Part I: Removing of Zn(II) from Polluted Water: Determination of Precipitation Limit Of Zn(II) Ion With 2-Hydroxy-1,2,3-Propanetricarboxylic Acid

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Abstract: Problem statement: The goal of this research was to investigate the condition for removing of Zn cation from water, through precipitation method with 2-hydroxy-1,2,3-propanetricarboxylic acid as ligand.

Approach: In this study we examined the precipitation of Zn(II) ion in water solutions of ZnSO$_4$ $\times$ 7H$_2$O (1$\times$10$^{-2}$ and 5$\times$10$^{-3}$ mol L$^{-1}$) with 2-hydroxy-1,2,3-propanetricarboxylic acid (1$\times$10$^{-1}$, 1$\times$10$^{-3}$ mol L$^{-1}$) in constant ionic strength of 0.6 mol L$^{-1}$ NaCl. We have determined the concentration region at which Zn(II) start to precipitate.

Results: From precipitation diagrams of zinc with 2-hydroxy-1,2,3-propanetricarboxylic acid, in ionic force 0.6 mol L$^{-1}$ NaCl, we have found that during decreasing the concentration of 2-hydroxy-1,2,3-propanetricarboxylic acid, in case of constant concentration of Zn(II), the limit of precipitation is shifted to lower values of pH. The solid phase is analyzed by IR spectroscopy.

Conclusion: From the IR spectroscopic analysis we can conclude that Zn(II) ion can precipitate with 2-hydroxy-1,2,3-propanetricarboxylic acid.

Key words: Environment, precipitation limit, Zn(II) ion, ligands, 2-hydroxy-1,2,3-propanetricarboxylic acid, IR spectroscopy

INTRODUCTION

Human activities can cause water pollution or can pollute river sediments (Montgomery, 1985). Components from organic or inorganic origin, within time they can sediment in lower part of river. The sediment from river contains heavy toxic metals, organic or inorganic components (Halamic et al., 2001). Water from river can contain ions (Cu, Cd, Zn, Pb, Al and Hg), depends on pollution, which are very toxic for water organisms. If these ions bind with different ligands (organic molecules), the metal toxicity will reduce. Natural water contains a lot of molecules and ions with organic and inorganic origin. Cations in natural water can be present as complex, but anions can be from human activities (phosphates and dicarboksilik acids), (Hammond, 1971) or can be present from natural humic acids and aminoacids (Flaig and Beutelspacher, 1975; Schnitzer and Khan, 1978). Investigation of the interactions between metals and ligands, is very important for Environmental chemistry.

Oceans and seas water contain metals, also zinc and other helate ligands in normal quantity but sometimes depends on pollution they can contain high level of these metals and ligands. We can find complexes which are not stable with different inorganic ligands, as example chloride ions, or complexes, which are stable and these are formed from metals and helate ligands from organic mater or formed from polluted water (Ibanez et al., 2007).

Toxic metals as zinc are considered as non toxic when it is complexes with helate ligands. Water organisms (fish’s) can eat these complexes, but it is not believed that these kinds of compounds can entry to the nutritive chain. But this should investigate very carefully in each case (Ibanez et al., 2007).

The Aim of this work was to investigate the condition for removing of Zn cation from water, through precipitation method with 2-hydroxy-1,2,3-propanetricarboxylic acid as ligand.

MATERIALS AND METHODS

In this study we used ZnSO$_4$ $\times$ 7H$_2$O, 2-hydroxy-1,2,3-propanetricarboxylic acid as a ligand, sodium hydroxide and sodium chloride. For this investigation
we have prepared some concentrated solutions which are stored on glass bottles in room temperature. Diluted solution we have prepared fresh for each series of precipitated systems. The precipitated systems are prepared using methods from Tezak et al. (1951).

Precipitated system, ZnSO$_4 \times 7$H$_2$O with 2-hydroxy-1,2,3-propanetricarboxylic acid, is investigated in the long region of concentration with ionic force of NaCl 0.6 mol L$^{-1}$.

As example, one series it’s prepared in this way:

- The solution was added in two line of test-tube. In the first line of test tubes is added the solution of ZnSO$_4 \times 7$H$_2$O with known concentration (as example 1×10$^{-1}$ mol L$^{-1}$). In second line of test tube we added the 2-hydroxy-1,2,3-propanetricarboxylic acid solution, also with known concentration (as example 1 mol L$^{-1}$). The second line of test tube we added NaCl in that way that ionic force to be 0.6 mol L$^{-1}$. After that we added the solution of NaOH to increase the pH value. The total volume in each test tube should be 10 mL. The differences till 10 mL, we have fill with distillate water

- Solution from the first line tubes was added to the solution of second test tube (7 times per 20 sec). All the concentration is calculated on the total volume after mixing, which means at 10 mL. The systems after mixed are stored on thermostat for 24 h in 25°C. To determine the precipitated diagrams, when the concentration of Zn ions stays unchanged, we have to change the concentration of 2-hydroxy-1,2,3-propanetricarboxylic acid. For that we used three deferent concentration of 2-hydroxy-1,2,3-propanetricarboxylic acid for one concentration of Zn(II) ion. We used concentration of 2-hydroxy-1,2,3-propanetricarboxylic acid 1×10$^{-1}$, 1×10$^{-2}$ and 1×10$^{-3}$ mol L$^{-1}$ for each concentration of Zn(II). For zinc (II) ion we used two concentration 1×10$^{-2}$ and 5×10$^{-3}$ mol L$^{-1}$. At all of these systems we added solution of NaCl in that way that ionic force to be 0.6 mol L$^{-1}$. Also we added the NaOH to change the pH values. Precipitated systems are monitors after 24 h. It is determinate the concentration which cause the difference between clear solution and precipitation. Then it is measured the pH value on the top of precipitate with pH meter, “Metrohm”

- Some precipitates are prepared in large quantity for quantity analysis. Systems have stored in thermostat for 24 h in the temperature of 25°C and then the pH value is measured on the top of precipitate. These systems are filtered (we used filtered paper with blue line for filtration) and are dried on the air. We used the IR spectra to characterize and to find the presence of organic components to precipitate. To record IR spectra we used spectrophotometer, “SHIMADZU 8400 S” with potassium bromide technique

**RESULTS**

Precipitation of zinc(II) with 2-hydroxy-1,2,3-propanetricarboxylic acid was investigated to concentration of zinc 1×10$^{-2}$ and 5×10$^{-3}$ mol L$^{-1}$ with different concentration of 2-hydroxy-1,2,3-propanetricarboxylic acid (1×10$^{-1}$, 1×10$^{-2}$ and 1×10$^{-3}$ mol L$^{-1}$). We have added the solution of NaCl because we want that general ionic force to be 0.6 mol L$^{-1}$. In this mixture we added the NaOH solution in that way that pH increase continually and from here to find at which pH values the Zn(II) ion will precipitate.

**DISCUSSION**

From the precipitation diagram of Zn(II) with 2-hydroxy-1,2,3-propanetricarboxylic acid we can see, that when concentration of zinc is 1×10$^{-2}$ mol L$^{-1}$ and concentration of 2-hydroxy-1,2,3-propanetricarboxylic acid 1×10$^{-1}$ mol L$^{-1}$ (Fig. 1) we have not the precipitate,
but the precipitation start when the concentration of 2-hydroxy-1,2,3-propanetricarboxylic acid is $1 \times 10^{-2}$ and $1 \times 10^{-3}$ mol L$^{-1}$ at the value of pH = 7.81 and 7.19, respectively. At pH = 10.27 the precipitate start when the concentration of Zn is $5 \times 10^{-3}$ mol L$^{-1}$ and concentration of 2-hydroxy-1,2,3-propanetricarboxylic acid is $1 \times 10^{-1}$ mol L$^{-1}$ (Fig. 2), but when concentration of 2-hydroxy-1,2,3-propanetricarboxylic acid is $1 \times 10^{-2}$ mol L$^{-1}$, precipitate start at pH = 10.03. When the concentration of 2-hydroxy-1,2,3-propanetricarboxylic acid is $1 \times 10^{-3}$ mol L$^{-1}$ precipitate start at pH = 6.96.

We have found that diagrams have not changed after a long stored and for that the time of 24 h was approved as time of achieved the equilibrium. To analyze the precipitate, some of test tubes are filtered and are dried in the room temperature. These precipitate are characterized with IR spectra (Fig. 4 and 5).

We have obtained also the IR spectra of 1,2,3-propanetricarboxylic acid (Fig. 3). Comparing the IR specters, we can conclude that we have interaction between Zn and 1,2,3-propanetricarboxylic acid.

To the 1,2,3-propanetricarboxylic acid IR spectra (Fig. 3) we see the peaks at 1710 cm$^{-1}$ which characterize the carboxyl group. At solid phase this peak is shifted at lower values, 1600 cm$^{-1}$ (Fig. 4 and 5). This tells us for the interaction of Zn with 1,2,3-propanetricarboxylic acid. The breit peak at 1100 cm$^{-1}$ is characteristic for the interaction of Zn-OH.

Fig. 2: Precipitate diagram of Zn(II) in concentration $5 \times 10^{-3}$ mol L$^{-1}$

Fig. 3: IR spectra of 1,2,3-propanetricarboxylic acid

47
Fig. 4: IR spectra of precipitate which is formed after interaction of Zn(II) with 1,2,3-propanetricarboxylic acid (c(ZnSO$_4$.7H$_2$O) = 5×10$^{-3}$ mol L$^{-1}$, c(1,2,3-propanetricarboxylic acid) = 1×10$^{-3}$ mol L$^{-1}$, pH = 9.46)

Fig. 5: IR spectra of precipitate which is formed after interaction of Zn(II) with 1,2,3-propanetricarboxylic acid (c(ZnSO$_4$.7H$_2$O) = 1×10$^{-2}$ mol L$^{-1}$, c(1,2,3-propanetricarboxylic acid) = 1×10$^{-2}$ mol L$^{-1}$, pH = 6.72)

**CONCLUSION**

To investigate the interaction between ligands and metals, which can be present in natural water, is very important for Environment. For that we have analyzed the precipitation diagrams of Zn(II) ion with 2-hydroxy-1,2,3-propanetricarboxylic acid. From our results we can conclude:

- Also from precipitation diagrams of zinc with 2-hydroxy-1,2,3-propanetricarboxylic acid at ionic force of 0.6 mol L$^{-1}$ NaCl, we can see that when the concentration of 2-hydroxy-1,2,3-propanetricarboxylic acid decrease, in case of constant concentration of zinc, the limit of precipitation will shift at lower values of pH.
- Solid precipitates are analyzed by IR spectrophotometer and the IR spectra which we have obtained are compared with IR spectra of 2-hydroxy-1,2,3-propanetricarboxylic acid. From the IR spectra of solid phase we can conclude that zinc
can react with 2-hydroxy-1,2,3-propanetricarboxylic acid

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