A STUDY TO DETERMINE THE CHEMICAL SPECIATION OF SELECTED HEAVY METALS IN ANAMMOX REACTOR

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Introduction

1. ANAMMOX BACTERIA

Anammox (anaerobic ammonium oxidation) process is an alternative process , that is studied for use in biological nitrogen removal in wastewater, to traditional nitrification and denitrification process. Annamox process is carried out by Annamox bacteria which is a special bacteria that operates in anaerobic conditions. Operating in anaerobic conditions result in reduction of the energy requirement for wastewater treatment, while producing less sludge thus making the sludge handling easier.

2. HEAVY METAL INHIBITION ON ANAMMOX BACTERIA

Annamox is a very common bacteria type that can be found easily in nature or man-made systems, though its sensitive to environmental conditions and influenced by a variety of inhibitory substances **(Isaka et al 2006; Gonzalez-Martinez et al. 2018)**. Sometimes, it can take up to six months to recover from an inhibition incident therefore it's mainstream usage is limited. Significant concentrations of heavy metals can be found in the some nitrogen-rich wastewater producing industries such as landfill leachates, livestock wastewaters, fertilizer industry wastewaters and metal refineries **(Baun and Chris-tensen 2004; Manipura et al. 2007; Lotti et al. 2012; Zhang et al. 2015b)**.These situation posing a threat to the potential use of annamox bacteria. Short-term and long term inhibitory effects of some heavy metals such as Cd^{2+} and Cu^{2+} on anammox bacteria are still being studied. Different threshold values have been evaluated from different studies **(Zhang et al.2016; Val del Rio et al. 2017)**, but it is well-known that, values are often related to the concentrations of metal in wastewater.

Objective

In this study, the theoretical speciation of some selected heavy metals, namely Cu and Cd heavy metals in a typcial synthetic anammox reactor was examined. The partitioning of heavy metals between solid and bulk phases impacts their bioavailability to Anammox bacteria and, therefore, their toxicity. For modeling, chemical speciation software (Visual MINTEQ) was used to predict the chemical speciation and behavior of heavy metals inside the Anammox reactor. By using the software heavy metal free-ion concentrations were simulated. The program was provided information on the wastewater composition and heavy metal concentrations. By running the model at a variety of concentrations, the influence of concentrations in the chemical speciation of heavy metals was comprehensively analyzed.

Material &Method

- Visual MINTEQ is the second most used chemical balance software application among researchers. It combines state-of-the-art explanations of sorption and complexation reactions with easy-to-use menus and options for importing and exporting data from or to Excel.
- In this thesis, Visual MINTEQ is used to observe in what quantities and how a specific heavy metals reacts with chemicals in synthetic water in an anammox reactor.

The following wastewater composition was used to determine the theoretical speciation of Cu^{2+} and Cd^{2+} separately in the Anammox feed wastewater

Table 1. Input data to be entered on Visual Minteq.

Compound	
NH_4^+-N / NO_2-N	200 / 220 mg/L
$NaHCO_3$	1.04 g/L
K_2HPO_4	174.2 mg/L
$CaCl_2$	73.5 mg/L
$MgCl_2$	102 mg/L
Trace Element Solution 1	1 ml/L
$Na_2EDTA{\cdot}2H_2O$: 10 g/L	
$FeSO_4$: 5 g/L	
Trace Element Solution 2	1ml/L
$Na_2EDTA{\cdot}2H_2O$: 10 g/L	
$ZnSO_4.7H_2O$: 0.43 g/L	
$CoCl_2.6\ H_2O$: 0.24 g/L	
$MnCl_2.4H_2O$: 0.99 g/L	
$CuSO_4.5H_2O$: 0.25 g/L	
$NiCl_2.6H_2O$: 0.19 g/L	
H_3BO_4 : 0.014 g/L	

In addition to the table, 1 mg/L, 2.5 mg/L, 5 mg/L, 7.5 mg/L,10 mg/L Cd^{2+} Cu^{2+} and was added respectively as varying compound.

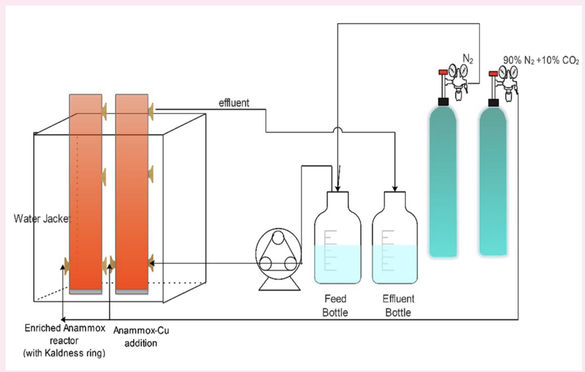

Figure 3. Reactor Setup used in experimental studies. Theoretical speciation was calculated using the feed composition of this reactor.

Figure 1. Screenshot of Visual Minteq screen to enter wastewater feed composition.

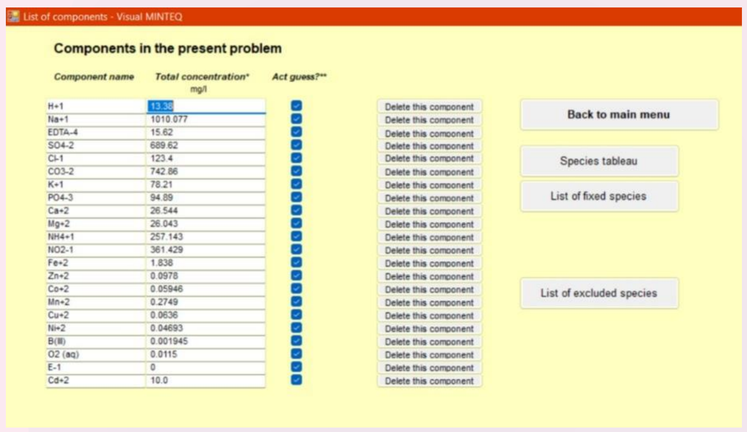

Figure 2. Screenshot of Visual Minteq screen shows components.

Output And Results

Table 2. Speciation of Cd^{2+} in the absence of bacterial adsorption.

	1 mg/L	2.5 mg/L	5 mg/L	7.5 mg/L	10 mg/L
$Cd(CO_3)_2^{-2}$	2.99E-08	5.46E-05	1.02E-05	6.30E-05	6.13E-05
$Cd(NH_3)_2^{+2}$	1.32E-08	2.28E-05	4.15E-06	2.80E-05	2.74E-05
$Cd(NH_3)_3^{+2}$	6.56E-11	2.05E-07	2.19E-08	1.33E-07	1.27E-07
$Cd(NH_3)_4^{+3}$	9.62E-14	5.44E-10	3.14E-11	1.86E-10	1.74E-10
$Cd(OH)_2$ (aq)	2.00E-11	3.52E-08	6.83E-09	4.24E-08	4.15E-08
Cd^{+2}	7.19E-06	3.79E-03	2.59E-03	1,.68E-02	1.73E-02
$CdCO_3$ (aq)	1.15E-06	1.12E-03	4.02E-04	2.54E-03	2.54E-03
$CdEDTA^{-2}$	1.00E+00	2.48	4.99	5.50	5.50
$CdH_2BO_3^+$	1.17E-12	1.10E-09	4.12E-10	2.16E-09	2.62E-09
$CdHPO_4$ (aq)	2.69E-06	2.39E-03	9.31E-04	5.99E-03	6.13E-03
$CdNH_3^{+2}$	5.80E-07	5.54E-04	2.04E-04	1.29E-03	1.30E-03
$CdOH^+$	1.10E-08	1.06E-05	3.87E-06	2.45E-05	2.46E-05

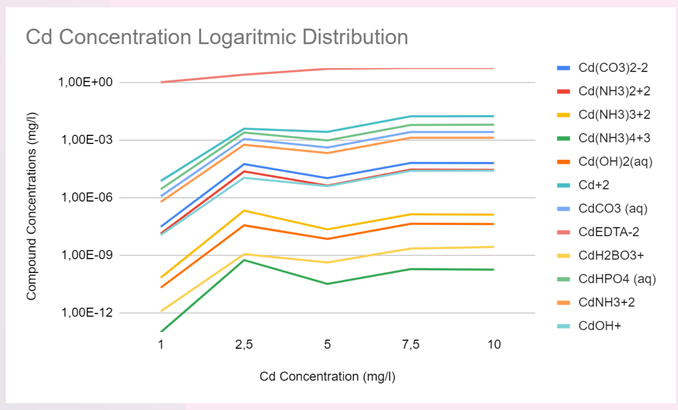

Figure 4. Cd^{2+} Concentration Logaritmic Distribution.

Table 3. Speciation of Cu^{2+} in the absence of bacterial adsorption.

	1 mg/L	2.5 mg/L	5 mg/L	7.5mg/L	10mg/L
$Cu(CO3)_2^{-2}$	1.12E-06	4.92E-05	1.21E-02	1.21E-02	1.21E-02
$Cu(OH)_2$ (aq)	2.12E-08	8.87E-07	2.16E-04	2.16E-04	2.16E-04
Cu^{+2}	2.67E-08	1.11E-06	2.72E-04	2.72E-04	2.72E-04
Cu-ads	1.53E-01	3.83E-01	6.19E-01	6.19E-01	6.19E-01
$CuCO_3$ (aq)	3.64E-06	1.56E-04	3.83E-02	3.83E-02	3.83E-02
$CuEDTA^{-2}$	8.46E-01	2.11E+00	3.37E+00	3.37E+00	3.37E+00
$CuHCO_3^+$	1.02E-08	4.39E-07	1.08E-04	1.08E-04	1.08E-04
$CuHEDTA^-$	1.44E-05	3.61E-05	5.75E-05	5.75E-05	5.75E-05
$CuHPO_4$ (aq)	3.55E-08	6.41E-07	1.49E-04	1.49E-04	1.49E-04
$CuOH^+$	7.18E-08	3.00E-06	7.32E-04	7.32E-04	7.32E-04
$CuOHEDTA^{-3}$	2.27E-04	5.67E-04	9.04E-04	9.04E-04	9.04E-04
$CuSO_4$ (aq)	8.71E-09	3.64E-07	8.89E-05	8.89E-05	8.89E-05

After the chemical speciation was determined, the precipitation and absorption values of cadmium and Cupper heavy metals in the synthetic reactor were investigated for different concentrations.

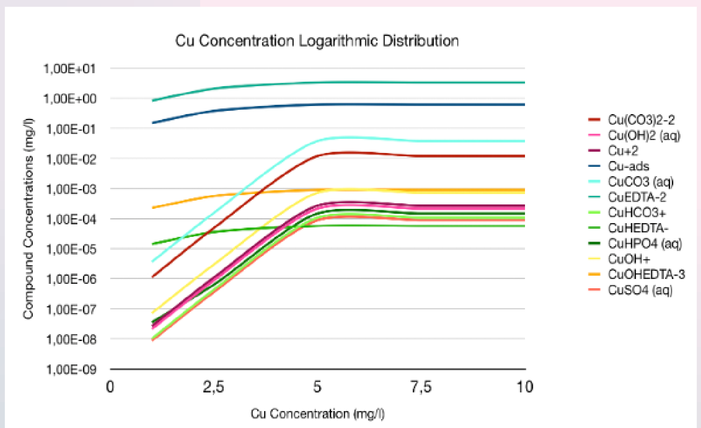

Figure 5. Cu^{2+} Concentration Logaritmic Distribution.

Table 4. Prediction of Bacterial Adsorption and Precipitation of Cd^{2+} at increasing concentrations.

Applied Cd (mg/L)	Cd free-ion concentration in mixed liquor	Soluble Cd Concentration	Precipitated Cd Concentration	Surface-bound Cd Concentration
1	4.68E-06	7.96E-01	0	0.20
2.5	1.69E-04	1.99	0	0.51
5	7.68E-04	3.98	0	1,02
7.5	0.016529	5.55	0.53	1.42
10	0.016988	5.55	3.03	1.42

Table 5. Prediction of Bacterial Adsorption and Precipitation of Cu^{2+} at increasing concentrations.

Applied Cu (mg/L)	Cu free-ion concentration in mixed liquor	Soluble Cu Concentration	Precipitated Cu Concentration	Surface-bound Cu Concentration
1	2.66E-08	8.46E-01	0	0.15
2.5	1.11E-06	2.12	0	0.38
5	2.72E-04	3.42	0.95	0.62
7.5	2.72E-04	3.42	3.45	0.62
10	2.72E-04	3.42	5.95	0.62

Conclusion

- The theoretical speciation of Anammox reactor in the presence of different cadmium and cupper concentrations and the inhibitive effect of these heavy metals was studied in this research.
- The theoretical results showed precipitation can be observed only after 7.5 mg/L of cadmium concentration. For cupper, precipitation began to observed at concentration of 5 mg/L.
- Specifically when Cu^{2+} concentration in the mixed liquor was 10 mg/L, approximately 59.5 % of total was removed abiotically by precipitation, Therefore only 3.42 mg/L of Cu^{2+} remain soluble in the system. These soluble portion of the Cu^{2+} available to anammox to impact on inhibition.
- On the other hand when cadmium concentration in the mixed liquor was 10 mg/L, precipitation percentage noted as 30.3 %, these indicates the remaining soluble portion is 5.55 mg/L in the system.
- The most dominant chemical speciation form for both heavy metal speciation was $CdEDTA^{2-}$ and $CuEDTA^{2-}$. $CdEDTA^{2-}$ concentration was observed 319 times more than Cd^{2+} concentration at 10 mg/L cadmium concentration. Because $CdEDTA^{2-}$ has a very complex structure, its inhibition effect on the anammox is far from critical levels.