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Effect of Chelating Agents on Metal Remobilization from Polluted Sediments

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Summary: Heavy metals can be remobilized from suspended materials and bottom sediments by changes in pH and redox potential conditions and by chelating with synthetic chelating agents such as EDTA and DTPA which are used in many industrial applications. Because of their low biodegradability, they are present in many aquatic systems where their strong chelating capacities can modify the transfer of toxic heavy metals between solid and liquid phases. In this study, the remobilization of several metals (Al, Cu, Pb, Fe, Mn and Zn) from polluted sediment in the presence of two different chelating agents EDTA and DTPA was investigated as a function of dissolutive equilibrium time, concentration of chelating agents and pH.

Introduction

Sediments can accept the pollutants from the depositing inputs, and act as carrier and temporary reservoirs of pollution because heavy metals are not permanently held by them and can be released back into the water column.[(1)] Within the sediment system, heavy metals will tend to reach equilibrium between the pore water and the solid phase. The partitioning equilibrium had shown to be influenced by some environmental factors such as: pH, redox potential, salinity, chelating agents, and temperature. [(2)] The three most commonly used types are the polyphosphate, hydroxycarboxylic acid and aminopolycarboxylic acid chelating agents. Aminopolycarboxylic acid chelating agents are used most frequently, because they bind metal ions more strongly than polyphosphates and maintain their sequestering ability over a wider pH range than hydrocarboxylic acid types.

Diethylenetriaminepentaacetic acid (DTPA), Ethylendiaminetetraacteic acid (EDTA), and their sodium salts, are used as chelating agents in the industry of soap, detergents, water treatment, metal finishing and plating, pulp and paper manufacture, synthesis of polymers, photographic products, textiles, scale removal and agriculture. They are synthetic complexing agents that have been utilized extensively as metal sequestrates by a wide variety of industries. The main uses of EDTA are in industrial cleaning, household detergents, photographic industry, pharmacy, textile and paper

manufacturing. Applications of DTPA include the inactivation of metal ions in the pulp and paper industry and use as a drug in heavy metal poisoning. [3]

EDTA occurs widely as a water pollutant because it is mostly used in aqueous solutions which are discharged after use via wastewater streams. Although EDTA is non-toxic to mammals at environmental concentrations, there is some concern about the potential of EDTA to remobilize toxic heavy metals out of sewage sludges and sediments.[4] The remobilization of heavy metals from natural sediment in the presence of DTPA has been the subject of few studies.

Experimental

Four sediment samples were collected along Rosetta branch near Kafr El-Zayat industrial area in August 2005 using hand corer sampler. Samples were analyzed for sediment texture and total heavy metals. The sample collected 100 meter downstream the industrial area was chosen for the experiment due to the high concentration of heavy metals. This sample was air dried at 25°C for two weeks, [5] crushed and sieved in 0.2 mm sieves to obtain a homogeneous sample.

A suspension of ratio 1 g : 1 L, sediment : water which is representative to natural surface sediment was prepared. This suspension was divided into four portions where EDTA (10^{-2} M) was added to the first portion, EDTA (10^{-4} M) was added to the second, DTPA (10^{-2} M) was added to the third and DTPA (10^{-4} M) was added to the fourth. The pH was adjusted once at pH 3 and the other at pH 7 for each portion at the start of each experiment and regulated during all the contact time by micro-addition of concentrated NaOH or HNO_3. The experiment was conducted in polyethylene flasks agitated on a vibrating table (170 rpm) at room temperature. Suspensions were analyzed after contact time 2, 4, 8, 16 and 32 hours.

Before analysis, samples were filtered through a 0.3 µm cellulose filter, acidified with HNO_3 and stored at 4°C. Samples were then analyzed for trace elements such as (Al, Cu, Pb, Fe, Mn and Zn) using Inductively Coupled Plasma-Mass Spectrometer (ICP-MS), Perkin Elmer, USA. Metals mobilization concentration is expressed in percentage of released metal to the total metal concentration in the original sediment sample.

Sediment Characterization

The sediment sample used was rich in sand and silt (loam) and highly polluted in Al, Mn, Fe, Pb, Cu, and Zn. The organic matter content (O.M.) determined by oxidation with potassium dichromate in acidic condition was 6.5 %. *Table (1*)

Table (1): Sediment characteristics

Al (mg/kg)	Mn (mg/kg)	Fe (mg/kg)	Pb (mg/kg)	Cu (mg/kg)	Zn (mg/kg)	O.M. (%)
178,000	3770	59800	20	140	320	6.5

Results and Discussion

Equilibrium time

The effect of the reaction time between water and the underneath sediment was studied using a bench experiment where the time needed to reach equilibrium between metal adsorption on solid phase (sediment) and release into liquid phase (water) "equilibrium time" was monitored through 32 hours.

In the presence of low concentration of EDTA (10^{-4} M) at pH 7, the results showed that equilibrium was reached after 16 hour for (Al, Zn and Mn) while for (Fe, Pb and Cu) equilibrium was not reached until the end of the experiment reaction time 32 hours. By increasing EDTA concentration (10^{-2} M), equilibrium was reached after 4 hour for (Fe), 16 hours for (Al) while the rest of metals studied (Cu, Mn, Pb and Zn) was not reached until the end of the experiment reaction time 32 hours.

In the presence of low concentration of EDTA (10^{-4} M) at pH 3, the results showed that equilibrium was reached after 8 hours for (Pb), 16 hour for (Al, Zn and Cu), while for (Fe and Mn) equilibrium was not reached until the end of the experiment reaction time 32 hours. By increasing EDTA concentration (10^{-2} M), equilibrium was not reached until the end of the experiment reaction time 32 hours for all studied metals.

In the presence of low concentration of DTPA (10^{-4} M) at neutral conditions, the results showed that equilibrium was reached after 8 hours for (Zn, Pb and Fe), while for (Al, Cu and Mn) equilibrium was not reached until the end of the experiment reaction time 32 hours. By increasing DTPA concentration (10^{-2} M), equilibrium was

reached after 8 hours for (Al, Mn and Pb), while for the rest of metals studied (Cu, Fe and Zn) it was not reached until the end of the experiment reaction time 32 hours.

Table (2): Release of metal as function of time in presence of EDTA

Reaction Time (hrs)			2	4	8	16	32
Metal	pH Value	Complexing agent Conc. (Molar)	Metal Conc. (%)				
Al	7	10^{-4}	0,50	0,40	0,44	0,25	0,24
		10^{-2}	12,92	15,67	13,97	12,47	12,16
	3	10^{-4}	0,61	0,71	0,62	0,73	0,79
		10^{-2}	6,35	6,07	6,63	8,03	10,34
Cu	7	10^{-4}	30,00	33,00	34,00	35,20	36,80
		10^{-2}	87,00	97,40	96,00	95,60	98,20
	3	10^{-4}	38,80	40,10	42,30	51,00	51,50
		10^{-2}	69,00	79,20	88,60	97,00	97,60
Fe	7	10^{-4}	3,70	2,04	1,08	0,68	1,62
		10^{-2}	55,85	59,87	60,44	61,71	62,10
	3	10^{-4}	5,08	6,76	6,61	7,98	10,02
		10^{-2}	24,41	25,92	30,95	38,96	43,48
Mn	7	10^{-4}	33,95	38,20	41,64	45,62	47,21
		10^{-2}	95,84	96,75	99,65	99,87	99,57
	3	10^{-4}	42,71	46,42	44,83	58,89	63,82
		10^{-2}	98,47	99,38	99,92	99,95	99,77
Pb	7	10^{-4}	3,26	3,04	3,04	3,48	4,40
		10^{-2}	24,35	51,30	45,65	55,65	58,70
	3	10^{-4}	0,00	0,22	0,00	0,00	0,00
		10^{-2}	10,43	16,78	16,96	21,30	36,52
Zn	7	10^{-4}	21,25	22,20	23,44	25,25	25,00
		10^{-2}	64,06	61,25	53,13	62,63	69,38
	3	10^{-4}	18,75	12,50	12,81	15,06	16,38
		10^{-2}	41,56	40,00	49,56	60,25	65,31

In the presence of low concentration of DTPA (10^{-4} M) at acidic conditions, the results showed that equilibrium was reached after 4 hours for (Zn), 16 hours for (Fe, Cu, Mn and Pb) while for (Al) equilibrium was not reached until the end of the experiment reaction time 32 hours. By increasing DTPA concentration (10^{-2} M), equilibrium was reached after 4 hours for (Pb), 8 hours for (Mn) and 16 hours for (Cu) while the rest of metals studied (Al, Fe and Zn) was not reached until the end of the experiment reaction time 32 hours.

Table (3): Release of metal as function of time in presence of DTPA

Reaction Time (hrs)			2	4	8	16	32
Metal	pH Value	Complexing agent Conc. (Molar)	Metal Conc. (%)				
Al	7	10^{-4}	0,94	0,91	0,60	0,38	0,56
		10^{-2}	16,12	18,71	15,70	14,21	14,52
	3	10^{-4}	0,26	0,37	0,18	0,26	0,48
		10^{-2}	7,98	8,03	6,85	8,26	10,62
Cu	7	10^{-4}	74,00	70,00	66,80	70,80	67,60
		10^{-2}	76,00	83,80	86,80	93,60	99,00
	3	10^{-4}	40,20	42,60	43,60	60,60	60,00
		10^{-2}	47,40	46,20	57,80	63,60	63,20
Fe	7	10^{-4}	5,55	4,16	2,66	2,49	3,01
		10^{-2}	46,35	47,89	45,44	45,64	52,78
	3	10^{-4}	6,52	7,53	8,39	10,92	10,72
		10^{-2}	25,42	29,26	32,44	39,13	42,47
Mn	7	10^{-4}	38,20	42,44	48,81	52,52	58,36
		10^{-2}	96,00	96,16	98,94	98,20	98,73
	3	10^{-4}	44,83	47,48	49,87	74,80	75,68
		10^{-2}	98,49	97,61	95,12	95,79	96,43
Pb	7	10^{-4}	10,87	12,61	23,09	22,17	21,26
		10^{-2}	23,04	25,22	26,52	27,35	27,30
	3	10^{-4}	19,13	23,48	25,00	28,70	29,70
		10^{-2}	29,83	37,83	36,96	38,26	41,74
Zn	7	10^{-4}	27,19	23,75	25,00	25,31	25,31
		10^{-2}	64,06	63,56	65,31	68,69	74,38
	3	10^{-4}	23,44	17,19	17,19	17,50	17,19
		10^{-2}	29,83	37,83	36,96	38,26	41,74

The decrease of metal mobilization by time may be attributed to an adsorption of the metal complex back to the sediment. A long term decrease of mobilization is expected due to the biodegradation of these complexes. **(6)**

Effect of chelating agent type

The release of metals as a function of chelating agent type either DTPA or EDTA was studied. Two experiments were conducted one using low concentrations of each chelating agent (10^{-4} M) and the other using high concentrations (10^{-2} M). Each experiment was conducted under acidic (pH 3) and neutral (pH 7) conditions.

Table (4): Effect of complexing agent type (concentration 10^{-4} M)

Complexing Agent Type		EDTA	DTPA
Metal	pH Value	Metal Conc. (%)	
Al	7	0,25	0,38
	3	0,73	0,26
Cu	7	35,20	70,80
	3	51,00	60,60
Fe	7	0,68	2,49
	3	7,98	10,92
Mn	7	45,62	52,52
	3	58,89	74,80
Pb	7	3,48	22,17
	3	0,00	28,70
Zn	7	24,25	25,31
	3	15,06	17,50

In presence of 10^{-4} M EDTA or DTPA, results showed that under acidic conditions (pH 3) DTPA has higher ability than EDTA to release all the metals under study except for Aluminum where EDTA has higher ability to release it than DTPA. Under neutral conditions (pH 7), the ability of DTPA for releasing all the metals under study was higher than EDTA for all studied metals.

This may be attributed to the higher stability constant of DTPA for all studied metals than that of EDTA with the same metals. **(7)** *Table (4*)

Table (5): Effect of complexing agent type (concentration 10^{-2} M)

Complexing Agent Type		EDTA	DTPA
Metal	pH Value	Metal Conc. (%)	
Al	7	12,47	14,21
	3	7,55	8,26
Cu	7	95,60	93,60
	3	97,00	63,60
Fe	7	61,71	45,64
	3	38,96	39,13
Mn	7	99,87	98,20
	3	99,95	95,79
Pb	7	55,65	27,35
	3	21,30	38,26
Zn	7	62,63	68,69
	3	60,25	58,13

In presence of 10^{-2} M EDTA or DTPA, results showed that under acidic conditions (pH 3), DTPA has higher ability than EDTA to release aluminum and lead, EDTA has higher ability than DTPA in releasing copper, and manganese, while

DTPA and EDTA nearly had the same ability to release zinc and iron. Under neutral conditions (pH 7), DTPA has higher ability than EDTA to release aluminum and zinc, EDTA has higher ability than DTPA in releasing copper, iron, manganese and lead. *Table (5*)

Effect of chelating agent concentration

The release of metals as a function of chelating agent concentration was studied at two concentrations 10^{-2} M and 10^{-4} M where two experiments were conducted using EDTA and DTPA under neutral (pH 7) and acidic (pH 3) conditions.

In table (6) it was clearly shown that metals release increase greatly in presence of higher concentration of EDTA both in neutral and acidic conditions, while metals release increase greatly in presence of higher concentration of DTPA both in neutral and acidic conditions.

Table (6): Effect of complexing agent concentration

Complexing Agent Conc. (Molar)			10^{-4}	10^{-2}
Metal	**Complexing Agent Type**	**pH Value**		
Al	EDTA	7	0,25	12,47
		3	0,73	7,55
	DTPA	7	0,38	14,21
		3	0,26	8,26
Cu	EDTA	7	35,20	95,60
		3	51,00	97,00
	DTPA	7	70,80	93,60
		3	60,60	63,60
Fe	EDTA	7	0,68	61,71
		3	7,98	38,96
	DTPA	7	2,49	45,64
		3	10,92	39,13
Mn	EDTA	7	45,62	99,87
		3	58,89	99,95
	DTPA	7	52,52	98,20
		3	74,80	95,79
Pb	EDTA	7	3,48	55,65
		3	0,00	21,30
	DTPA	7	22,17	27,35
		3	28,70	38,26
Zn	EDTA	7	24,25	62,63
		3	15,06	60,25
	DTPA	7	25,31	68,69
		3	17,50	58,13

This is attributed for both EDTA and DTPA to the following equation:

$$\text{ligand} + \text{metal} \leftrightarrow \text{metal-ligand}$$

So by increasing the ligand concentration, the reaction will be shifted to the right hand side so metal-ligand complex concentration increase.

Effect of pH

The release of metals as a function of pH level either neutral or acidic was studied. Two experiments were conducted in presence of EDTA and DTPA. Each experiment was conducted once using high concentration of chelating agent and other using low concentration.

It was shown that in presence of 10^{-4} M of EDTA the amount of released Al, Fe, Mn, and Cu in acidic conditions is higher than that released in neutral conditions while more amounts of Pb and Zn released in neutral conditions than in acidic conditions. In presence of 10^{-2} M of EDTA, the amount of Al, Cu, Fe, Pb and Zn released in neutral conditions is higher than in acidic conditions, while more Mn is released in acidic conditions than in neutral conditions. *Table (7)*

Table (7): Effect of pH (using EDTA complexing agent)

pH Value		7	3
Metal	**Comlpexing agent conc. (Molar)**	**Metal Conc. (%)**	
Al	10^{-4}	0,25	0,73
	10^{-2}	12,47	8,03
Cu	10^{-4}	35,20	51,00
	10^{-2}	95,60	97,00
Fe	10^{-4}	0,68	7,98
	10^{-2}	61,71	38,96
Mn	10^{-4}	45,20	58,89
	10^{-2}	99,87	99,95
Pb	10^{-4}	3,48	0,00
	10^{-2}	55,65	21,30
Zn	10^{-4}	24,25	15,06
	10^{-2}	62,63	60,25

It was shown that in presence of 10^{-4} M of DTPA the amount of released Fe, Mn, and Pb in acidic conditions is higher than that released in neutral conditions while more amounts of Cu, Al and Zn are released in neutral than in acidic conditions. In

presence of 10^{-2} M of DTPA, the amount of Al, Cu, Fe, Mn, and Zn released in neutral conditions is higher than that in acidic conditions while Pb released in acidic conditions is higher than in neutral conditions. *Table (8)*

This may be attributed to the higher competition abilities of these chelating agents than binding sites of sediment fractions at neutral pH conditions in case of both EDTA and DTPA complexing agents. These results are in good agreement with the diagrams shown by [8, 9] which had indicated that the degrees of complexations of ligands with heavy metals as function of pH were lower in acidic and alkaline conditions.

Table (8): Effect of pH (using DTPA complexing agent)

pH Value		7	3
Metal	**Complexing agent Conc. (Molar)**	**Metal Conc. (%)**	
Al	10^{-4}	0,38	0,26
	10^{-2}	14,21	8,26
Cu	10^{-4}	70,80	60,60
	10^{-2}	93,60	63,60
Fe	10^{-4}	2,49	10,92
	10^{-2}	45,64	39,13
Mn	10^{-4}	52,52	74,80
	10^{-2}	98,20	95,79
Pb	10^{-4}	22,17	28,70
	10^{-2}	27,35	38,26
Zn	10^{-4}	25,31	17,50
	10^{-2}	68,69	58,13

Conclusion

DTPA complexing ability is slightly higher than EDTA, it is poorly biodegradable. The time required by EDTA complexing agent to reach dissolutive equilibrium ranged from 16 to more than 32 hours which is the maximum time of

the experiment, while for DTPA complexing agent the time needed to reach dissolutive equilibrium ranged from 8, 16 to more than 32 hours.

The solublization of metals from polluted solids in the presence of complexing agents is the result of a competition between solid adsorption and solubilization by complexation depending on the complexing affinity of the complexing agent for a metal and on the affinity between the solid and a metal. Desorption order can be controlled by either the solid or the complexing agent. An increase of mobilization was noticed with the increase of complexing agent's concentration.

This study shows that EDTA and DTPA should be taken into account in environmental problems. Although a little risk is predicted for the metals trapped in the sediments to remobilize; except in accidental pollution, a similar study would be necessary to determine the optimal quantity of complexing agent that could increase the ability of the metal bound to the sediment to remobilize.

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