSSION**

As it was discussed before, the sample of fresh water was taken from Sardabroud River and the saline water was taken from Caspian Sea. The physicochemical parameters at the location, where the samples were taken, are summarized below in Table 3.

Percentage removal and concentrations of the investigated heavy metals (Cu, Mn, Ni, Pb, and Zn) are presented in Table 4. It can be mentioned that lowest and highest removal efficiency at various salinities

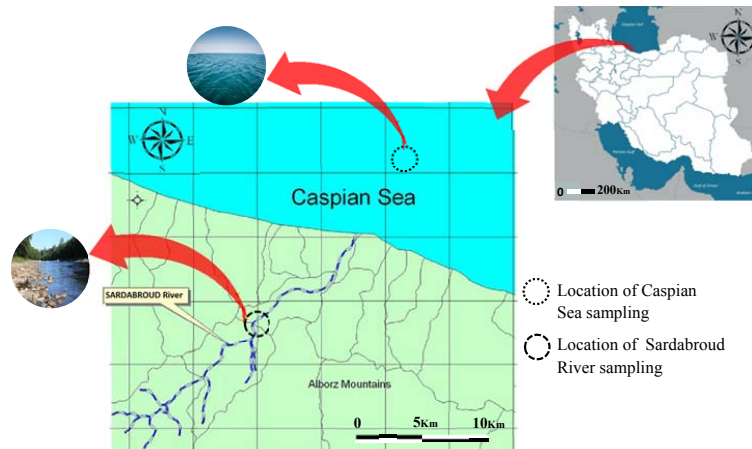


Fig. 1: Location of Sardabroud River and Caspian Sea

Table 1: Mixture proportionality of saline and fresh water in 6 aquariums

Aquarium	Volume of freshwater (L)	Volume of seawater (L)	Volume of Aquarium (L)	Salinity (‰)
1	0.5	0.044	0.544	1
2	0.5	0.135	0.635	2.5
3	0.5	0.262	0.762	4
4	0.5	0.453	0.953	5.5
5	0.5	0.770	1.270	7
6	0.5	1.405	1.905	8.5

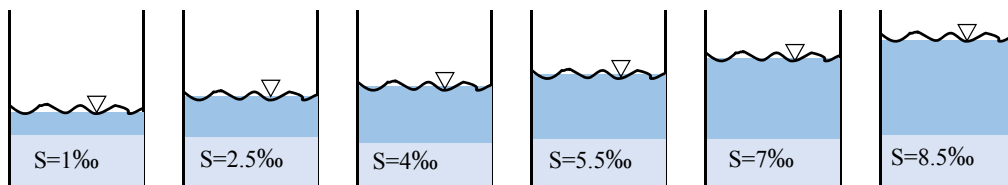


Fig. 2: A diagram showing the mixture of freshwater and saline water

Table 2: Summary of methods and apparatus for determining various parameters

Parameters	Methods/apparatus of measurement
pH/Eh	Eh/ pH meter (metrohm 744)
EC	Bante instruments
Do	Do meter (Inolab WTW)
Salinity	Bante instruments
TDS	Bante instruments
Mn, Cu, Pb, Ni, Zn	ICP-OES (Varian Vista MPX model)

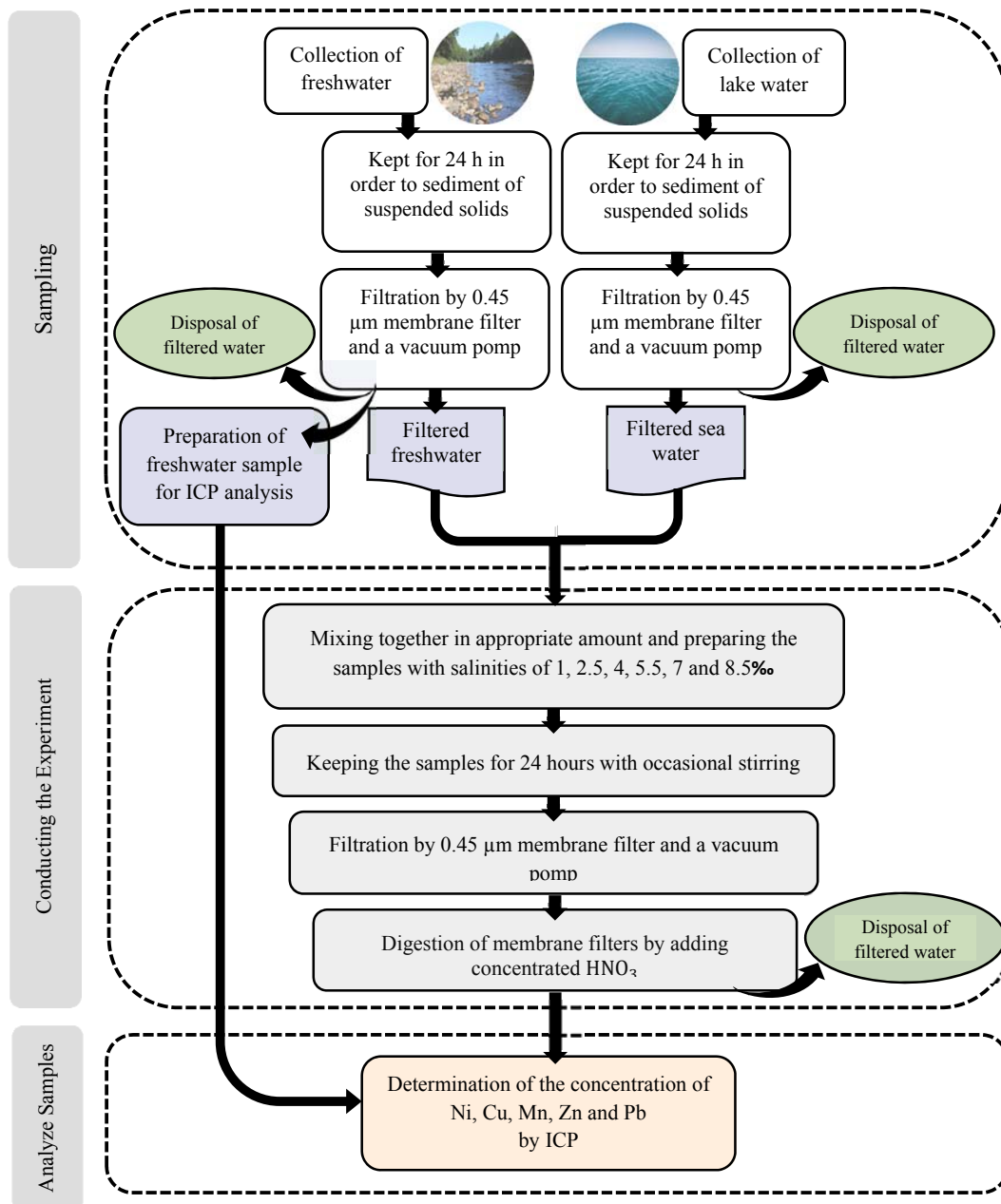


Fig. 3: A flow chart describing the experimental methodology

Table 3: Fresh and saline water important physicochemical parameters at the location of sampling

	S(‰)	pH	TDS (µg/L)	EC (µs/cm)	DO (mg/L)	Eh (mV)
Fresh water	0.07	8	152	305	8	175
Saline water	11.5	8.48	9260	18480	9.71	140

Table 4: Laboratory removal efficiency of metals during mixing of Sardabroud River water with Caspian Sea water

Sample	Cu (µg/L)	Mn (µg/L)	Ni (µg/L)	Pb (µg/L)	Zn (µg/L)	S (%)	pH	DO (mg/L)	EC (µs/cm)	TDS (µg/L)	Eh (mV)
River Water	24	60	24	72	312	0.07	8	8	305	152	175
1	1.5 (6.25)*	3.5 (5.83)	2 (8.33)	3.5 (4.86)	19 (6.09)	1	8.4	7.9	2020	1014	138
2	3 (12.5)	2 (3.33)	6 (25)	2 (2.78)	58 (18.59)	2.5	8.32	8	4560	2280	143
3	3.6 (15)	1.2 (2)	3.6 (15)	1.2 (1.67)	42.6 (13.65)	4	8.37	7.5	7310	3650	142
4	1.5 (6.25)	1 (1.67)	1.5 (6.25)	1 (1.39)	28.5 (9.13)	5.5	8.2	7.5	9760	4880	140
5	2 (8.33)	1 (1.67)	1.5 (6.25)	1 (1.39)	29.5 (9.46)	7	8.45	6.8	12260	6130	137
6	4 (16.67)	2 (3.33)	2 (8.33)	2 (2.78)	56 (17.95)	8.5	8.48	6.4	14690	7340	135

\*Values within parenthesis show removal efficiency of heavy metals.

Table 5: Natural removal efficiency of metals during mixing of Sardabroud River water with Caspian Sea water

Sample	Cu (µg/L)	Mn (µg/L)	Ni (µg/L)	Pb (µg/L)	Zn (µg/L)	S (%)
River water	24	60	24	72	312	0.07
1	1.5 (6.25)*	3.5 (5.83)	2 (8.33)	3.5 (4.86)	19 (6.09)	1
2	1.5 (6.25)	0 (0)	4 (16.67)	0 (0)	39 (12.5)	2.5
3	0.6 (2.5)	0 (0)	0 (0)	0 (0)	0 (0)	4
4	0 (0)	0 (0)	0 (0)	0 (0)	0 (0)	5.5
5	0 (0)	0 (0)	0 (0)	0 (0)	0 (0)	7
6	0.4 (1.67)	0 (0)	0 (0)	0 (0)	0 (0)	8.5
Total	4 (16.67)	3.5 (5.83)	6 (25)	3.5 (4.86)	58 (18.59)	-

\*Values within parenthesis show removal efficiency of heavy metals.

belongs to Pb and Ni, respectively. The maximum removal of Ni and Zn occurs at the second aquarium (salinity=2.5‰). However, the maximum removal of lead and Manganese was achieved at the first aquarium (between the salinities of 0.07 and 1‰). It is also interesting to mention that the flocculation of all considered elements declines at salinity of 5.5‰ and increase at salinity of 8.5‰. However, Table 4 does not illustrate the actual conditions throughout the mixture of fresh water and saline water. In fact,

in every stage, when the flocculation process occurs, some part of the colloidal metals are removed from the fresh water and the amount of these metals in fresh water decreases (Saeedi *et al.*, 2003; Biati and Karbassi, 2012). Thus, in establishing the natural position of estuarial mixture, the flocculates formed in each stage should be deducted from that of the prior stage (Table 5). The data presented in Table 5 is discussed as natural conditions that occur in an estuary.

According to data shown in Table 5, Mn and Pb have the lowest removal efficiency and their flocculation rate is not greater than 4.86% and 5.83% at different salinities, respectively. Thus, Pb and Mn are demonstrating conservative behavior, although other metals including Ni, Cu and Zn are non-conservative. The conservative behaviors of Pb and Mn are in contrast with the nearby estuaries (Biati and Karbassi, 2012). The removal efficiency

of considered elements in Sardabroud River is in Eq. 1.

$$\text{Ni}(25\%) > \text{Zn}(18.59\%) > \text{Cu}(16.67\%) > \text{Mn}(5.83\%) > \text{Pb}(4.86\%) \quad (1)$$

The optimum removal efficiency mostly occurs between the salinities of 1 and 2.5‰ (primary mixing steps) which acknowledges the results of

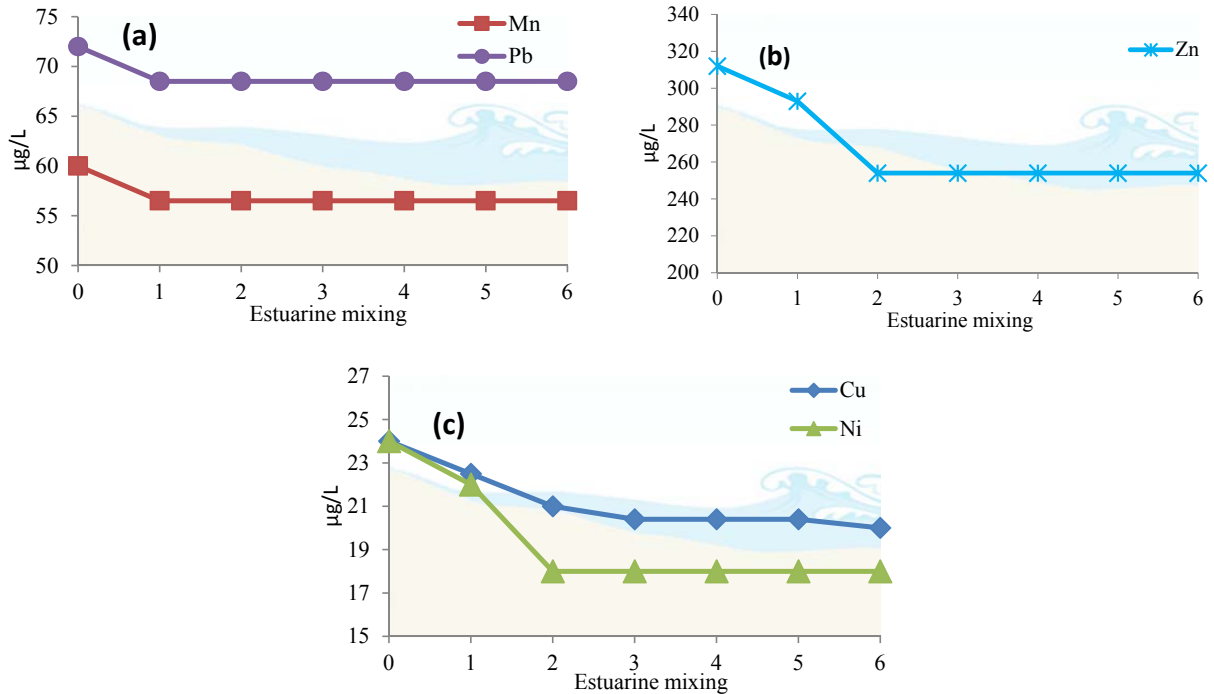


Fig. 4: Reduction trend of concentration of Pb and Mn (a), Zn (b), Cu and Ni (c) due to flocculation process in Sardabroud's estuary

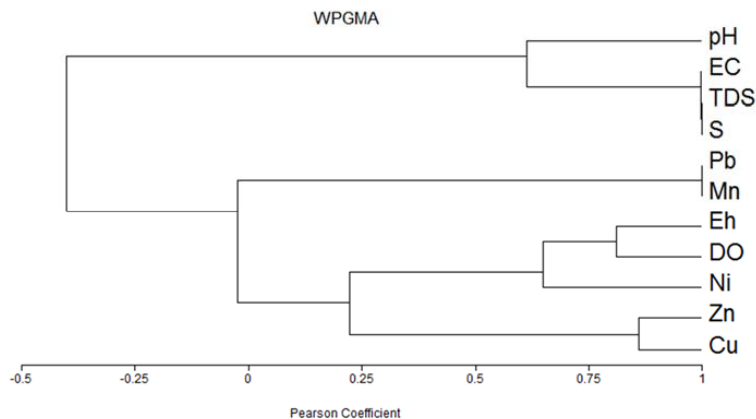


Fig. 5: Dendrogram of cluster analysis with MVSP software

Table 6: Load of dissolved metals released into the Caspian Sea before and after flocculation process

Element	Initial concentration in river ( $\mu\text{g/L}$ )	Mean annual discharge before flocculation (ton/yr)	Pollution loads released into the Caspian Sea after flocculation (ton/yr)
Cu	24	3.41	2.84
Zn	312	44.3	36.06
Pb	72	10.22	9.7
Ni	24	3.41	2.56
Mn	60	8.52	7.8

other investigations (Bewers *et al.*, 1974; Duinker and Nolting, 1976). Reduction trend of concentration of heavy metals during estuarine mixing are shown in Fig. 4.

According to dendrogram of cluster analysis (Fig. 5), DO and Eh are grouped with Nickel at relatively high similarity coefficients and it indicates that DO and Eh are highly effective in reducing the concentration of Nickel by flocculation process. Also, electrical conductivity, salinity, TDS and pH do not play any function in the flocculation of studied metals which is in accordance with obtained results of other researchers (Fazelzadeh *et al.*, 2012; Biati and Karbassi, 2012; Karbassi *et al.*, 2014).

Lead and manganese are connected to pH, EC, TDS, Salinity, Eh and DO (Fig. 5) at low correlation coefficients. Thus, in order to identify the effective factors on the removal of these two metals in this estuary, further researches are suggested.

The average discharge of Sardabroud River is about  $\text{m}^3$  per year and the initial concentrations of colloidal metals in Sardabroud water is Zn(312  $\mu\text{g/L}$ ), Cu(24  $\mu\text{g/L}$ ), Pb(72  $\mu\text{g/L}$ ), Mn(60  $\mu\text{g/L}$ ) and Ni(24  $\mu\text{g/L}$ ). Thus, the amount of dissolved zinc, copper, lead, nickel and manganese which transferred into the Caspian Sea from Sardabroud River would be 44.30 ton, 3.41 ton, 10.22 ton, 8.52 ton and 3.41 ton per year, respectively. The outcomes of this investigation indicate that 18.59%, 16.67%, 4.86%, 5.83% and 25% of dissolved loads of Zn, Cu, Pb, Mn and Ni, respectively, come into the particulate phase during estuarine mixing. Therefore, the total pollution loads released into the Caspian Sea reduces from 69.86 to 58.96 ton per year (Table 6).

## CONCLUSION

In this study, the flocculation trend of colloidal copper, manganese, nickel, zinc and lead during mixing of Sardabroud River water with the Caspian Sea water was performed to study the effect of

physicochemical parameters on removal efficiency of mentioned heavy metals. In addition, performance of natural self-purification in Sardabroud's estuary was examined. The experimental study reveals that the flocculation of Cu, Zn, Pb, Ni and Mn occurs at various salinities (1 to 8.5‰). The results of analysis show that the maximum efficiency of metal removal belongs to Nickel comparing to other metals and its flocculation rate is intensified by dissolved oxygen and Eh, according to the statistical analysis. Due to low correlation coefficient between pH, TDS, salinity, EC and studied heavy metals, these parameters are not effective in flocculation trend of Cu, Zn, Pb, Ni and Mn. Also, it was found that all the studied metals (except Pb and Mn) show non-conservative behavior. The experimental results indicated that without flocculation, the amount of colloidal elements discharged into the Caspian Sea is as Cu (3.41 ton/yr), Zn (44.30 ton/yr), Pb (10.22 ton/yr), Ni (3.41 ton/yr) and Mn (8.52 ton/yr). However, after the flocculation process, the amount of these dissolved elements is dramatically reduced to Cu (2.84 ton/yr), Zn (36.06 ton/yr), Pb (9.7 ton/yr), Ni (2.56 ton/yr) and Mn (7.8 ton/yr). It can be concluded that natural flocculation process avoid releasing whole of dissolved metals in to the sea and metal pollution loads reduced in a natural process. So, it points out the importance of flocculation process in natural self-purification of estuarine zone.

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## CONFLICT OF INTEREST

The authors declare that there are no conflicts of interest regarding the publication of this manuscript.

## ABBREVIATIONS

<i>CA</i>	Cellular acetate
<i>Cu</i>	Copper
<i>DO</i>	Dissolved oxygen
<i>EC</i>	Electrical conductivity
<i>Eh</i>	Redox potential
<i>Eq</i>	Equation
<i>g/L</i>	Gram per liter
<i>h</i>	Hour
<i>HNO<sub>3</sub></i>	Nitric acid
<i>ICP-OES</i>	Inductively coupled plasma-optical emission spectrometry
<i>km</i>	Kilometer
<i>km<sup>3</sup></i>	Kilometer square
<i>L</i>	Liter
<i>µg/L</i>	Microgram per liter
<i>µm</i>	Micrometer
<i>mL</i>	Milliliter
<i>Mn</i>	Manganese
<i>mV</i>	Millivolt
<i>MVSP</i>	Multivariate statistical package
<i>m<sup>3</sup>/s</i>	Cubic meter per second
<i>Ni</i>	Nickel
<i>Pb</i>	Lead
<i>‰</i>	Per mile
<i>TDS</i>	Total dissolved solids
<i>S</i>	Salinity
<i>WPG</i>	Weighted pair group
<i>yr</i>	Year
<i>Zn</i>	Zinc

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