

**BEHAVIOUR OF SOME HEAVY METALS IN
WATER-SEDIMENT SYSTEM OF EL-SALAM
CANAL AS AFFECTED BY ADDED MnO₂**

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ABSTRACT: Mn and Fe oxides are one of the most soil and sediment components affecting various chemical redox reactions under anaerobic conditions. The effect of MnO₂ on the behaviour of some heavy metals was studied in sediment samples taken from El-Salam Canal. It is shown that all sediment suspensions reach reducing conditions after a few days of submergence. Addition of MnO₂ importantly enhanced the removal of As, Cu, Ni and Pb from the overlying water particularly at the first period of waterlogging. This effect indicates the possible role of some native sediment components such as MnO₂ on the removal of some heavy metals through some redox chemical reactions which can convert such metals to insoluble or immobile forms which reduce their environmental hazard effect.

INTRODUCTION

El-Salam Canal is one of the national promising projects involves the reuse of drainage waters. Bahr Hadous drain (1.905 billion m³) and El-Serw drain (0.435 billion m³) are the main

sources for the water of the canal in addition to Nile water (2.11 billion m³) (DRI, 1993).

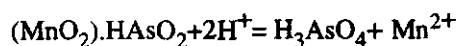
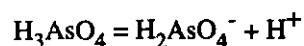
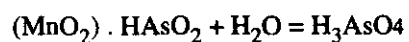
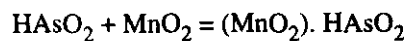
The canal extends through deposits of varying modes of formation including fluvial, marine, lacustrine and aeolian

(Said, 1990). Its total length is about 242 km divided into two parts viz, 87 and 155 km in western and eastern banks of Suez Canal, respectively.

About 400,000 feddans in North Sinai will be reclaimed using El-Salam Canal water, (JICA, 1996). Heavy metal content in the water could be a limiting factor for the reuse of drainage water for agriculture. In this respect, Shawky et al., (1994) found that the water of Bahr Hadous drain contains high levels of Cu, Pb, Cd and Co. However, Farag and Mehana (2000) found that the concentration of heavy metals (Fe, Mn, Zn, Cu, Pb, Cd, Co, Ni) in El-Salam Canal water are much lower than their maximum permissible limits for irrigation water. The role of transition metal oxide/hydroxide minerals such as Mn oxide, in redox reactions in soils and aqueous sediments is pronounced (Stumm and Morgan, 1970 ; Oscarson et al., 1981). Mn oxide, occurs as

suspended particles, in surface water and as coatings on soil and sediments. Mn (III/IV) can play an important role in soils and sediments via oxidation of inorganic cations. Both advantageous and deleterious effects to environmental quality can be involved. The positive side, involves oxidation of arsenite (As III) to arsenate (As V) by Mn (III/IV) oxides (Oscarson et al., 1980). The negative side is oxidation of chromic (Cr III) to chromyl (Cr VI) which is very mobile in soils and sediments (Amacher and Baker, 1982). As (V) can be reduced to As (III) by bacteria and phytoplankton (Andreae and Klumpp, 1979).. Johnson and Pilson (1975) concluded that As (III) could be oxidized to As (V) under sea water conditions. Mn (III/IV) oxides play an important role in the abiotic oxidation of As (III) to As (V) (Oscarson et al., 1980 & 1981). This is very vital effect because As (III) is very toxic pollutant and more soluble

and mobile (Deuel and Swoboda, 1972) than As (V). When As (III) added to MnO_2 , it can be oxidized to As (V) (Oscarson et al., 1981) or sorbed on the oxide surface. The oxidation of As (III) by MnO_2 can be shown by Oscarson et al., (1983) as follows :



Each mole of As (III) oxidized releases about 1.5 moles H^+ into the system. pH will be lowered but around ~ 7.0. Each mole of As (III) oxidized to As (V) results in a mole of Mn (IV) to be reduced to Mn (II) which can be partially dissolved in solution (Oscarson et al., 1981).

On the other hand, manganese oxide, and hydroxide, may also catalyze the oxidation of other heavy metals such as Cu^{2+} , Ni^{2+} , and Pb^{2+} by disproportionation to

Mn^{2+} and MnO_2 (Hem, 1978). The disproportionation results in vacancies in the Mn oxide structure. Since the Mn^{2+} and Mn^{3+} in the oxides, have similar physical size, as Cu^{2+} , Ni^{2+} and Pb^{2+} , these metals can occupy the vacancies in the Mn oxide and became part of the structure, with disproportionation or with other redox processes involving Mn oxide, the solubility of the metals can be affected.

The aim of the current study is to investigate the effect of Mn oxide on the behavior of As (III), Cu (II), Ni (II) and Pb (II) in the sediments of El-Salam Canal.

MATERIALS AND METHODS

Five sediment samples and five water samples were collected from Bahr Hadous Drain intersection point with El-Salam Canal. The sampling was repeated five Km far along. The sediment samples were air dried and crushed to pass a 2 mm sieve before use. The samples were analysed for total form of Fe,

Mn, Cu, Pb, Ni and As after digested in acid mixtures (Chapman and Pratt, 1961). pH of the samples was determined using a standard method. Some physical and chemical properties of the sediment samples are presented in Table 1. Some chemical characteristics of the water samples are shown in Table 2.

All experiments were carried out on soil suspensions made up by putting 50 g of sediment and 140 ml of deionized water in 250 ml conical flasks. All flasks were received 10 ml solutions in order to add $5 \mu\text{g l}^{-1}$ from As^{3+} , Cu^{2+} , Ni^{2+} , Pb^{2+} using NaAsO_2 , $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ and $\text{Pb}(\text{CH}_3\text{COO})_2$. As such sediment to water suspensions of 1/3 was obtained.

The experiment carried out in ten flasks, half of them treated with 0.2% freshly prepared MnO_2 (birnessite) (Mckenzie, 1971) while the rest were left without treating. Each treatment was repeated 3 times. All flasks

were flushed with nitrogen gas and continuously stirred for half an hour at the beginning of the experiment. After that, all flasks were incubated under closed system conditions at $20^\circ\text{C} \pm 1.0^\circ\text{C}$. There were a set of flasks for every period of determination.

After 0, 2, 4, 6, 8, 10, 12 and 14 days, redox potential (Eh) and pH were measured using platinum and glass electrodes, respectively while a calomel electrode was used as a reference. Suspensions were centrifuged and filtered and the filtrates were analysed for Fe, Mn, As, Cu, Ni and Pb according to standard methods.

RESULTS AND DISCUSSION

Redox potential evolution

The redox potential (Eh) is one of the most important sediment physico-chemical parameters expressing its reducing power.

The evolution of the redox potential measured at intervals following submergence is given

Table (1) : Some physical and chemical properties of the sediments used

No.	Texture	CaCO ₃ (g kg ⁻¹)	Organic Matter (g kg ⁻¹)	Total N (g kg ⁻¹)	CEC (c mol kg ⁻¹)	pH (1 : 25)	Fe ₂ O ₃ (g kg ⁻¹)	Total Fe %	Total Mn (mg kg ⁻¹)	Total heavy metals(mg kg ⁻¹)			
										As	Cu	Ni	Pb
1	Clay	29.6	1.9	1.4	35.2	7.78	14.6	6.62	1095	2.90	32.1	18.2	28.2
2	Clay	30.1	1.3	1.1	35.7	7.76	13.9	6.58	1036	2.62	30.6	18.1	28.3
3	Clay	27.8	1.3	1.0	35.4	7.79	13.1	6.67	1012	2.33	29.2	17.6	27.7
4	Clay	31.0	1.0	1.2	34.9	7.72	12.8	6.66	1003	2.21	29.7	17.8	27.9
5	Clay	21.9	1.8	1.3	33.8	7.71	11.9	6.41	1006	2.06	29.9	17.7	26.3

Table (2): EC (dSm^{-1}), pH and concentrations of total heavy metals ($\mu\text{g l}^{-1}$) in water samples at different studied locations along El-Salam Canal.

Sample No.	EC dSm^{-1}	pH	Heavy metals concentration $\mu\text{g l}^{-1}$					
			Fe	Mn	As	Cu	Ni	Pb
1	1.22	7.83	1832	165.2	7.6	19.7	33.7	22.4
2	1.20	7.79	1522	152.1	6.2	15.1	27.6	23.12
3	1.26	7.95	1493	150.3	5.8	13.1	28.2	17.60
4	1.18	7.86	1309	132.1	4.1	11.4	25.1	10.90
5	1.23	7.82	1220	121.7	3.8	11.8	19.6	8.60

in Table (3). Data reveal that redox potential rapidly decreased, reaching reducing conditions within a few days. A rapid decline was associated with the non MnO_2 treated samples reaching Eh values of 0.0 to -27mV comparing to 10 to -12 mV for sediment samples, treated with MnO_2 after 2 days of flooding. Atta and Cleemput (1981) found that a rapid decline in redox potential is characteristic of soils with a low content of

reducible iron and manganese and a high content of easily oxidizable organic matter. It is note worthy that although the relatively high content of the native manganese in the five sediment samples (Table 1), but it could be mostly subjected to conversion to well crystalline form via aging processes, hence its reduction under such conditions could be lower than the freshly precipitated form. The former is characterized by its

Table (3): Evolution of sediment suspension Eh (mV) as affected by MnO₂ addition during the term of incubation

Sediment No.	MnO ₂ %	Time, days								
		0	1	2	4	6	8	10	12	14
1	0.0	300	90	0.0	-72	-123	-153	-205	-220	-230
	0.2	315	100	10.0	-63	-100	-142	-182	-193	-197
2	0.0	305	82	-21	-83	-127	-162	-209	-230	-234
	0.2	310	93	-12	-61	-105	-143	-178	-196	-199
3	0.0	302	90	-27	-92	-121	-167	-212	-235	-239
	0.2	315	83	-8	-71	-103	-148	-187	-189	-191
4	0.0	305	100	-22	-93	-112	-170	-215	-241	-245
	0.2	312	82	-9	-76	-105	-141	-189	-196	-198
5	0.0	307	102	-23	-95	-117	-179	-220	-236	-239
	0.2	310	87	-10	-71	-102	-146	-167	-202	-206

hard reducibility comparing to the freshly prepared one (Ponnamperuma, 1972). The total changes in Eh between the initial and final values were 512, 509, 506, 510 and 516 mV for MnO₂ treated sediment samples, respectively. The corresponding values for the non treated sediment were 530, 539, 541, 549 and 546 mV. This indicates that MnO₂ addition maintains the redox potential of the system at higher Eh values.

pH

Data in Table (4) show that the pH of the sediment suspensions changes towards the neutral side after submergence. This effect was found true with all sediment samples under study. Patrick and Mikkelsen (1971) reported that the pH of acid soils increases upon water logging, and the opposite was that for alkaline soils. This tendency indicates that the pH of suspensions is buffered around neutrality by some substances produced as a result of reduction processes.

Iron and manganese compounds in the form of hydroxides and carbonates and carbonic acid are likely to involve as buffering pH materials under such conditions (Ponnamperuma, 1972).

Water soluble Fe

The effect of MnO₂ addition on the water soluble Fe is presented in Table (5). It is clear that in the case of absence of MnO₂ which possesses a relatively low Eh values (Table 3) the considerable increase in water soluble Fe occurred after 4 days of incubation. This delaying period, can be due to the well known fact that manganese compounds are reduced before iron ones. The relatively low amounts of water soluble Fe in all sediment samples treated with MnO₂ may be due to the higher Eh of the system.

MnO₂ addition poisoned the redox system at a relatively high oxidized state (Patrick and Mikkelsen, 1971). Under such conditions, relatively few

Table (4): Evolution of sediment suspension pH as affected by MnO₂ addition during the term of incubation

Sediment No.	MnO ₂ %	Time, days								
		0	1	2	4	6	8	10	12	14
1	0.0	7.79	7.53	7.50	7.43	7.33	7.26	7.20	7.13	7.11
	0.2	7.78	7.56	7.49	7.33	7.21	7.18	7.14	7.12	7.10
2	0.0	7.78	7.56	7.43	7.38	7.20	7.14	7.11	7.10	7.10
	0.2	7.79	7.62	7.41	7.36	7.21	7.15	7.10	7.08	7.06
3	0.0	7.79	7.71	7.43	7.30	7.26	7.20	7.13	7.11	7.11
	0.2	7.79	7.61	7.45	7.32	7.24	7.20	7.12	7.10	7.10
4	0.0	7.73	7.63	7.41	7.30	7.21	7.17	7.15	7.11	7.10
	0.2	7.74	7.60	7.42	7.32	7.23	7.16	7.11	7.10	7.10
5	0.0	7.26	7.63	7.40	7.31	7.19	7.16	7.10	7.08	7.05
	0.2	7.25	7.65	7.42	7.36	7.18	7.15	7.13	7.11	7.03

Table (5): Water soluble Fe^{2+} concentration (mg l^{-1}) in the sediment suspensions as affected by MnO_2 addition during the term of incubation

Sediment No.	MnO_2 %	Time, days								
		0	1	2	4	6	8	10	12	14
1	0.0	0.01	0.13	0.62	0.66	0.70	0.75	0.32	0.22	0.12
	0.2	0.01	0.09	0.21	0.27	0.35	0.42	0.20	0.13	0.10
2	0.0	0.02	0.26	0.76	0.81	0.92	0.76	0.37	0.26	0.14
	0.2	0.02	0.08	0.26	0.32	0.33	0.40	0.25	0.12	0.12
3	0.0	0.11	0.29	0.68	0.71	0.81	0.89	0.42	0.29	0.16
	0.2	0.11	0.09	0.22	0.30	0.36	0.41	0.27	0.13	0.10
4	0.0	0.01	0.23	0.76	0.88	0.93	0.95	0.43	0.23	0.17
	0.2	0.01	0.07	0.23	0.37	0.40	0.43	0.23	0.14	0.12
5	0.0	0.02	0.29	0.60	0.72	0.81	0.87	0.51	0.26	0.16
	0.2	0.02	0.09	0.20	0.23	0.32	0.35	0.27	0.14	0.14

amounts of Fe are converted to water soluble Fe via reduction and hence remain in a solid form (Rabenhorst and James, 1992 ; Leonard et al., 1995 ; Rabenhorst, 1997 and Hussein and Rabenhorst, 1999).

Table (5) also reveal that water soluble Fe continued to increase in all sediment samples from 4 to 10 days then sharply declined by the end of the incubation course. This effect may be due to the precipitation of water soluble Fe by sulfide ions formed as a result of reduction of SO_4^{2-} under such extremely reduced conditions as shown in Table 3 which indicates that all sediment samples have Eh values between -191 and -254 mV which satisfy the reduction of SO_4^{2-} to S^{2-} ions (Jakoben et al., 1981).

Water soluble Mn

Data in Table 6 depict that flooding of sediment samples resulted in an increase in water soluble-Mn in all studied treatments particularly when

MnO_2 was added. It is worthwhile to note that water soluble Fe started to increase only after 4 days (Table 5), while water soluble Mn started to increase almost immediately after submergence. The differences among the two elements may be due to the high positive redox potential required for Mn reduction comparing to Fe. Saoud et al., (1986) attributed these effects to the differences in solubility between Fe and Mn compounds.

The final lowest concentration values of water soluble Mn may be due to its precipitation as Mn sulfide (Ponnamperuma, 1972).

Water soluble As

Data in Table 7 manifest the effect of the oxidizing power of the MnO_2 treated sediment samples with respect to As (III). It is shown that MnO_2 addition caused a sharp decrease in the water soluble As (III) content in all sediment samples during the initial period of incubation. This suggests as was found by

Table (6): Water soluble Mn²⁺ concentration (mg l⁻¹) in the sediment suspensions as affected by MnO₂ addition during the term of incubation

Sediment No.	MnO ₂ %	Time, days								
		0	1	2	4	6	8	10	12	14
1	0.0	1.01	1.79	1.81	1.21	1.01	0.80	0.61	0.32	0.21
	0.2	1.21	3.86	3.92	3.12	2.96	1.21	1.11	0.71	0.32
2	0.0	1.10	1.62	1.68	1.12	1.01	0.62	0.52	0.21	0.18
	0.2	1.20	3.13	3.52	3.02	2.81	1.10	0.96	0.62	0.29
3	0.0	1.20	1.52	1.62	1.10	0.92	0.53	0.42	0.24	0.17
	0.2	1.30	3.21	3.70	3.00	2.65	1.21	0.86	0.50	0.23
4	0.0	1.22	1.43	1.52	1.13	0.86	0.46	0.39	0.26	0.18
	0.2	1.35	3.51	3.81	3.12	5.25	1.31	0.76	0.43	0.25
5	0.0	1.20	1.36	1.42	1.11	0.93	0.52	0.22	0.29	0.17
	0.2	1.30	3.62	3.94	3.01	2.46	1.03	0.71	0.46	0.28

Table (7): Water soluble As³⁺ concentration (mg l⁻¹) in the sediment suspensions as affected by MnO₂ addition during the term of incubation

Sediment No.	MnO ₂ %	Time, days								
		0	1	2	4	6	8	10	12	14
1	0.0	3.64	3.01	2.12	1.13	0.87	0.36	0.22	0.17	0.11
	0.2	3.65	2.02	1.32	0.91	0.36	0.20	0.13	0.10	0.02
2	0.0	3.62	3.12	2.13	1.19	0.96	0.42	0.26	0.16	0.10
	0.2	3.62	2.11	1.34	0.82	0.38	0.23	0.16	0.08	0.02
3	0.0	3.60	3.31	2.16	1.22	0.91	0.51	0.29	0.18	0.11
	0.2	3.61	2.02	1.37	0.65	0.41	0.21	0.16	0.09	0.01
4	0.0	3.43	3.06	2.19	1.23	0.98	0.59	0.31	0.19	0.11
	0.2	3.42	2.11	1.42	0.56	0.45	0.26	0.17	0.08	0.06
5	0.0	3.42	3.11	2.22	1.36	0.86	0.66	0.33	0.18	0.10
	0.2	3.41	2.01	1.51	0.69	0.51	0.21	0.12	0.07	0.02

Oscarson et al. (1981) that Mn (IV) oxides were very effective abiotic oxidant with respect to As (III). This behavior means that at the initial period of submergence, as MnO_2 is subjected to reduction, it acts as As (III) oxidant, hence water soluble As decreases. The conversion of As (III) to As (IV) through the oxidation of As (III) by MnO_2 leveled off with elapsing time. Luh et al., (1973) and Gohda, (1974) stated that manganese is the main sediment component responsible for the oxidation of As (III). Deuel and Swoboda, (1972) cleared the difference in solubility between As (III) and As (V). As (V) has very low solubility comparing to As (III).

The oxidation of As (III) to As (V) by Mn (IV) is a thermo-dynamically favorable (Oscarson et al., 1980 ; Oscarson et al., 1981). It was found that synthetic Mn (IV) oxide was very effective on lowering the concentration of added As (III) to the sediment samples. This was

found true under all sediment samples.

Since the reduced state As (III) (arsenite) is much more toxic (Webb, 1966 and Penrose, 1974) and more soluble and mobile than the oxidized state As (V), consequently, the obtained data is of great importance with respect to aquatic environmental quality.

After 12 days of submergence, data in Table (7) reveal that the As (III) concentration reaches the lowest values which may be due to its precipitation as sulfide under the extremely low redox potential conditions (Table 3).

The MnO_2 treated sediment samples had a higher Eh than the untreated sediments (Table 3). The lower the redox potential of the system, the more energy was required to affect the transfer of electrons from As (III) to the sediment because the electron activity is greater (Sparks, 1995).

Cu, Ni and Pb

Data in Tables (8, 9,10) reveal that Mn (IV) oxide was very

Table (8): Water soluble Cu^{2+} concentration (mg l^{-1}) in the sediment suspensions as affected by MnO_2 addition during the term of incubation

Sediment No.	MnO_2 %	Time, days								
		0	1	2	4	6	8	10	12	14
1	0.0	4.64	4.01	2.10	1.81	1.61	1.21	1.02	0.76	0.21
	0.2	4.65	2.22	1.72	1.02	1.03	0.72	0.61	0.21	0.11
2	0.0	4.82	4.10	2.21	1.71	1.51	1.36	1.12	0.65	0.11
	0.2	4.81	2.36	1.65	1.02	0.92	0.61	0.73	0.21	0.10
3	0.0	4.92	4.32	2.36	1.82	1.63	1.30	1.16	0.93	0.19
	0.2	4.92	2.13	1.51	1.23	0.82	0.71	0.52	0.36	0.12
4	0.0	4.82	4.13	2.11	1.96	1.52	1.21	1.11	0.82	0.21
	0.2	4.81	2.10	1.46	1.32	0.73	0.61	0.43	0.21	0.11
5	0.0	4.63	4.01	2.22	1.81	1.71	1.13	1.11	0.96	0.20
	0.2	4.61	2.13	1.78	1.11	0.70	0.72	0.37	0.12	0.11

Table (9): Water soluble Ni²⁺ concentration (mg l⁻¹) in the sediment suspensions as affected by MnO₂ addition during the term of incubation

Sediment No.	MnO ₂ %	Time, days								
		0	1	2	4	6	8	10	12	14
1	0.0	4.82	4.21	2.01	1.96	1.73	1.38	1.12	0.82	0.11
	0.2	4.83	2.01	1.63	1.43	1.11	0.82	0.51	0.35	0.10
2	0.0	4.85	4.32	2.11	1.81	1.65	1.22	1.02	0.76	0.09
	0.2	4.84	2.10	1.53	1.36	1.22	1.03	0.41	0.21	0.08
3	0.0	4.83	4.13	2.23	1.62	1.53	1.45	1.02	0.65	0.12
	0.2	4.82	2.32	2.02	1.26	1.41	1.11	0.51	0.31	0.09
4	0.0	4.76	4.22	1.96	1.71	1.46	1.36	1.06	0.71	0.13
	0.2	4.75	2.04	1.52	1.12	1.00	0.89	0.62	0.22	0.08
5	0.0	4.75	4.36	1.82	1.82	1.23	1.21	1.07	0.63	0.11
	0.2	4.74	2.11	1.33	1.12	1.03	0.83	0.73	0.21	0.11

Table (10): Water soluble Pb^{2+} concentration ($mg\ l^{-1}$) in the sediment suspensions as affected by MnO_2 addition during the term of incubation

Sediment No.	MnO_2 %	Time, days								
		0	1	2	4	6	8	10	12	14
1	0.0	4.70	2.2	1.70	1.50	1.21	1.10	0.93	0.21	0.11
	0.2	4.68	1.5	1.00	0.92	0.30	0.20	0.10	0.01	0.01
2	0.0	4.62	2.1	1.60	1.4	1.22	1.12	0.96	0.23	0.13
	0.2	4.60	1.4	1.02	0.91	0.36	0.22	0.11	0.02	0.01
3	0.0	4.60	2.2	1.72	1.5	1.29	1.14	0.82	0.26	0.16
	0.2	4.61	1.3	1.23	0.82	0.37	0.25	0.13	0.01	0.01
4	0.0	4.58	2.1	1.63	1.32	1.20	1.16	0.87	0.29	0.13
	0.2	4.58	1.3	1.10	0.82	0.30	0.27	0.12	0.01	0.01
5	0.0	4.53	2.2	1.51	1.33	1.27	1.18	0.81	0.27	0.16
	0.2	4.52	1.4	1.12	0.96	0.36	0.24	0.11	0.02	0.02

effective in removing Cu, Ni and Pb from the overlying water of the studied sediment suspensions.

MnO₂ treated sediment samples exhibited a sharp decrease in water soluble Cu, Ni and Pb particularly during the initial period of incubation, where after, a gradual decrease was noted in all sediment samples by then, a sharp decline was noted by the end of incubation period. The first decrease in water soluble Cu, Ni and Pb particularly in MnO₂ treated sediment samples can be due to catalyzing the oxidation of these heavy metals by disproportionation to Mn²⁺ and MnO₂ (Hem, 1978, Sparks, 1995). The decrease in water soluble forms of these elements thereafter may be due to destruction of MnO₂ via reduction reactions which can be noted from the increase in the concentration of water soluble Mn (Table 6). The net result is the liberation of heavy metals which adsorped on the surface of MnO₂.

The final decrease in the concentration of water soluble forms of these elements may be due to the precipitation of these metals as sulfides under the extremely low redox potential (Table 3). Stumm and Morgan (1970) pointed out that on the basis of solubility product constants of sulfide compounds, elements such as Pb, Co, Ni, Hg, Ag, Cu and Zn remain essentially fixed in reducing sidements of the pore water with a sulfide concentration of 10⁻⁹ mol per litre. The solubility product of metal sulfides are 6.3 x 10⁻³⁶, 3.2 x 10⁻⁸, 1.4 x 10⁻¹⁵, 3.2 x 10⁻¹⁹ and 3.2 x 10⁻²⁷ for Cu S, Fe S, Mn S, Ni S and Pb S, respectively.

REFERENCES

- Amacher, M.C. and D.E. Baker (1982) : Redox reactions involving chromonium, plutonium and manganese in soils. Doe/Dp/ 04515 - 1. State Univ. Univ. Park, PA.
- Andreae, M.O. and D. Klumpp (1979) : Biosynthesis and

- release of organo-arsenic compounds by marine algae. Environ. Sci. Technol. 13 : 738 - 741.
- Atta, S.K. and O. Van Cleemput (1981) : Redox potential characteristics and nitrate reduction in some Egyptian soils. Alex. Sci. Exch. 2 : 176 - 185.
- Chapman, H. and P.F. Pratt (1961) : Methods of Analysis for Soils, Plants and Waters, Univ. of California, Division of Agric. Sci.
- Deuel, L.E. and A.R. Swoboda (1972) : Arsenic solubility in a reduced environment. Soil Sci. Amer. Proc. 36 : 276 - 278.
- Drainage Research Institute (DRI), (1993) : Drainage Water, Vol. III Drainage Water Reuse Project.
- Farag, F.M. and T.A. Mehana (2000) : Studies on the quality of El-Salam Canal water and its sources, Conferences of Social and Agric. Develop. of Sinai, El-Arish. 523 - 533.
- Gohda, S. (1974) : The content and oxidation state of arsenic and antimony in coastal water of Japan. J. Oceanogr. Soc. Jap. 30, 163 - 167.
- Hem, J.D. (1978) : Redox processes at the surface of manganese oxide and their effects on aqueous metal ions. Chem. Geol. 21 : 199 - 218.
- Hussein, A.H. and M.C. Rabenhorst (1999): Variability of properties used as differentiating criteria in tidal marsh soils. Soil Sci., 164: 48-56.
- Jakobsen, P. ; W.H. Patrick, Jr. and B.G. Jillians (1981): Sulfide and methane formation in soils and sediments. Soil Sci., 132: 279-287.
- Japan International Cooperation Agency (JICA) (1996) : The feasibility study on the North Sinai integrated rural development project, Phase II, Interim Report.

- Johnson, D.I. and M.E.A. Pilson (1975) : The oxidation of arsenite in sea water. *Environ. Butt.* 8, 157 – 171.
- Leonard, L.A. ; A.C. Hine and M.E. Luther (1995): Surficial sediment transport and deposition processes in a vuncus roemerianus marsh, West-Central Florida. *J. Coastal. Res.*, 11: 322-336.
- Luh, M.D. ; K.A. Barker and D.E. Henley (1973) : Arsenic analysis - and toxicity- a review. *Total Environ.* 2 : 1 – 12.
- Mckenzie, R.M. (1971) : The synthesis of birnessite, cryptomelane, and some hydroxides of manganese. *Mineral. Mag.* 38 : 493 – 505.
- Oscarson, D.W. ; P.M. Huang; C. Defosse and A. Herbillon (1981) : Oxidative power of Mn (IV) and Fe (III) oxides with respect to As (III) in terrestrial and aquatic environments. *Nature (London)* 29 : 50 – 51.
- Oscarson, D.W. ; P.M. Huang and U.T. Hammer (1983) : Oxidation and sorption of arsenite by manganese dioxide as influenced by surface coatings of iron and aluminum oxides and calcium carbonate. *Water, Air, Soil Pollut.* 20 : 233 – 244.
- Oscarson, D.W. ; P.M. Huang and W.K. Liaw (1980) : The oxidation of arsenite by aquatic sediments. *J. Environ. Qual.* 9 : 700 – 703.
- Oscarson, D.W. ; P.M. Huang and W.K. Liaw (1981) : Role of manganese in the oxidation of arsenite by fresh water lake sediments. *Clays and Clay Minerals*, 29 (3) : 219 – 225.
- Patrick, W.H. and D. Mikkelsen (1971) : Plant nutrient behavior in flooded soil. In (*Fertilizer Technology and Use*) 2nd (Edition). *Soil Sci. Soc. Amer., Mad. Wis., USA.*
- Penrose, W.R. (1974) : Arsenic in the marine and aquatic environments, analysis, occurrence and significance ;

- CRC Crit. Rev. Environ. Cont., 4 : 465 – 482.
- Ponnamperuma, F.N. (1972): The chemistry of submerged soils. Adv. Agron. 24, 29 - 96.
- Rabenhorst, M.C. (1997): The chrono-continuum: An approach to modeling pedogenesis in marsh soils along transgressive coast line. Soil Sci., 162: 2-9.
- Rabenhorst, M.C. and B.R. James (1992): Iron sulfidization in tidal marsh soils. P. 203 - 217. In R.W. Fitzpatrick and H.C.W. Skinner (ed.) Biomineralization Processes of Iron and Manganese in Modern and Ancient Environments. Catena Suppl. 21, Catena Verlag, Germany.
- Said, R. (1990) : The Geology of Egypt. Balkema, Rotterdam, Molom, 734.
- Saoud, A.A. ; O. Van Cleemput and L. Baert (1986) : Behavior of iron and manganese in soils under flooded and field capacity conditions. Alex. Sci. Exch. 7 (2) : 133 – 153.
- Shawky, S. ; P. Osta Pezuk and M. Rossbach (1994) : Comparative analysis of water and sediments from fresh water compartment in Egypt and Germany. German-Egyptian Seminar on Environmental Research, Cairo, March 21 – 23.
- Sparks, D.L. (1995) : Environmental Soil Chemistry, Academic Press. INC.
- Stumm, W. and J.J. Morgan (1970): Aquatic Chemistry. Wiley-Interscience, New York.
- Webb, J.I. (1966) : Enzyme and Metabolic Inhibitors. Vol. 3 Ch. 6, Academic Press, New York, 595 – 790.

تأثير إضافة ثاني أكسيد المنجنيز على سلوك بعض المعادن الثقيلة في نظام راسب - ماء لترعة السلام

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تمت دراسة تأثير إضافة ثاني أكسيد المنجنيز على سلوك بعض المعادن الثقيلة في نظام راسب - ماء في رواسب جمعت من القاع علي مسار ترعة السلام ابتداء من إلتقائها مع مصرف بحر حادوس ثم بعد كل ٥ كم علي ذلك المسار.

أوضحت النتائج أن العينات تحت الدراسة قد وصلت إلي مرحلة الإختزال بعد أيام قليلة من الغمر وإستمر الإنخفاض في جهد الأكسدة والإختزال حتى نهاية التجربة.

إتضح أن ثاني أكسيد المنجنيز المضاف قد شجع على إزالة المعادن الثقيلة Pb ، Ni ، Cu ، As من الماء حيث تحولت إلي صورة غير ذائبة خاصة في الفترات الأولى من الغمر بالماء. أما في الفترات المتأخرة ومع إنخفاض جهد الأكسدة والإختزال إلي قيم شديدة السالبة فإن إنخفاض تركيز الصورة الذائبة في الماء من تلك العناصر يرجع إلي تحولها إلي كبريتيدات تلك المعادن شحيحة الذوبان.

نتائج التجربة توضح أهمية بعض مكونات الرواسب مثل ثاني أكسيد المنجنيز في إزالة بعض المعادن الثقيلة من الماء وتحويلها إلي صورة غير ذائبة مما يقلل من تأثيرها الضار على البيئة.