Investigation on the complexation properties of chlortetracycline with Iron and Aluminum

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Abstract

Chlorotetracycline (CTC) is widely used for enhancement of growth in animal farms. However, it can end up in wastewater and surface water. Complexation of CTC with metals is an important issue than may enhance the toxicity and persistence. Determination of stability constants of complexes is a good measure to compare the affinity of CTC towards different metals.

OBJECTIVES

- Determination of the stability constant of CTC–metal complexes of two metal ions Fe(III), Al(III) through famous Bjerrum Procedure and also
- Study the complexation process with X-ray photoelectron spectroscopy (XPS) and Fourier transform infrared spectroscopy (FTIR).

PRINCIPLE

The reaction is:

$$M + nL \leftrightarrow ML_n$$

The stability constant (B) is defined as follows:

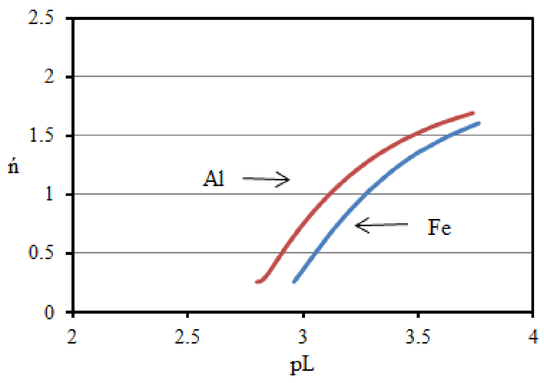
$$B = \frac{[ML_n]}{[M][L]^n}$$

METHODOLOGY

Bjerrum Method

In this method, three solution, containing a strong acid, acid+CTC and acid+CTC+metal ion are titrated against strong base and the data are used to calculate CTC-metal complexation stability constant (logB). The corresponding values of pL (a function of CTC concentration) at ń (a function of metal concentration) equal to 0.5 and 1.5 gives log B_1 and log B_2 respectively.

RESULTS

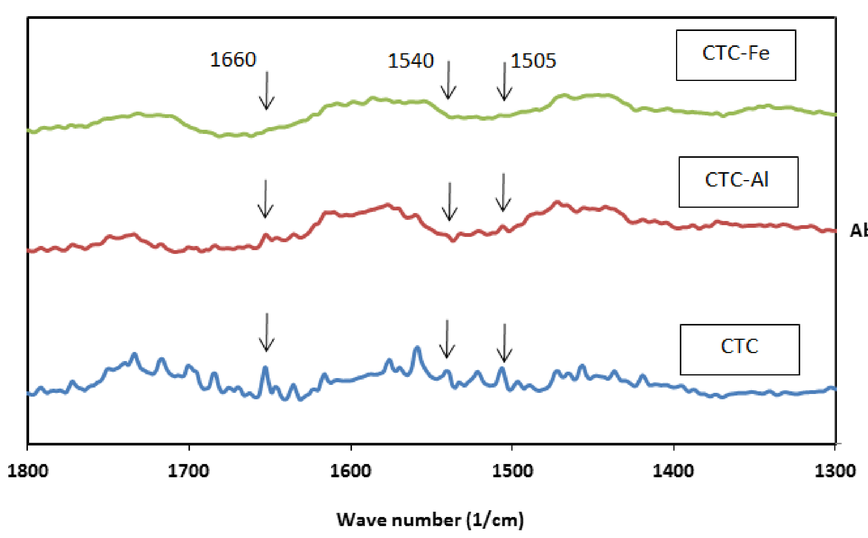


Stability constants of CTC-Al and CTC-Fe complexes

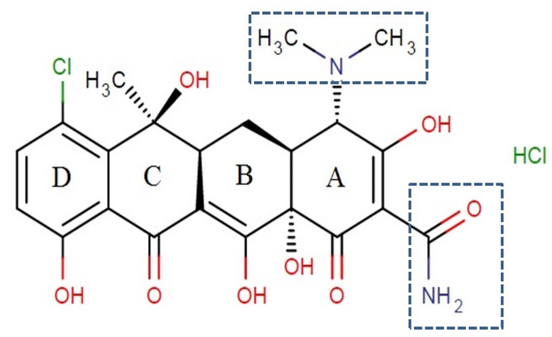
Complex	Log B1	Log B2
CTC-Fe	3.05	3.64
CTC-Al	2.91	3.48

Analysis

FTIR



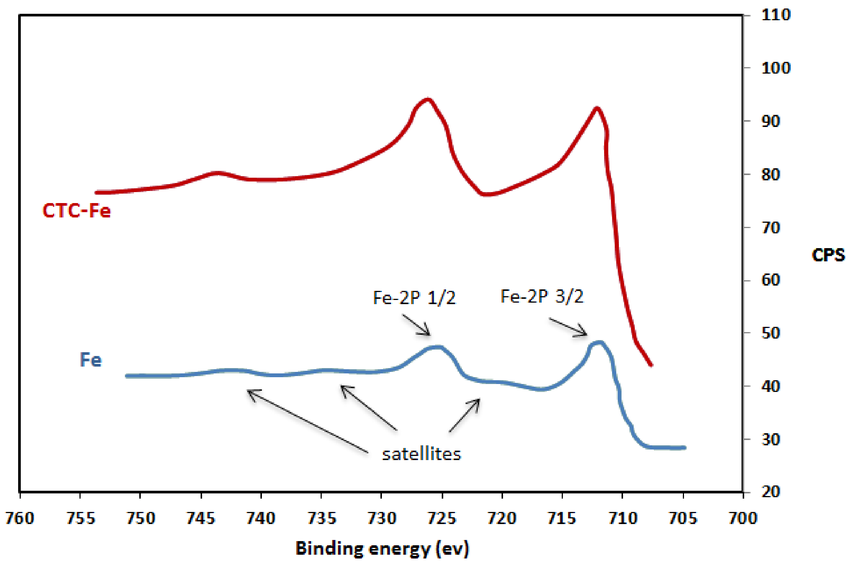
FTIR spectra of CTC, CTC-Al and CTC-Fe complexes



Molecular structure of CTC

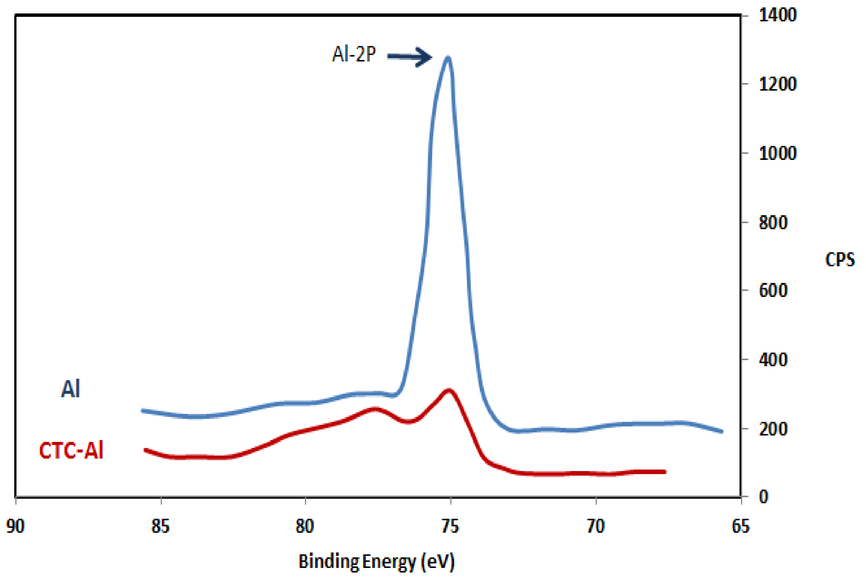
- The intensity of carbonyl (1660 cm^{-1}) and amino (1540 cm^{-1}) groups of amide in ring A and also amino moiety (1505 cm^{-1}) of the dimethylamine group in ring A decreased.
- These changes indicate that two functional groups (that is marked by dashed line molecular structure) participated in the complexation reaction.
- For iron, the decrease is intensities are more remarkable than those for aluminum which admits the higher value of stability constant.

XPS



XPS spectra of Fe and CTC-Fe complex

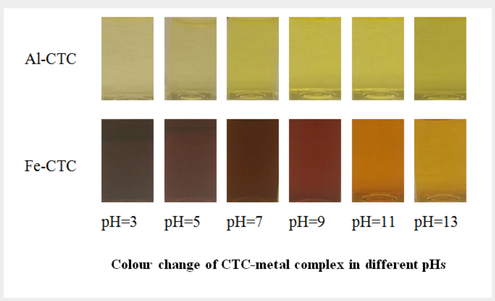
- ✓ The XPS spectra of Fe(III) complex shows a doublet peaks at 711.48 and 725.16 eV and three satellites positions are representative of Fe(III). However in CTC-Fe the shape is remarkably different (in terms of doublet positions and number of satellites) that confirms the chemical state of Fe is changed as a result of complexation.
- ✓ The XPS spectra of Al(III) complex shows a single peak at around 75 eV that is the characteristic of Al(III). However for CTC-Al complex a doublet is observed that means the chemical statues of Al is considerably changed.



XPS spectra of Al and CTC-Al complex

CONCLUSIONS

- CTC forms strong complex with iron and aluminum.
- The first and second stability constants were measured to be 2.91 and 3.48 for CTC-Al complex and 3.05 and 3.64 for CTC-Fe complex.
- High values of stability constants indicate that their persistence and toxicity are increased in wastewater and wastewater sludge.
- The FTIR spectra showed that the amine and amide groups of CTC participate in complexation.
- Also XPS spectra showed that the chemical status of FE(III) and Al(III) underwent fundamental changes after complexation.



Colour change of CTC-metal complex in different pHs

REFERENCES

1- Agwuh, Kenneth N., and Alasdair MacGowan. "Pharmacokinetics and pharmacodynamics of the tetracyclines including glycylcyclines." Journal of Antimicrobial Chemotherapy 58.2 (2006): 256-265.

2- Albert, Adrien. "Avidity of terramycin and aureomycin for metallic cations."Nature 172 (1953): 201.

3- Irving, H. M., & Rossotti, H. S. (1954). The calculation of formation curves of metal complexes from pH titration curves in mixed solvents. *Journal of the Chemical Society (Resumed)*, 2904-2910.

4- Chen, Gao, Ling Zhao, and Yuan-hua Dong. "Oxidative degradation kinetics and products of chlortetracycline by manganese dioxide." *Journal of hazardous materials* 193 (2011): 128-138.

5- Gu, Cheng, and K. G. Karthikeyan. "Interaction of tetracycline with aluminum and iron hydrous oxides." *Environmental science & technology* 39.8 (2005): 2660-2667.

6- Chastain, Jill, and Roger C. King, eds. Handbook of X-ray photoelectron spectroscopy: a reference book of standard spectra for identification and interpretation of XPS data. Eden Prairie, MN: Perkin-Elmer, 1992.