

# Experimental study on the effect of salinity change on Fe and Cr removal from estuary water

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**Abstract.** Freshwater metal contaminants which in the estuary tend to precipitate into intertidal surface sediments during freshwater-seawater mixing because of heavy water chemical reaction. The impacts of ferric hydroxide on the removal rate of Cr with increasing pH and salinity were conducted by laboratory simulation experiment. The removal rate of Cr by ferric hydroxide decreased with increasing pH from river water to seawater in the estuary; this is because pH changed the Zeta potential of ferric hydroxide. And with increasing salinity, the removal rate of Cr by ferric hydroxide firstly decreased and then increased. On the hand,  $\text{Na}^+$  entering the sliding surface, which could improve Zeta potential and stability of ferric hydroxide colloid, which leads to the amount of Cr removal by colloid aggregation decreased. On the other hand, there was competitive adsorption between  $\text{Cl}^-$  and  $\text{CrO}_4^{2-}/\text{HCrO}_4^-$ . In this study, Fe was the key factor of heavy metal Cr distribution with pH change.

## 1 Introduction

An estuary acts as a zone of land-sea interaction in which runoff from the land mixes with seawater. It is a water body where freshwater, brackish water and seawater are present simultaneously [1]. There are complex interfaces and interactions among physics, chemistry, biology, and geology in an estuary, which makes the study in this area difficult [2, 3]. During freshwater-seawater mixing, the salinity and acidity increase from estuarine water to seawater, i.e. from 0 to 35 ppt and pH = 6.9 to 8.1, respectively [4]. Changes of salinity and pH could lead to the formation of  $\text{Fe}(\text{OH})_3$  colloids when the dissolved Fe in freshwater interacts with alkaline seawater, which can then affect the interaction process of Fe with Cr and other heavy metals. The impacts of salinity and suspended particulate matter in freshwater-seawater mixing zone on partition coefficient ( $K_d$ ) have been reported [5], noting that heavy metals such as As, Cd and Cr were more susceptible to variations in salinity. Therefore, it is meaningful to investigate the interaction theory between Fe and Cr when the salinity and pH changes in the estuary. In this study, simulated interior batch experiments were used, keeping the value of pH in the reaction system, and increase the concentration of NaCl to represent the changes of salinity in the estuary area, then the Fe and Cr were monitored to investigate the interaction between them with long-term salinity changes in the estuary.

## 2 Materials and Methods

To begin, 48.396 g of  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  and 1.4145 g of  $\text{K}_2\text{Cr}_2\text{O}_7$  (China National Pharmaceutical Group Corporation, Beijing, P.R. China) were added respectively to dissolved 1 L and 500 mL of deionized water and stored in the dark at 4 °C. Then, 0.1M NaOH and 10 %  $\text{HNO}_3$  solutions (China National Pharmaceutical Group Corporation, Beijing, P.R. China) were prepared using with deionized water.

In order to better simulate the salinity change of estuary water, the measured values of water samples in Dagu River estuary were used as a reference to prepare solutions of 0, 10, 20 and 30 ppt to which 300  $\mu\text{L}$  Fe solution and 100  $\mu\text{L}$  Cr solution were added to produce initial concentrations of  $\text{Fe} = 3000 \mu\text{g/L}$  and  $\text{Cr} = 100 \mu\text{g/L}$  in the different salinity solutions. These solutions were adjusted to  $\text{pH} = 7.00 \pm 0.10$  and then 10 mL samples were extracted to measure Zeta potential. The residual liquid was then agitated by magnetic stirring at a rotating speed of 200 r/min. After 0, 5, 10, 20, and 30 minutes, and then 3, 6, 9, 12, 24, and 48 to 240 hours, 10 mL liquid was removed that was added a 1 to 2 drop solution of 10 %  $\text{HNO}_3$  to prevent metal hydrolysis, and the pH value subsequently monitored by a pH regulator and the concentration of Fe and Cr then determined by ICP-OES.

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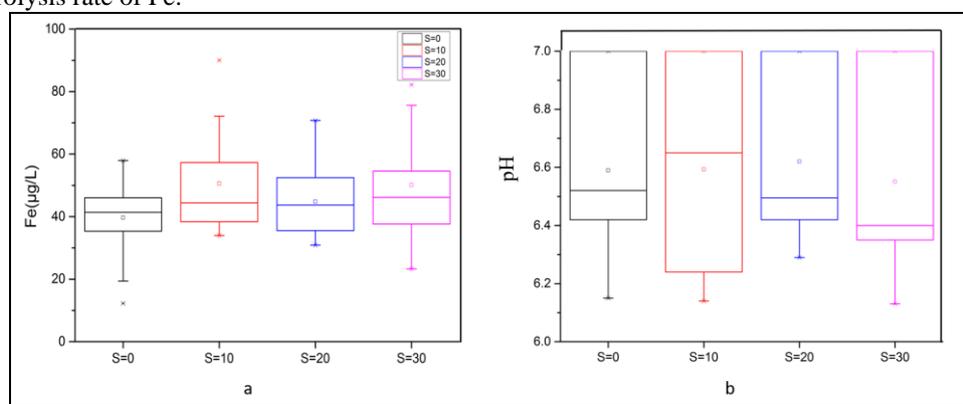
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### 3 Results and discussion

#### 3.1 Concentration changes of dissolved Fe and pH with time

The initial concentration of Fe in the different salinity solution ( $S = 0, 10, 20,$  and  $30$  ppt) was is  $3000 \mu\text{g/L}$ , for which the pH value is  $7.00 \pm 0.10$ . As shown in Figure 1, the dissolving Fe was formed into  $\text{Fe}(\text{OH})_3$  colloids in all groups at the start time, because it was observed that the dissolving Fe disappeared when the concentration of  $\text{Fe} \leq 558 \mu\text{g/L}$ . The concentration of dissolving Fe is greatest in group 1 ( $S = 0$  ppt) compared with other groups ( $S = 10, 20$  and  $30$  ppt), indicating that the hydrolysis rate of Fe was the fastest in group1 and the salinity is an impact factor to retard the hydrolysis rate of Fe, but not the important factor because the decrease of concentration is not obvious. It has been reported that  $\text{Cl}^-$  can slow down the formation rate of iron oxides [6, 7]. It is the most effective on decreasing the hydrolysis rate of Fe in the group 2, for which the salinity is 10 ppt because it is shown in Figure 1(a) that the quartile and the median concentrations of Fe are both higher than the concentration of Fe in other groups. So, this result may indicate that the interaction between Cr and Fe will be greatly affected in water environment with salinity around 10 ppt.

As we know, the most important impact factor on the hydrolysis rate of Fe is pH and the higher value of pH, the lower the concentration of dissolving Fe, which indicates that the most of the dissolved Fe in water was hydrolyzed. Figure 1(b) shows the distribution of pH as a function of salinity, illustrating that the pH is the most impact factor on the hydrolysis rate of Fe.



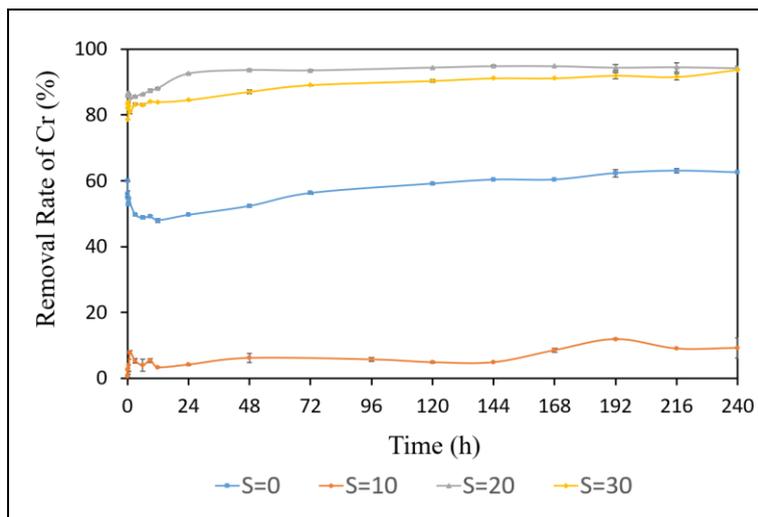
**Fig. 1.** Box and whisker plots of dissolved iron concentration for different salinity (a) and pH as a function of solution salinity (b).

#### 3.2 Concentration change of dissolved Cr with time

The experiment of the salinity change from 0 to 30 ppt represents the changing of salinity of the freshwater runoff to the sea in the estuary area. Salinity will affect the thickness and interface energy of the colloidal compression electric double layer, thus affecting the species and adsorption efficiency of the adsorbed ions [8]. In general, the change of ionic strength, i.e., salinity, is more likely to affect the diffusion layer of the colloidal double layer. Hayes and Leckie classified the adsorption types into two: beta-plane adsorption is susceptible to the influence of electrolytes, and o-plane adsorption is not susceptible to the influence of electrolytes [9].

The initial concentration of Cr the difference salinity solution ( $S = 0, 10, 20$  and  $30$  ppt) was is  $100 \mu\text{g/L}$ , for which the value of pH is  $7.00 \pm 0.10$ . The removal efficiency of Cr varies with salinity (Fig. 2), which indicates that the adsorption of beta-plane is the main function and the main form of the product is the outer complex. Therefore, is the removal rate of Cr first decreases and then increases with the increase of salinity. At a salinity of 10 ppt, the removal amount of Cr is the least, less than 10%. As salinity increases to 20 ppt, nearly 90% of Cr is removed, with Cr now present at 30 ppt.

We can also determine from Figure 2, the interaction of Cr and salinity in different groups at three time periods. At the beginning of the reaction, the removal rate of Cr reaches a high level, and this is due to the hydrolysis of Fe at the moment of  $\text{pH} = 7$ . During this time, Fe removed Cr by adsorption, entrainment, and co-precipitation for one hour, during which the removal rate of Cr and Cr content decreased. After 24 hours, the removal rate of Cr decreased slightly in each salinity group, due to the instability of product structure and the re-release of the immobilized and unstable Cr into the solution. From 24 hours to the end of the experiment at  $>240$  hours, the removal rate of Cr continued to increase, which may be the adsorption on the surface of the product, and the continuous binding of Cr to the binding site of the product surface would remove Cr from the solution. Thus, the removal efficiency of Cr varies with salinity at first increases, then decreased, and finally and rose again (Fig. 2).

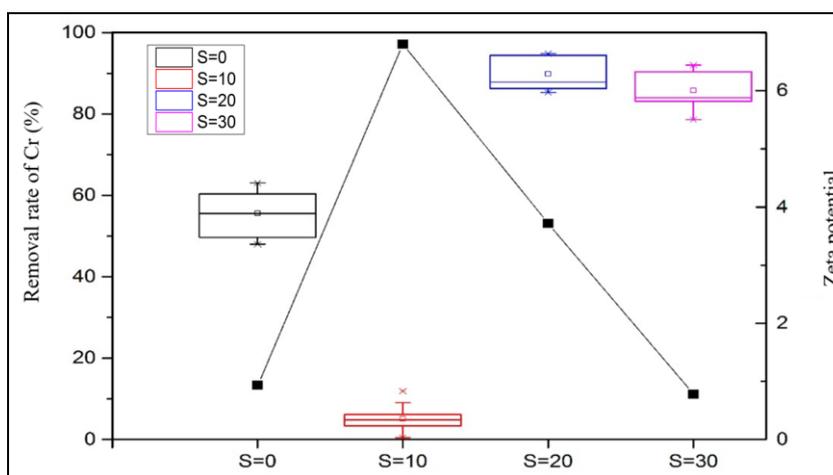


**Fig. 2.** Change of Cr removal rate with time.

### 3.3 The Zeta potential of ferric hydroxide formed under different salinity

The double layer structure of colloid consists of adsorption layer and a diffusion layer. There is an abstract boundary between the fixed adsorption layer and the diffusion layer, which boundary is the adsorption layer inside and the diffusion layer outside. Therefore, it is called a sliding surface. The potential on the sliding surface is Zeta potential, and it can affect colloid stability.

At a salinity of 10 ppt, the removal rate of Cr decreased abruptly, accompanied by a sudden increase of Zeta potential because the introduction of high concentration NaCl, and many  $\text{Na}^+$  into the sliding surface and diffusion layer, resulting in the formation of iron hydroxide colloid Zeta potential increased. It has been pointed out that when the concentration of the electrolyte is high, the adsorption potential of colloid for counter-ion will be full, and then the adsorption of the same ion will begin [10], which makes the Zeta potential increase with the increase of ion strength. With the increase of Zeta potential, the repulsion force between particles and the stability of colloids increases, so it is not easy to agglomerate. Therefore, the removal rate of Cr decreases with the ratio of Cr removed by colloidal agglomeration and entrainment decreases. By contrast,  $\text{Cl}^-$  ions will form competitive adsorption with  $\text{CrO}_4^{2-}/\text{HCrO}_4^-$  due to the same negative charge, which also results in a low removal rate of Cr. When the salinity is increasing to 20 and 30 ppt, negative ions in solution, such as  $\text{Cl}^-$ , enter the colloid diffusion layer.  $\text{Cl}^-$  present in the diffusion layer will be squeezed into the adsorption layer by the electrostatic repulsion force, so that the diffusion layer becomes thinner and the Zeta potential decreases, as expected from the compressed double layer theory [11]. As the Zeta potential decreases, the repulsive force between particles decreases and the stability decreases, the flocculation of  $\text{Fe}(\text{OH})_3$  produces a large amount of precipitation, which adsorbs the Cr in the sweeping solution, so the removal rate of Cr becomes higher.



**Fig. 3.** Box plot of Cr removal rate versus Zeta potential.

## 4 Conclusions

In this study, we simulated the changes of salinity and pH in the estuary by a laboratory simulation experiment and observed the change of Fe through time. It was observed that this was the key factor in the concentration change of the

heavy metal Cr with pH change. The removal rate of Cr by ferric hydroxide scavenging decreased with increasing pH from river water to seawater composition; this is because pH changed the Zeta potential of ferric hydroxide. The removal rate of Cr by ferric hydroxide first decreased with increasing salinity and then increased. The initiation of Na<sup>+</sup> entering into the sliding surface, which improves the Zeta potential and stability of the Fe(OH)<sub>3</sub> colloid, leads to a decreased amount of Cr removal by colloid aggregation. Competitive adsorption between Cl<sup>-</sup> and CrO<sub>4</sub><sup>2-</sup>/HCrO<sub>4</sub><sup>-</sup> was observed.

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