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ORIGINAL RESEARCH PAPER

Role of estuarine natural processes in removal of trace metals under emergency situations

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ABSTRACT: Estuaries are well known for their potential in removing metal from fresh water to provide micro-nutrients to aquatic life. In the present investigation, we have tried to bring out the metal removal potential of estuaries during accidental spills. For this purpose artificial river water containing high concentration of Mn, Cu, Zn, Ni and Pb were mixed with sea water at different salinity regimes. Water samples were taken from a station on the main branch of Tajan River that flows in to the Caspian Sea. For this purpose, solutions with a concentration of 5 mg/L of each studied metal (Mn,Cu, Zn, Pb) were prepared in Tajan River water. The salinity regimes include 3, 6, 8, 10 and 11 ppt. It was noted that metal concentration decreased by increasing salinity. Metals were flocculated at different rates: Cu (88%) > Ni (86%) > Pb (84%) > Mn (74%).Thus, as average about 80% of total elemental content flocculates. Hence, it was concluded that a large amount of micro nutrients is carried by the river and flocculated in the estuary where the river water mixes with the sea water which may play a vital role in supplying nutrients to the aquatic animals. Cluster analyses have shown that Mn and Ni are governed by EC, pH and salinity.

KEYWORDS: *Estuary; Environment; Heavy Metal; Nutrients; Pollution*

INTRODUCTION

Estuaries of rivers are affected by different pollutions and materials carried by the rivers into the sea. These pollutions including petroleum hydrocarbons, heavy metals and radioactive materials enter the rivers through industrial and urban wastewater (Pejman *et al.*, 2011). Due to being rich in nutrients (phosphate and nitrate), estuaries are also the habitat of numerous living organisms (Heidaria *et al.*, 2014). According to the studies and investigations, the concentrations of heavy metals in river water is more than the concentration of those in sea (Nasehi, 2013); therefore, it may be concluded that estuaries act as a filter and separate heavy metals from micro nutrients (Karbassi *et al.*, 2015a). Various factors such as water retention time and adsorption of heavy metals by suspended particles lead to the separation of heavy metals from water in estuaries (Kalani *et al.*, 2014). The most significant factor in the flocculation process is the mixture of fresh and salt water. Due to providing micro nutrients, it is of the considerable significance in geochemical cycles of dissolved elements and aquatics (Karbassi *et al.*, 2015b). The mixture of riverine freshwater and saline water from seas in estuary results in the flocculation of heavy metals especially in the upper part of the estuary where lower salinity regimes are observed (Gerringa *et al.* 2001; Karbassi *et al.* 2008a;

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Shamkhali Chenar *et al.* 2013; Valikhani *et al.,* 2014). During the mixing of river water and seawater in estuary, dissolved elements come into the particulate phase due to flocculation mechanism (Boyle *et al.* 1977; Karbassi *et al.* 2008b,c). Therefore, estuarine processes can affect elemental composition of the sea water (Troup and Bricker 1975; Nouri *et al.* 2008). The estuarine flocculation process provides valuable nutrient resource for main organisms (Meybeck, 1988). 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; Akoto *et al.*, 2008; Mensi *et al.*, 2008; Lee and Mohamed, 2009; Ahmed *et al.*, 2010).Estuaries are known as the confluence of fresh and salt water and due to high production of flora and fauna, they are one of the most productive marine ecosystems (Nouri *et al.,* 2009; Viswanathan *et al.*, 2010). Thus, estuaries have biodiversity and the fish migrating to the rivers to spawn pass through this area, and the fries live in this area for a while when heading towards the sea (Basavarajappa *et al.*, 2011; Kalani *et al.,* 2014). Given the richness of nutrients, the estuary may have a crucial role in providing nutrients for the aquatics and become a habitat for many marine organisms (Visvanathan, 2010; Vaezi *et al.*, 2014).

Given the importance of the issue and considering the fact that there is not sufficient information available on the process of flocculation, absorption and rejection of heavy metals and role of flocculation process in

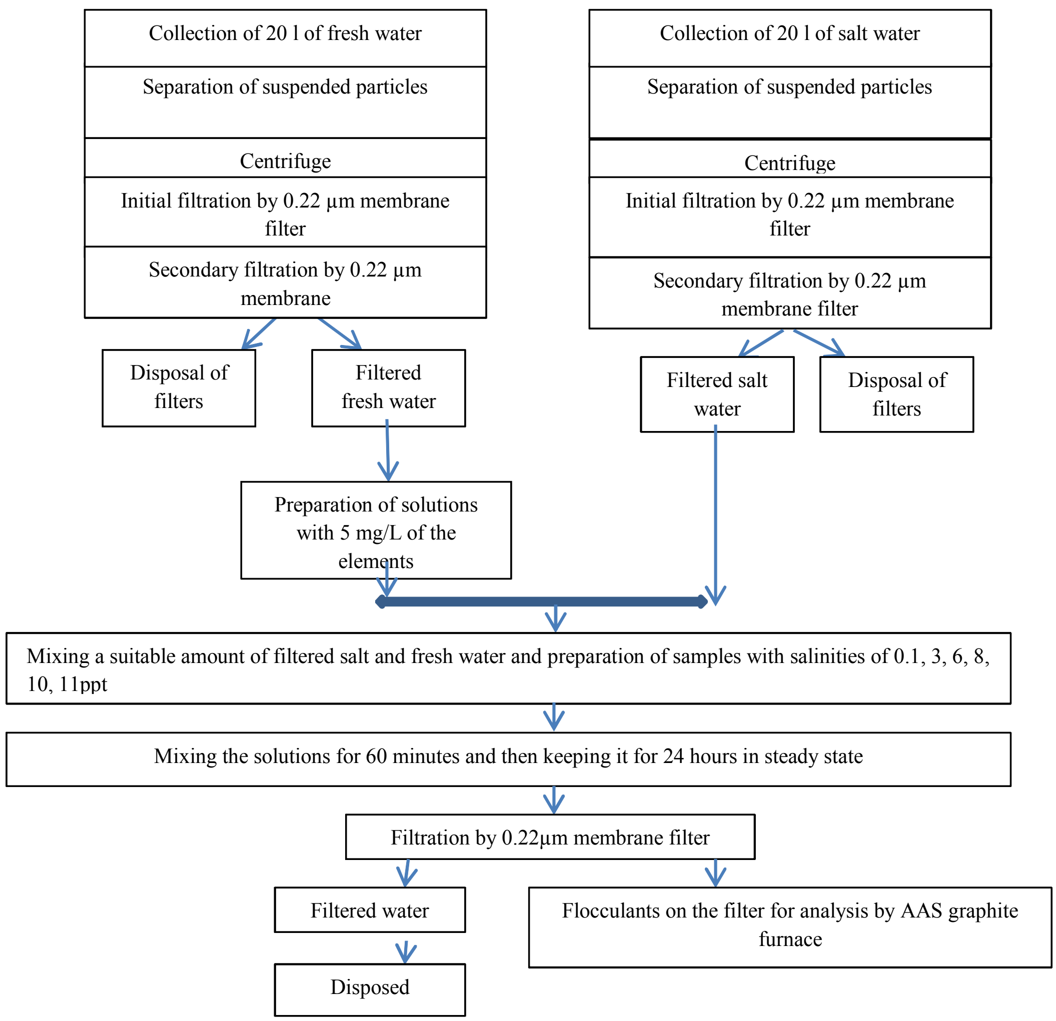

Fig. 1: Method statement flowchart of flocculation process

Fig. 2: Sampling location in Tajan River
(The sampling place is marked with a triangle)

providing nutrients for aquatics in estuary of rivers entering the Caspian Sea, further studies and tests are required in order to provide a more comprehensive understanding of these processes. For this reason, this study is an attempt to pursue various objectives such as the investigation of method, the amount of flocculation of the water (for the first time up to 5 mg/L), capability of the estuary to separate dissolved heavy metals, and the role of salinity, electrical conductivity and pH in flocculation in the estuary.

This study has been performed in Tajan River of Mazandaran Province nearby Caspian Sea in 2015.

MATERIALS AND METHODS

Fresh water sample was taken from Kord Kheyl station on the main branch of Tajan River. Salt water sampling place was selected 16 km off the coast of the Caspian Sea where the salinity is stable (Fig. 2). After sample collection, fresh and salt water samples were transferred to the laboratory and remained steady for 24 hours during which their suspended solids were deposited. Then, 15 ml of the supernatant of each sample was removed, and the whole water was filtered using 0.23 micrometer membrane filter and a vacuum pump. Subsequently, five solutions with a concentration of 5 mg/L of the heavy metals i.e. Mn, Ni, Cu, Zn and Pb were prepared by adding the standard solution to the river water with a salinity of about 0.1 ppt.

The mixed samples of fresh and saline waters were slowly stirred for 60 min. and kept for 24 h. in order to flocculate. Finally all samples were filtered using 0.2 µm filter and a millipore vacuum pump. After that, the collected flocs on filters were transferred into beakers and then 5 ml of nitric acid were added to each beaker waiting for decomposition of membrane filters without heating. The solution were made up to volume and analyzed by atomic absorption spectrophotometry, Perkin Elmer 410 equipped with graphite furnace. River water sample with a salinity of 0.1 ppt and the fabricated sample with salinities of 3, 6, 10, 8, 10 and 11 were also measured for parameters such as pH and EC immediately after filtration. The Silver nitrate titration method was applied to measure the salinity (Fig. 1).

RESULTS AND DISCUSSION

In previous years, the flocculation process was investigated and expressed on the basis of the lab processes. In recent years, the researchers have sought to return the lab activities to the natural states and to report the results of flocculation concentrations as a natural and lab report. This study is an attempt to investigate the both aforementioned states separately.

Laboratory flocculation of elements

The results of this state are presented in Table 1, and Figs. 3 to 12 illustrate changes in flocculation concentration in various regimes of pH in estuary of Tajan River. As shown in Table 1, the maximum flocculation concentration in the salinity of 3 ppt belongs to Cu, and the minimum flocculation concentration in the salinity of 3 ppt is seen for Mn. Total flocculation is computed and presented in Table 1. For instance, total flocculation for Zn is 16.35 mg/L.

Table 1: Flocculation Amount of Elements (Zn, Cu, Mn, Ni, Pb) in the remaining elements in fresh water in the (Laboratory) condition (mg/L)

Cu	Pb	Mn	Ni	Zn	Salinity ppt
Concentration of flocculants	Concentration of flocculants	Concentration of flocculants	Concentration of flocculants	Concentration of flocculants	
0	0	0	0	0	0.1
3.7	3.1	0.3	1.6	2.3	3
3.7	3.3	1	2.4	2.8	6
4	3.7	2.4	3.4	3.3	8
4.3	4	3.3	4	3.8	10
4.4	4.2	3.7	4.3	4.15	11
16.4	**18.3**	**10.7**	**15.7**	**16.35**	**-**

* The figures in the last row represent the total flocculants for each column.

Table 2: Flocculation amount of elements (Zn, Cu, Mn, Ni and Pb) in the remaining elements in the (Natural) fresh water (mg/L)

Cu	Pb	Mn	Ni	Zn	Salinity (ppt)
Concentration of flocculants	Concentration of flocculants	Concentration of flocculants	Concentration of flocculants	Concentration of flocculants	
0	0	5	0	0	0.1
3.7	3.1	4.7	1.6	2.3	3
3.7	0.2	4	0.8	0.5	6
0.5	0.4	2.6	1	0.5	8
0.3	0.3	1.7	0.6	0.5	10
0.1	0.2	0.4	0.3	0.35	11
4.6	**4.2**	**3.7**	**4.3**	**4.15**	**-**

* The figures in the last row represent the total flocculants for each column.

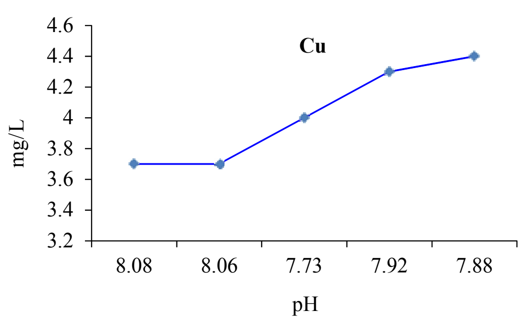

Fig. 3: The concentration of Cu in different pH at Tajan estuarine in the Laboratory state

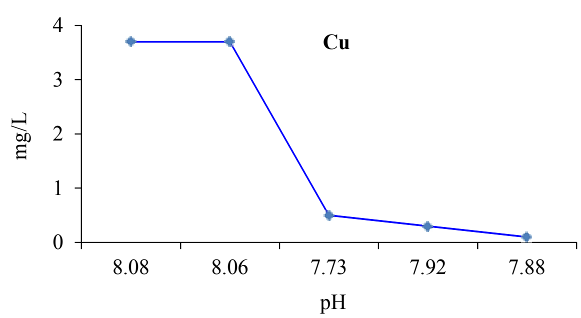

Fig. 4: The concentration of Cu in different pH in the Natural state

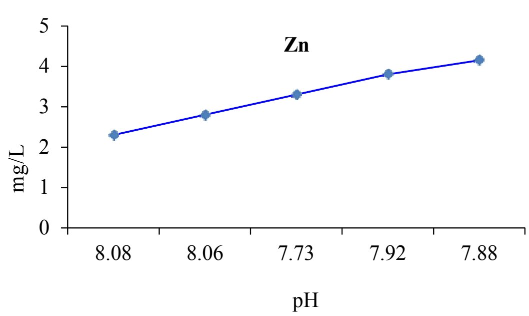

Fig. 5: The concentration of Zn in different pH in the Laboratory state

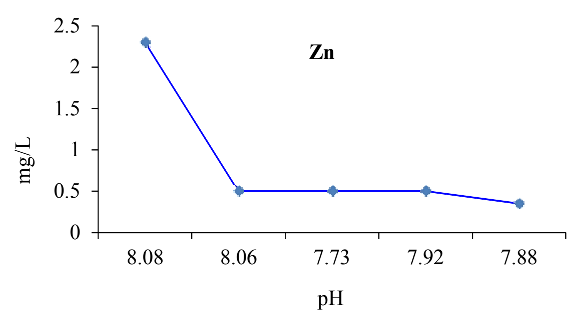

Fig. 6: The concentration of Zn in different pH in the Natural state

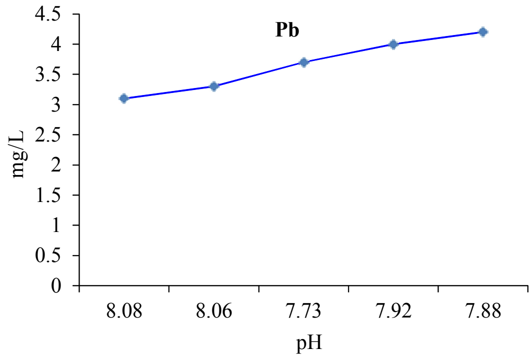

Fig. 7: The concentration of Pb in different pH in the Laboratory state

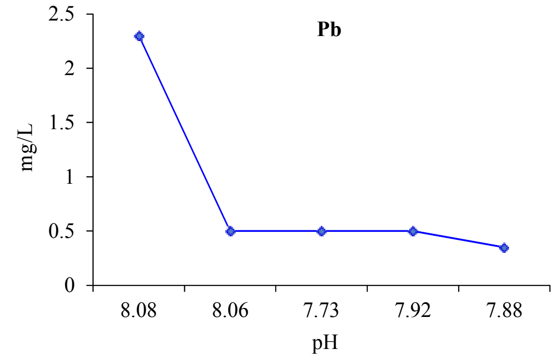

Fig. 8: The concentration of Pb in different pH in the Natural state

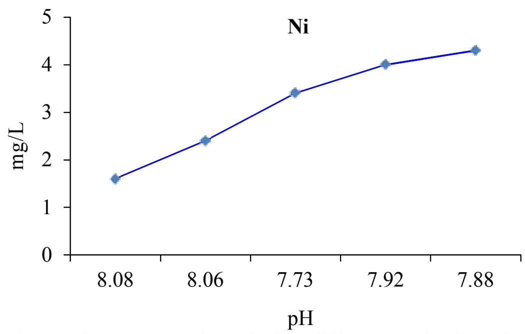

Fig. 9: The concentration of Ni in different pH in the Laboratory state

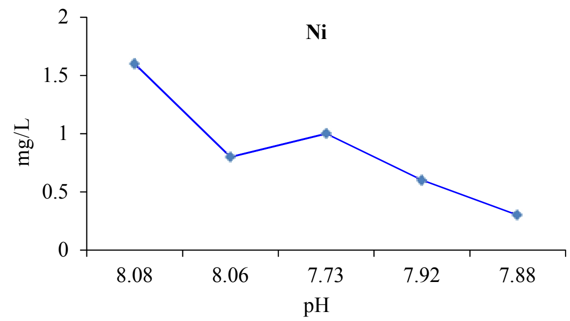

Fig. 10: The concentration of Ni in different pH in the Natural state

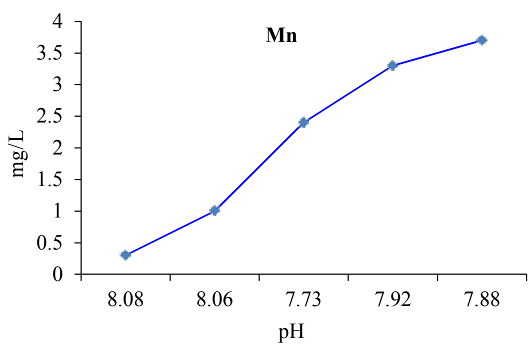

Fig. 11: The concentration of Mn in different pH in the Laboratory state

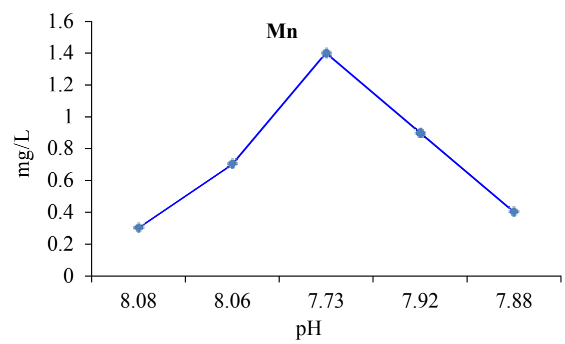

Fig. 12: The concentration of Mn in different pH in the Natural state

However, the total concentration of the artificially added element to the solution is about 5 mg/L. Obviously, this amount of flocculation may not be real. Thus, it is necessary to investigate the natural state.

Natural flocculation of elements

Since the five aquariums are filled up with fresh water of Tajan River on equal basis; thus they do not show the real flocculation during estuarine processes (Figs 3, 5, 7, 9 and 11). These are shown in Figs. 3 to 8 as stated before. Table 2 demonstrates the results of natural state and Figs. 4, 6, 8, 10 and 12 show the flocculation concentration under natural state of flocculation of elements.

Interpretation of figures

Cu: The maximum flocculation of Cu is in the salinity of 3 ppt, and by increasing the concentration in 6 ppt,

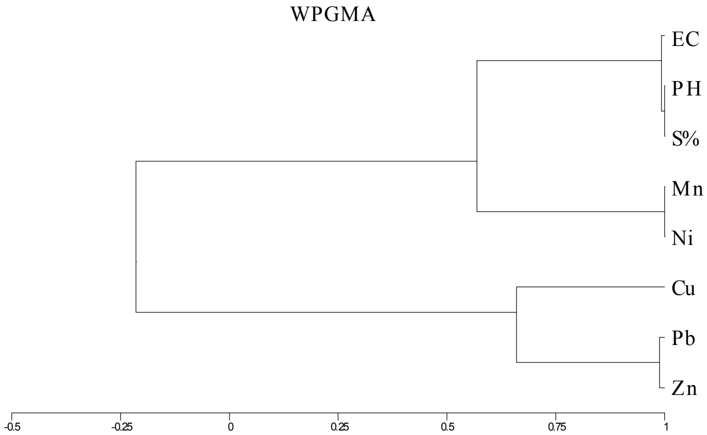

Fig. 13: Dendrgram of cluster analysis of chemical elements and other physic-chemical characteristics in flocculation process in the (Natural) condition

even some amount of flocculated copper is dissolved again. Hence, the maximum and minimum flocculation of copper are in the salinities of 3 and 6 ppt, respectively.

Zn: Maximum flocculation concentration of zinc is in salinity of 3 ppt, and the flocculation concentration decreases by increased salinity.

Pb: The maximum flocculation concentration of lead is also observed in salinity of 3 ppt, so that about 62% of dissolved lead flocculates in this salinity. Generally, the flocculation concentration again decreased by increased salinity.

Mn: In the case of manganese, it is noticed that this element flocculates slightly in salinity of 3 ppt; however, the flocculation increases by increased salinity so that the maximum flocculation is in the salinity of 8 ppt. Afterwards,
the flocculation concentration decreases by increased salinity.

Ni: In salinity of 3 ppt, about 32% of this element flocculates, and in salinity of 6 ppt, the flocculation concentration decrease. Similar to manganese, copper and lead, increased flocculation concentration is seen in salinity of 8 ppt, and again the flocculation concentration decreases by increased salinity. Table 3 presents flocculation concentrations of elements and their percentages.

Table 3: Flocculation concentration of elements (Zn, Mn, Ni, Cu and Pb) with different salinity regimes in the (Natural) condition (mg/L)

Zn	Pb	Ni	Cu	Mn	S (%)
2.3	3.1	1.6	3.7	0.3	3
(46)*	(62)	(32)	(74)	(6)	
0.5	0.2	0.8	-	0.7	6
(10)	(4)	(16)	(0)	(14)	
0.5	0.4	1	0.5	1.4	8
(10)	(8)	(20)	(6)	(28)	
0.5	0.3	0.6	0.3	0.9	10
(10)	(6)	(12)	(6)	(18)	
0.35	0.2	0.3	0.1	0.4	11
(7)	(4)	(6)	(2)	(8)	

* The numbers in parenthesis are expressed as percentage

CONCLUSION

To identify the mechanisms and parameters which may control the flocculation concentration, the salinity, electrical conductivity and pH were measured, and correlation coefficients between the elements and these parameters were calculated. Consequently, cluster analysis was applied for a better presentation. Cluster analysis used in the present investigation is based on weighted pair group (WPG).therefore the intra-relationship amongst studied parameters is brought out and the governing factors responsible for flocculation are highlighted.

Cluster Analysis of Parameters in Natural State

Cluster analysis of parameters in natural state comprises of two clusters of A and B is shown in dendrogram (Fig. 13). In cluster A, Pb and Zn are linked by the similarity coefficient of 0.998. Then Cu has a relationship with Pb and Zn in similarity coefficient of 0.70, and these three elements have relationships with one another without bearing any relationships with pH, EC and salinity. It is observed that flocculation concentration of these three elements is not affected by pH. In cluster B, salinity, EC and pH are related in similarity coefficient of 0.998. Subsequently, these three factors are connected to Mn and Ni in similarity coefficient of 0.65. This reveals that flocculation concentration of Mn and Ni is mainly controlled by salinity, electrical conductivity and pH. The very low similarity coefficient between clusters A and B indicated that governing factors for studied metals differs. More detailed studies are required to know about the flocculation processes of Zn and Pb.

According to Table 3, it can be concluded that the rate of flocculation of elements in the estuary is as follows:

Cu (88%) > Ni (86%) > Pb (84%) > Zn (83%) > Mn (74%)

and the rate of the remaining metals in solution is contrary to the above relation

Mn (26%) > Zn (17%) > Pb (16%) > Ni (14%) > Cu (12%)

SUMMARY

- A high percentage of river elements, before entering the sea, is separated due to flocculation process in the estuary and coastal shores which may be an important source of nutrients for aquatics.
- A major part of studied metals flocculate at lower salinity regimes.
- Flocculation percentages of the elements in Tajan River are as follows:
- Cu (88%) > Ni (86%) > Pb (84%) > Zn (83%) > Mn (74%)
- The tests show that concentrations of the elements and micro nutrients in the river water are much higher than those in the sea water.
- Dendrogram of the cluster analysis of the heavy metals in natural state in the estuary of Tajan River shows that the concentration of Ni and Mn is mainly affected by pH, EC and salinity, except for Zn, Pb and Cu the concentrations of which are not affected by the salinity, electrical conductivity and pH.
- Flocculation processes provide micro nutrients to aquatic ecosystems while acting as a self-purification mechanism for metal contents in freshwater. It is well known that metals are present in colloidal form in river water. These colloidal metals are being bonded together to form larger particles. Hence metals are removed from water in the form of flocs.

CONFLICT OF INTEREST

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

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