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HEAVY METAL LEVELS AND ADSORPTION CAPACITY OF NILE RIVER SEDIMENTS*

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Determination for organic carbon and analyses of Cd, Cu, Mn, Pb and Zn were carried out on extractions (exchangeable and residual phases) of the fraction smaller than 63 μm of Nile sediment samples. Also, the fraction sediment samples were treated by synthetic solutions of metals with different concentrations. According to the index of geoaccumulation, the sediment samples are unpolluted by Mn, Cu and Zn, but they have high accumulation of Cd and Pb. The elevated concentrations of Cd and Pb can be attributed to lithogenic origin and anthropogenic sources (manufactures of metal alloys, batteries, and plastics; fertilizers and pesticides; and corrosion of galvanized materials). The adsorption data suggests that the pH is the important factor in the control of metal ions adsorption onto the bed sediments. Nile sediments exhibited high capacity for sorption of heavy metals, especially Pb and Cd followed by Zn, Cd, and Mn. The adsorption of metal ions on Nile sediments follows the Langmuir and Freundlich isotherm models. Statistical analysis was applied to the results and exhibited good and interesting relationships.

Keywords: Heavy metals; sediment; pollution; adsorption; river Nile

INTRODUCTION

Heavy metal pollution of aqueous streams is a major environmental problem facing the modern world [1]. Heavy metals added to a river system by natural or manmade sources during their transport are distributed between the aqueous phase, and suspended and bed sediments. The fraction in the sediment is expected not to present direct danger, if the metal ions are tightly bound to it and subsequently settle to the bottom in the course of time. This state of affairs is maintained until there is remobilisation from the sediment due to changing environmental conditions in the system [2]. Sediments are repositories for physical and biological debris and sinks for a wide variety of chemical [3].

* This paper is dedicated to spirit our guide the late Prof. Dr. R.M. Awadallah (1943 – 1999).

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In recent years, the analysis of bottom sediments has been used to determine the extent and sources of trace metals contamination in aquatic environment [4]. Sediments have the capacity to accumulate trace metals and other contaminants over time and so give a time-integrated assessment of contamination they may have occurred in the waterbody [5]. There are close relationships between heavy metal ions and sediments, such as suspended particles, bed loads, and bottom sediments, in river water. River sediments adsorb most of the heavy metal ions in river water [6]. Palheiros *et al.* [7] have studied the adsorption of cadmium onto a river bed sediments and reported that pH is the most important parameter in the control of cadmium adsorption onto riverbed sediments.

In Egypt, the river represents the life for Egyptians. Thus a number of authors have studied river Nile (water and sediment) chemistry. Soltan [8] studied the sediment quality of the river Nile and the distribution of some trace elements in the bulk sediments of the river Nile. He concluded that the alkaline pH values of the Nile sediments reduce the release of the metals from sediments to water. The relationship between heavy metals in mud sediments and beach soil of the river Nile was investigated by Awadallah *et al.* [9].

Against this background the objectives of this study are to assess the degree and sources of Nile sediment pollution related to heavy metals to quantify a possible mobilization of heavy metals from the sediment to the waterbody, and to estimate the maximum capacity of Nile sediments from metals discharged into water by different ways with the help of the adsorption process.

EXPERIMENTAL

Sampling

By means of a spring – loaded Ekman dredge sediment sampler made of stainless steel, sediment samples were collected at nine stations (behind High Dam (1), behind Aswan barrage (2), Abu El Riesh, Aswan (3), Qena (4), Sohag (5), Assiut (6), El Menya (7), Beni Suef (8) and Giza (9)) along the river Nile, Egypt (Figure 1) during December, 1998. The samples were dried in air then in an electrical oven at 105°C. Suspended matter samples at behind High Dam and Aswan barrage were separated by filtering 5 liters of each water sample (samples (1) and (2)) through a glass – fiber filter (Millipore type AP 40). The glass – fiber filter was washed several times with de-ionized water by vacuum via Gooch crucible. The filter was dried at 105°C after removing the filter from the filtration apparatus for 1hr. The filter was weighed before use. Water samples were collected just

below the water surface using Nansen bottle sampler [10], which previously soaked in 10% nitric acid and thoroughly rinsed with de-ionized distilled water.

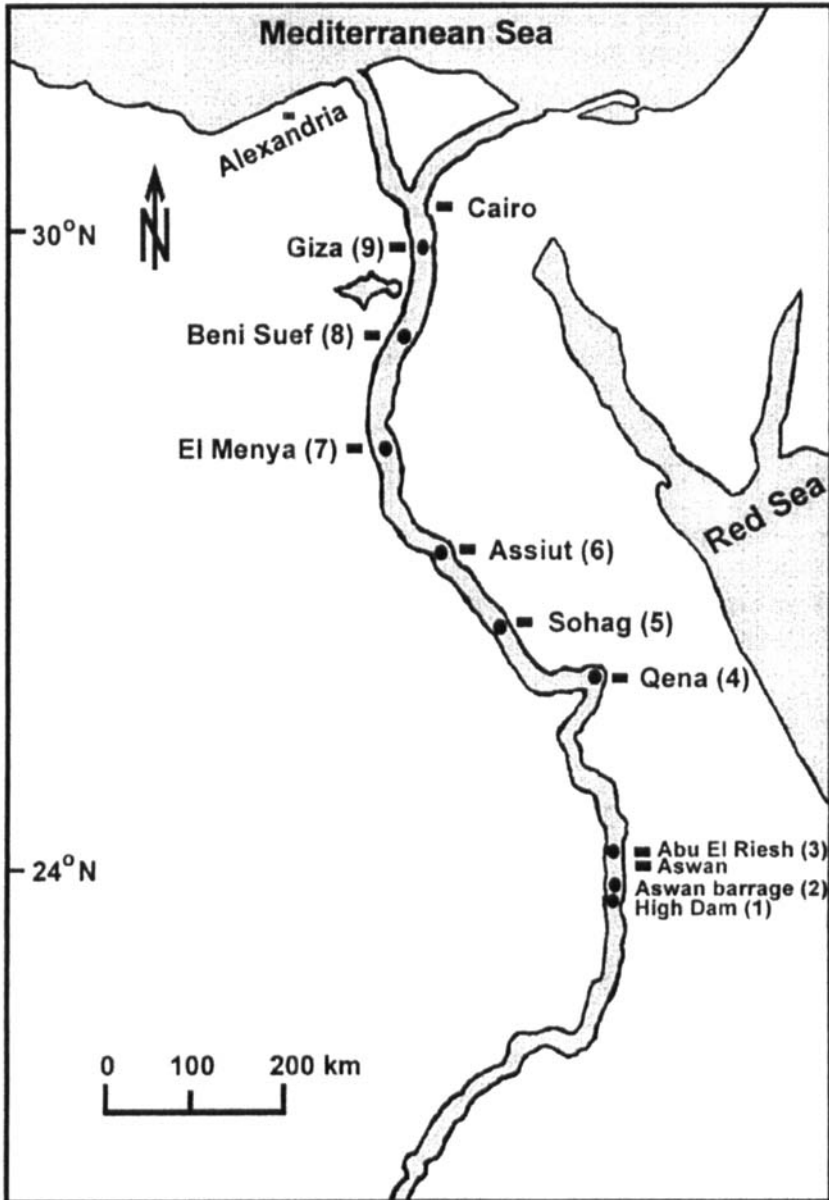


FIGURE 1 Map of Egypt showing the locations from which samples came (•)

Fractionation of particles

200 g from each dried sample was sieved through nylon sieve to obtain the size fraction $<63 \mu\text{m}$. The fractionation is imperative to base metal analyses and the size fraction $<63 \mu\text{m}$ is commonly used^[4]. Each fraction was stored in clean polyethylene bottle until needed for the experiments.

Chemical extraction

A) Exchangeable phase

The exchangeable phase was extracted at room temperature with 25 ml of 1M $\text{CH}_3\text{COONH}_4$ (ammonium acetate)/g dry weight sediment fraction whereas shaken at 15000 rpm for 4h. The adsorbed phase was separated by centrifugation, decanted into a sample bottle and acidified to pH 1.5.

B) Total metal concentration (residual phase)

One gram of each dried sediment fraction, dried suspended matter and USGS – G₂ geological standard^[11] were digested with a mixture of conc. HF, HCl and HNO_3 in a Teflon beaker. Digestion was repeated three times to ensure complete dissolution and digestion. The residue of extraction was dissolved in 50 ml of 20% HCl and rewarmed at 80°C for 20 min. The solution was made up to 50mL with de-ionized water.

Adsorption experiments

Batch adsorption experiments were conducted by equilibrating 1 g of each sediment sample fraction ($<63 \mu\text{m}$) with 25 ml of metal ions (mixture from Cu, Cd, Mn, Pb and Zn) solution with known concentrations. Initial concentrations of metal ions were held to 5, 10, 20, 50 and 100 mg/L, the pH of resulting solution approximately equal 5. Constant stirring of the solutions was maintained for 1h on a water bath shaker at 25°C then the contents of the flask were filtered through Whatman 0.45 μm filter paper and subsequently analysed for residual concentration of metal ions (non-adsorbed). The adsorbed metal ion concentrations were calculated by the difference between the initial concentration and non-adsorbed concentration.

Effect of pH on adsorption

To evaluate the effect of acidic pH on the adsorption of metals, we selected the samples no. 2 (behind Aswan barrage) and 9 (Giza) to application this experi-

ment. Samples 2 and 9 were selected as a representation for south and north of Nile river stream (Figure 1). 1 g of each sediment sample fraction was treated with 25 ml of metal ions solution (100 mg/L) as the above procedure and the pH of solution was adjusted to desirable pH (2, 4 and 6) using dilute HNO₃ acid solution. To knowledge the effect of neutral and alkaline pH on the behaviour of metal ions in the waterbody, we selected the samples no. 2 and 9 to application this experiment. 1 g of each sediment sample fraction was treated with 25 ml of metal ions solution (100 mg/L) and the pH of solution was adjusted to desirable pH (7, 8 and 9) using dilute NaOH solution. The concentration of available metal ions in the filtrated solution was determined in each batch. The standard solution (100 mg/L for each metal in the mixture) of metals without sediment samples were adjusted in three conical (25 mL in each conical) to pH 7, 8 and 9 to knowledge the quantity of precipitated metals under different pH values and wherefore, we can calculate the quantity of metals which adsorbed on the sediment fraction.

Measurements and analysis

All chemicals were purchased from BDH, Sigma, Aldrich, and E. Merck (A.R., 99.9%). Loss on ignition at 550°C was used as an estimate of sediment organic matter content. The metal concentrations of the samples (Cu, Cd, Mn, Pb and Zn) were measured by Sp 1900 Pye Unicam recording flame atomic absorption spectrophotometer at their respective wavelengths using hollow cathode lamps (air – acetylene burner was used). The working atomic absorption spectroscopic standard solutions (1 mg mL⁻¹) for the elements were prepared by diluting the stock solutions using de-ionized water. The samples and standard solutions were run in six replicates consequently. The precision of the results was estimated by triplicate analysis. The accuracy and precision of the analytical results were estimated as standard deviation for six replicates of samples.

Statistical analysis

The statistical analysis of the database of the chemical analysis of sediment samples was performed using the Minitab program data analysis (Minitab Release 10.1. Copyright (C), Minitab Inc., 1994).

RESULTS AND DISCUSSION

Trace metal associations with different sediment phases

The trace metals distribution along the river Nile for the two extraction systems (Table I) revealed that NH₄OAC extracts the readily exchangeable metals (Cd;

1.8 – 13.5 μgg^{-1} , Cu; 0.25 - 4 μgg^{-1} , Mn; 15.5 – 62 μgg^{-1} , Pb; 55 – 462.5 μgg^{-1} , and Zn; 18.3 – 56 μgg^{-1}) and represent a minor fraction of the total metal concentration of the solid. Without exception, trace metal concentrations found in the residual fraction (HF – HNO₃ – HCl system) were higher than those observed in the exchangeable fraction (Cd; 16.3 – 206 μgg^{-1} , Cu; 26.3 – 93.8 μgg^{-1} , Mn; 112.5 – 342.5 μgg^{-1} , Pb; 550 - 2613 μgg^{-1} , and Zn; 173.8 – 611.3 μgg^{-1}). These metals (within the crystal structure of primary and secondary minerals) are not expected to be released in solution over a reasonable time span under the conditions normally encountered in nature. Cu, Pb, Zn and organic carbon show higher levels in the mud sediments deposited behind the High Dam wall (Lake Nasser) as a result of fishers activity in the lake including effluents of Fisher boats, making Fisher Factory, and tourist villages.

TABLE I Selected physicochemical parameters (mean of six samples) of Nile sediment samples

Locality	Pb			Cd			Cu			Mn			Zn			TOC* %	pH	mv
	A	B	C	A	B	C	A	B	C	A	B	C	A	B	C			
(1) Behind High Dam	195	2613	7.5	1.8	72.5	2.4	0.25	93.8	0.27	15.5	112.5	13.8	56	611.3	9.2	8.6	7.42	-39
(2) Behind Aswan Barrage	117.5	1700	6.9	13.5	190	7.1	1.25	53.8	2.3	53.3	287.5	18.6	20.3	223.8	9.1	7.92	7.63	-51
(3) Abu El Rieah, Aswan	462.5	787.5	58	2.8	93.8	3	2	63.8	3.1	62	342.5	18.1	29.8	280	10.6	8	7.31	-21
(4) Qena	197.5	612.5	32	3	30	10	4	45	8.9	26.3	187.5	14	21.3	260	8.2	5	7.05	-6
(5) Sohag	90	1538	5.9	4.8	16.3	29	0.5	57.5	0.9	25	208.8	12	21	233.8	9	6	7.21	-10
(6) Assiut	65	700	9.2	2.5	51.3	4.9	0.25	42.5	0.6	28.8	158.8	18.1	18.3	173.8	10.5	6.93	7.55	-28
(7) El Menyeh	267.5	2313	11.6	8.8	206	4.3	0.25	71.3	0.35	36.3	221.3	16.4	20.8	300	6.9	5.94	7.11	-7
(8) Beni Suef	97.5	550	17.7	2.8	81.3	3.4	0.25	26.3	0.95	38	175	21.7	21.3	200.5	10.6	7	7.07	-6
(9) Giza	55	1713	3.2	2.8	108	2.6	0.50	35	1.4	26.3	256.3	10.3	22.5	338.5	6.6	7	6.89	10
Mean	171.9	1392	17	4.75	94.3	7.4	1.02	54.3	2.08	34.6	216.7	15.9	25.7	262.4	8.97	6.93	7.24	-17
SD	122.5	793.9	16.9	3.66	62	8	1.19	19.2	2.56	13.9	66.1	3.42	11.1	146	1.42	1.07	0.23	17.9

* Total organic carbon

A Readily exchangeable metal, $\mu\text{g/g}$

B Total metal concentration $\mu\text{g/g}$

C Percent of the exchangeable metal / Total metal (% A/B)

Assessment of sediment quality

The background approach is the one of chemical methods for assessing sediment quality. This method compares the actual data with sites comprising natural or insignificant pollutant concentrations. The index of geoaccumulation [12] compares the measured concentration of the elements in the fine grained sediment fraction (Cn) with geochemical background values (Bn) in fossil clay and silt sediments (0.22 $\mu\text{g Cd g}^{-1}$; 45 $\mu\text{g Cu g}^{-1}$; 850 $\mu\text{g Mn g}^{-1}$; 20 $\mu\text{g Pb g}^{-1}$ and 95 $\mu\text{g Zn g}^{-1}$) [13] as follows:

$$I_{\text{geo}} = \log 2 \text{ Cn} / 1.5 \cdot \text{Bn}$$

The index of geoaccumulation (Table IIa) consists of 7 grades, whereby the highest grade (6) reflects 100-fold enrichment above background values. The assessment of sediment samples according to this index is summarised in Table IIb. Highest rates of accumulation at different levels for sediment samples have been found for Cd and Pb, while they were rather unpolluted by Zn, Cu and Mn. Similar results were obtained for sediments of the Rhine, Elbe and Weser rivers in Germany [14].

TABLE IIa Index of Geoaccumulation (I_{geo}) of trace metals in sediments

I_{geo}	Pollution Intensity
>5	very strong pollution
>4 – 5	strong to very strong
>3 – 4	strongly polluted
>2 – 3	moderate to strong
>1 – 2	moderately polluted
>0 – 1	unpolluted to moderate
<0	unpolluted

TABLE IIb Assessment of Nile sediment samples (mean of six samples) according to the index of geoaccumulation

Locality	1	2	3	4	5	6	7	8	9
Metals									
Pb	6.44	5.82	4.71	4.35	5.68	4.54	6.26	4.19	5.83
Cd	7.35	8.22	7.70	6.05	5.17	6.83	8.84	7.49	7.90
Cu	0.47	-0.09	-0.08	-0.17	-0.23	-0.66	0.07	-1.35	-0.94
Mn	-3.5	-2.15	-1.90	-2.76	-2.61	-3	-2.52	-2.86	-2.31
Zn	2.1	0.65	0.97	0.86	0.71	0.28	1.07	0.49	0.74
Average	2.57	2.49	2.28	1.66	1.74	1.6	2.74	1.59	2.24
SD	3.98	3.88	3.46	3.16	3.19	3.57	4.17	3.77	3.94

Generally, for the comparison of nine sediment samples in river Nile, the I_{geo} has been used. El Menya sediment sample exhibited highest overall accumulation followed by the samples from behind High Dam and behind Aswan barrage.

In both behind High Dam and Aswan barrage samples, Cd, Pb, in addition Zn (behind High Dam sample) is typically influencing the average factors enrichment. A portion of the above metal concentrations were from lithogenic origin, because the sediment in this region consists of fine granite particles from igneous rocks present in the main stream and sides of the river Nile. In addition, the slow flow rate of water at these regions leads to precipitate the suspended matter, which covers the most water surface, whereas the suspended matter play as transport pathway for metals. The analysis of suspended matter samples (Table III) supported the above interpretation. The suspended matter at these regions (ranged between 35 to 55 mg/L in samples (1) and (2), respectively) consists of green algae, fine clay, aquatic plants and organic matter, which is transported into the sediment by flocculation and sedimentation (Fig. 2a* – e*). Gaad [15] has reported metal uptake for various microorganisms (bacteria, algae and fungi), for example, cadmium represented up to 40% of the dry weight of *Zooglea remigera*, while the accumulation of lead by *Pseudomonas fluorescens* ranged from 32 to 35% from its dry weight.

TABLE III Heavy metal content ($\mu\text{g g}^{-1}$ DM) in selected suspended matter samples from river Nile waters

Metals	Pb	Cu	Zn	Cd	Mn
Locality					
(1) Behind High Dam	210	47.3	157	35.5	251
(2) Behind Aswan barrage	181	53	148	43	270

Highest metals accumulation of sediment at El Menya are to anthropogenic sources resulting from agricultural, industrial, and domestic discharges, whereas the river Nile stream penetrates the city center. Related to the anthropogenic origin, the concentrations of cadmium and lead in sediments result from the discharge of alloys, batteries, paints and coating manufactures. In addition, fire protection systems, fungicides, and electrical equipment can be suggested^[16].

Adsorption characteristics of sediment samples

A-Adsorption capacity of sediment samples

According to experimental results we have mapped the adsorption isotherms of sediment samples adsorbing Cd, Cu, Mn, Pb and Zn. These are shown in

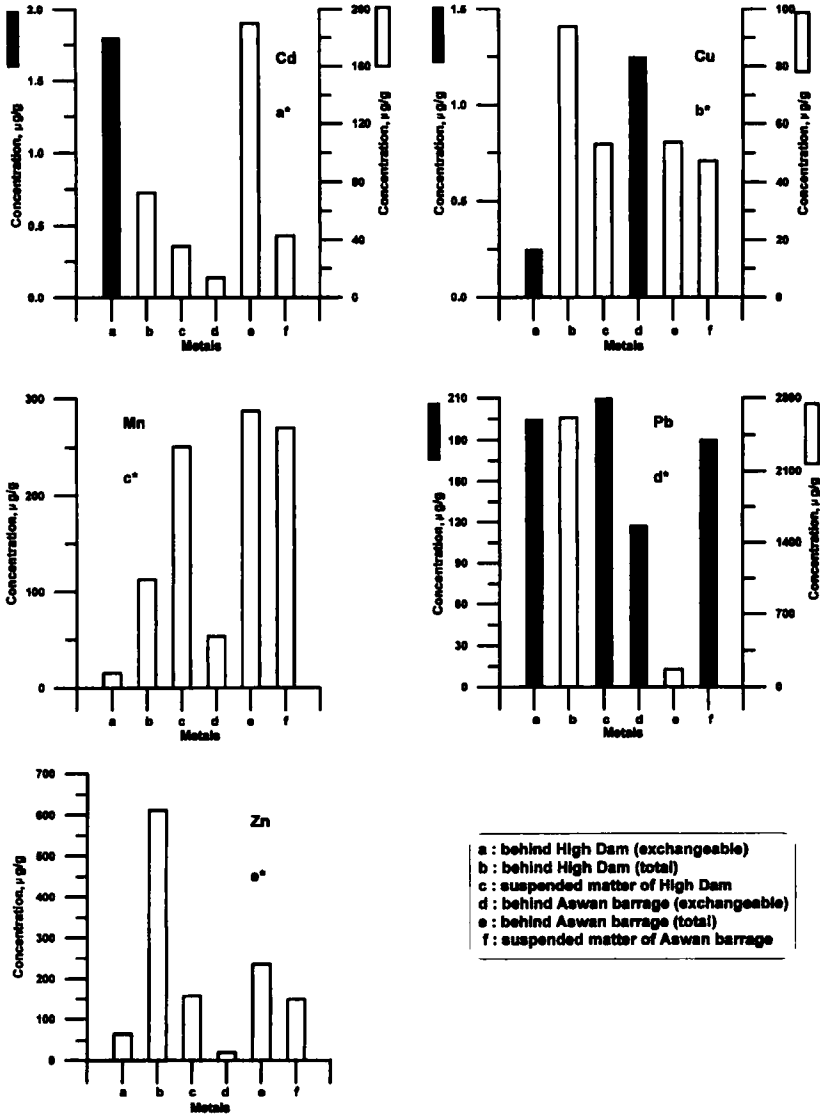


FIGURE 2a-e The relationship between metals contents in sediment and suspended matter samples at behind High Dam and Aswan barrage

Figure 3(a – e). The adsorption value of Pb is the largest, then in descending order are Cu, Zn, Cd, and Mn. The adsorption values of Pb and Cu show only a small difference. The largest adsorption value for Pb and Cu may be attributed to the very low solubility product of lead hydroxide, copper hydroxide followed by

Zn, Cd, and Mn hydroxides (Table IV). Mn hydroxide has a highest solubility product in this series and so adsorption is small. It can therefore be inferred that adsorption of these metals on sediment samples may be due to the formation of their insoluble hydroxide in a neutral medium. A similar behaviour was observed by Ajmal *et al.* [17].

TABLE IV The relationship between the percent adsorption (mean of nine samples) of metals (adsorbate concentration = 100 mg/L) and the solubility product of their hydroxides

<i>Metal ion</i>	<i>Metal hydroxide</i>	<i>K_{sp}</i>	<i>% adsorption</i>
Pb ²⁺	Pb(OH) ₂	1.4 × 10 ⁻²⁰	97.11
Cu ²⁺	Cu(OH) ₂	5.6 × 10 ⁻²⁰	93.78
Zn ²⁺	Zn(OH) ₂	7.68 × 10 ⁻¹⁷	44.77
Cd ²⁺	Cd(OH) ₂	5.33 × 10 ⁻¹⁵	40
Mn ²⁺	Mn(OH) ₂	4 × 10 ⁻¹⁴	11.6

In general, at low concentration of adsorbate ions (5 and 10mg/L), the mean uptake in the case of Cu, Pb, Zn and Cd ranged from 98.9 to 91.61% compared with Mn (83.35 – 85.24%). On the other hand, at higher solute concentrations (100 mg/L), the maximum removal of Pb, Cu, Zn, Cd and Mn is 97.11, 92.78, 44.77, 40 and 11.6%, respectively. At high sorbate concentrations, a smaller fraction of the sorbate species is sorbed and at high enough concentrations, the sediment sample has occupied all available sorption sites and is no longer sorbed at all [18]. Relative high sorptive abilities of sediment samples may be due to the high organic matter contents (Table I) in the Nile sediment samples (ranged between 5.94 – 8.6% organic carbon). Davis [19] and Sigg [20] reported that the important geochemical phases for the adsorption of metal ions are the contents of organic matter, manganese oxides, iron oxides, and clays.

The adsorption data for the investigated samples have been analysed with the help of Langmuir and Freundlich models to evaluate the mechanistic parameters associated with the adsorption process. Langmuir's isotherm assumes uniform energies of adsorption onto the surface and no transmigration of adsorbate in the plane of the surface [2]. The linear form of Langmuir isotherm equation is represented by the following equation:-

$$1 / q_e = 1 / Q^\circ + 1 / bQ^\circ C_e$$

Where q_e is the amount adsorbed (mg/g), C_e is the equilibrium concentration of the adsorbate ions (mg/L), Q° and b are Langmuir constants related to maximum adsorption capacity (mono layer capacity) and energy of adsorption, respectively. When $1/q_e$ is plotted against $1/C_e$, a straight line with slope $1/bQ^\circ$

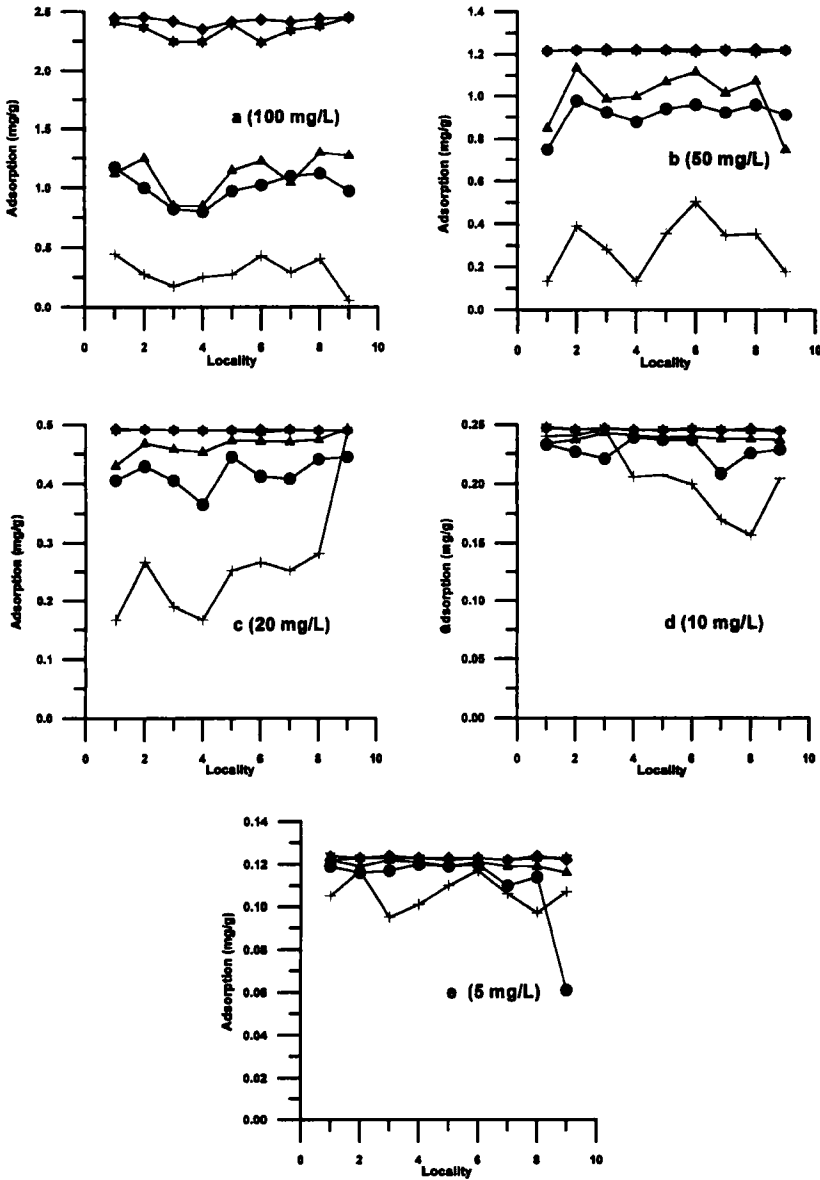


FIGURE 3a-e Adsorption of Pb (◆), Cd (◐), Cu (*) (●), Mn (+) & Zn (▲) on sediment samples (<63 μm) at different adsorbate concentrations

and intercept $1/Q^{\circ}$ is obtained (Figure 4a – e), which shows that the adsorption of metal ions follows the Langmuir isotherm model. The Langmuir parameters (Q°

and b) are calculated from the graphs (Figure 4a – e). The adsorption of metals (Pb, Cu, Cd, Mn, and Zn) by the sediments were significantly correlated with the adsorption maximum capacity and binding energy constant of the Langmuir equation. Parameters of Langmuir equation are useful in describing the sediment retention capacities. The maximum adsorption capacities of Nile sediment samples for Pb, Cu, Cd, Mn and Zn were about 22, 3630, 446, 9, and 42 times that of their intrinsic concentrations, respectively. This indicates that the sediment samples were far from saturation.

As with the Langmuir model, the adsorption data for Pb, Cu, Cd, Mn, and Zn has also been analysed using logarithmic form of Freundlich isotherm as shown in the following equation: –

$$\log q_e = \log K_F + 1/n \log C_e$$

Where q_e is the amount adsorbed (mg/g), C_e is the equilibrium concentration of the adsorbate ions (mg/L), K_F and n are Freundlich constants related to adsorption capacity and adsorption intensity, respectively. When $\log q_e$ is plotted against $\log C_e$, a straight line with slope $1/n$ and intercept $\log K_F$ is obtained (Figure 5a – e). This reflects the satisfaction of Freundlich isotherm for the adsorption of these metals.

B- Effect of pH on adsorption

The pH value is an important parameter, which affects adsorption of heavy metals on sediments [2,6,21,22]. The effect of pH on adsorption of investigated metals is shown in Figure 6(a – e). The adsorption experiments were carried out on the pH's 2, 4, 6, 7, 8 and 9. The visual observation clearly indicated the absence of any precipitation from synthetic solution until pH 6. To eliminate the effect of hydrolysis and sedimentation of ions with rises of pH; the influence of pH's 7, 8 and 9 on the synthetic solution of the adsorbate ions (100mg/L) without sediment samples was studied.

It is apparent from Figure 6(a – e) that the adsorption of lead ions occurs even in acidic medium, whereas the adsorption maximized in sample no. 2 (98.4%) and sample no. 9 (98.6%) at pH 4 and sharply decreased at pH 7 to 8.43 and 8.8% for samples no. 2 and 9, respectively. At pH 9, the adsorption percent became nil and 0.15 for these samples. Ajmal *et al.* [17], Zhou and Kot [6], Benjamin and Leckie [23], and Srivatava *et al.* [24] observed a similar behaviour. The high adsorption of Pb at lower pH indicates a high adsorption intensity [25].

A critical value of pH is 6, where the maximum adsorption percent of Cu ion onto sediment samples are 99.37 and 99.07% for samples no. 2 and 9, respectively. An abrupt decrease in the adsorption efficiency occurred at pH 7 reaching

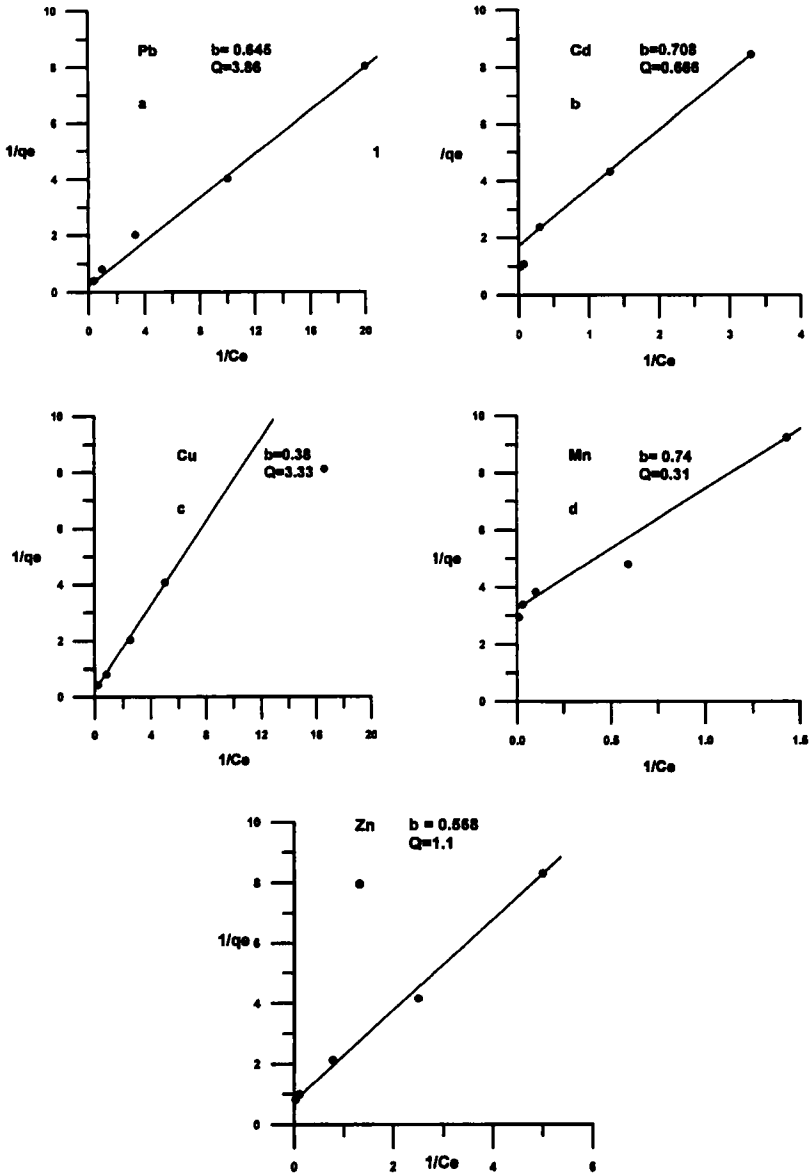


FIGURE 4a-e Langmuir adsorption isotherm for Pb, Cd, Cu, Mn & Zn

to 1.34 and 1.40% for these samples. Finally, at pH 9, the adsorption efficiency became nil. Many authors [6,24,26] have reported a similar behaviour.

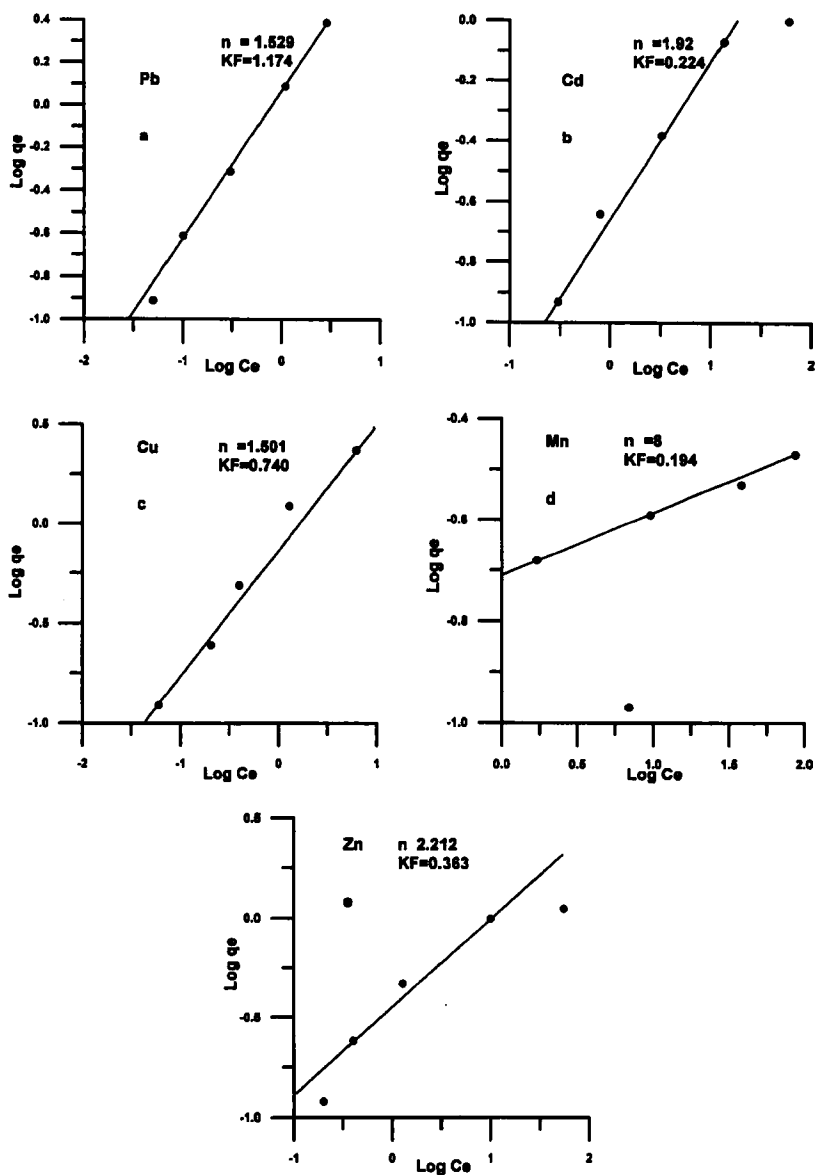


FIGURE 5a-e Freundlich adsorption isotherm for Pb, Cd, Cu, Mn & Zn

A general increase in adsorption with increasing pH of solution has been observed for Cd up to pH 8 (maximum adsorption for samples no. 2 and 9 are

73.8 and 71.2%), respectively. As the pH is further increased beyond 8 – 9, the onset of metal hydrolysis and precipitation may start. Decrease of Cd adsorption takes place at pH 9 with the corresponding adsorption percent being 52.67, 51.87% for samples no. 2 and 9, respectively. Similar results for Cd adsorption were obtained from Lake Chapala sediment [27]. Hansen and Maya stated that by increasing the ionic strength, the Cd adsorption curves shifted towards higher pH. Christensen [28] also reported a 2 – 3 fold increase in the adsorption capacity of cadmium on soils for a pH increase of one unit. Adsorption efficiency gradually increased from pH 2 (61 and 53% for samples 2 and 9) to pH 4 (reached to 66 and 59%, respectively) and reached to maximum adsorption at pH 6 with 71% adsorption for the two samples.

Sudden decrease in Zn adsorption efficiency with increasing pH has been observed at pH 7 (8 and 15% for samples no. 2 and 9) until pH 9 (0.96 and nil for samples 2 and 9), respectively. In view of the efficiency of metals adsorption, manganese exhibited lower adsorption values at the different pH values relatively to the investigated metals. This may be attributed to the intrinsic adsorption constants, whereas cations that form strong inner – sphere aqueous complexes are often strongly and specifically adsorbed when the same ligand is involved in solution and at sorbent surface. Conversely, species forming weak aquocomplex or ion pairs tend to be weakly adsorbed [29,30].

There is evidence that the adsorption tendency of divalent transition elements by hydrous oxide and sediments often follows the Irving – Williams order [31]. This suggests that the sequence of decreasing adsorption tendency is $\text{Cu} > \text{Zn} \geq \text{Ni} > \text{Co} > \text{Fe} > \text{Mn} > \text{Ca}$. The adsorption of Mn rises from 18.2 – 16.95 at pH 2 to 28.6 – 22% at pH 8 (maximum adsorption) for samples 2 and 9, respectively, and it falls with increasing basicity of the medium (at pH 9) to 15.7 – 14.9%. Generally, increase in adsorption with increasing pH of solution has been observed for Pb, Cu and Zn in acid medium (up to pH value 6 except Pb at pH 4) and at high pH's, chemical precipitation becomes a more dominant mechanism in metals removal.

Experimentally, the available Pb, Cu, and Zinc ions (soluble) in standard synthetic solution (without sediment sample) which contains 100 mg/L for each metal (mixture) at pH's 7, 8 and 9 being 10.5, 1.7 and 1.2 mg/L Pb; 1.43, 0.44 and 0.17 mg/L Cu; 59, 20, 1.38mg/L Zn, respectively (Figure 7). On the other hand, Cd and Mn in the synthetic solution (100mg/L), exhibited a behaviour different from the above metals, the available Cd and Mn ions in standard solution being 95, 85, & 60 mg/L Cd and 99.5, 92.1 and 48.4mg/L Mn at pH's 7, 8 and 9, respectively (Figure 7). Thus, this experiment demonstrates the adsorption behaviour of Cd and Mn on sediment samples at pH 8.

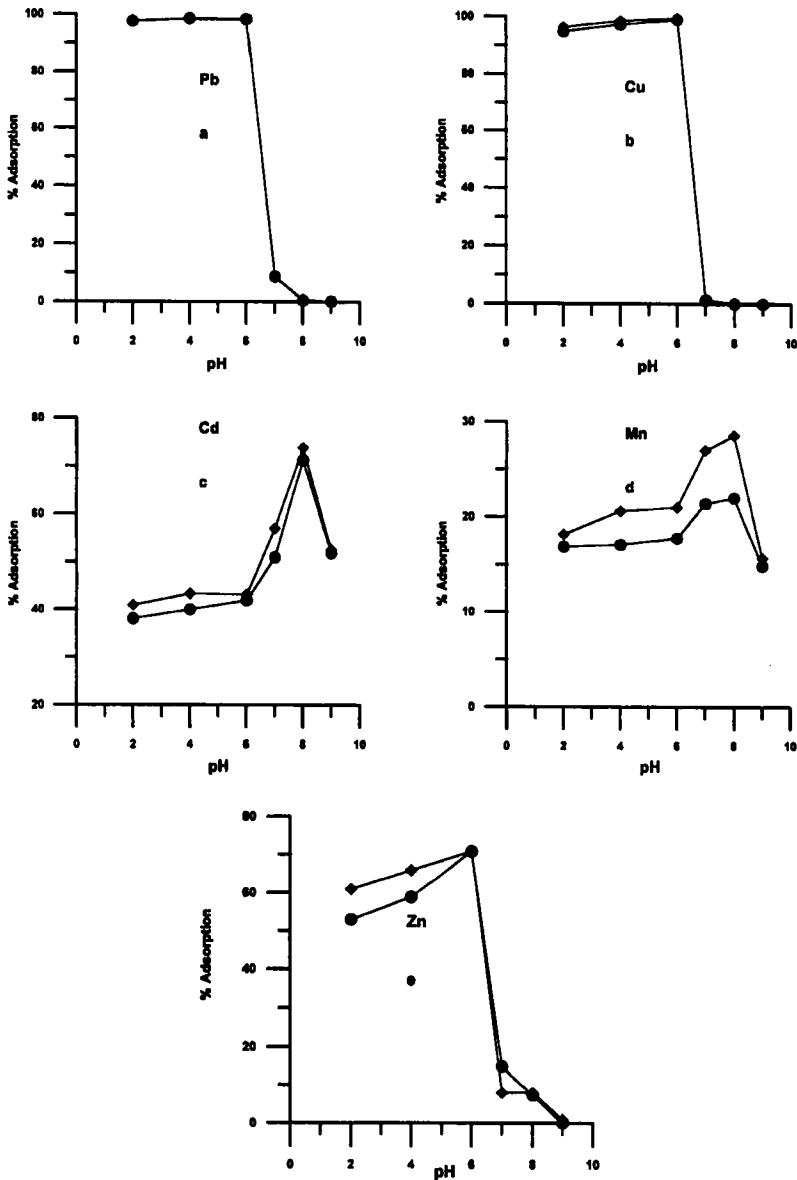


FIGURE 6a-e Effect of pH on adsorption of Pb, Cu, Cd, Mn and Zn on Nile sediments[sample 2 (♦) & sample 9 (•)] (adsorbent dose = 40 g/L; adsorbate concentration = 100 mg/L)

The high percent adsorption of Pb may be related to the solubility product of this metal (Table IV). Ajmal *et al.* (1995) stated that the maximum adsorption of

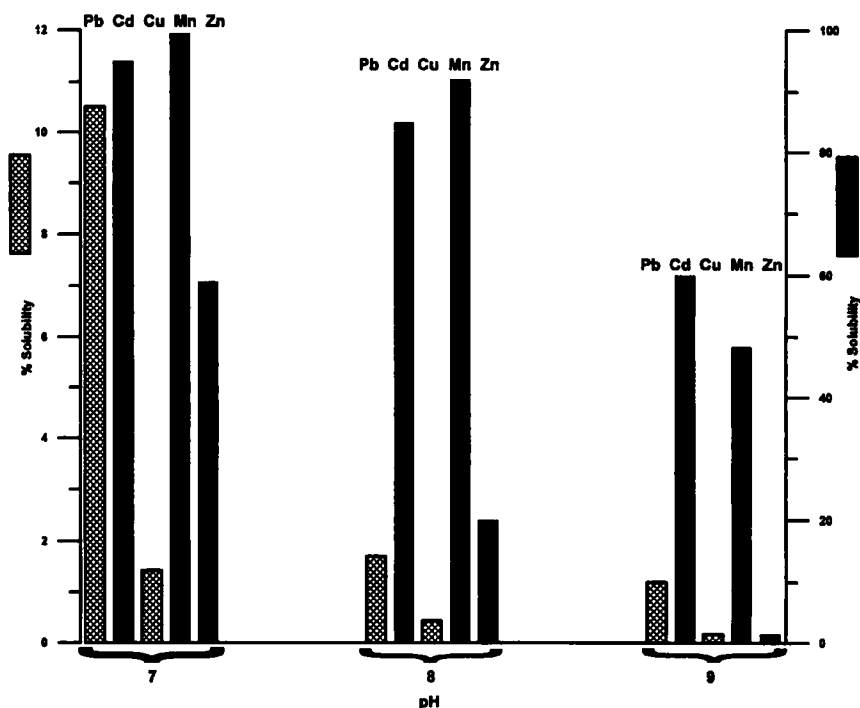


FIGURE 7 Effect of pH values on solubility of Pb, Cd, Cu, Mn & Zn present in standard solution (100 mg/L for each metal)

lead on pyrolusite in a neutral medium as well as on hydrous manganese oxide might be attributed to the very low solubility product of lead hydroxide followed by Zn and Cd. In this study, the percent adsorption of metals inversely proportional with their solubility products. Therefore, it can be inferred that adsorption of these metals on sediment samples may be due to the formation of their insoluble hydroxides in a neutral medium.

Efficiency of sorption process as a function of pH value

An increase in the pH of natural systems tends to favor removal of most trace elements (especially cations) from solution. Their removal is usually by adsorption and / or by precipitation (sorption) in solids that become insoluble with increasing pH. The trace elements may precipitate in their own pure solids, but most often are coprecipitated as trace species in the major elements solids. We can see from Table V that the sorptive capacity of sediment samples increases with the increase of pH value for the different metals.

TABLE V Sorption capacity (%) of some heavy metals on sediment samples (mean of samples no. 2 & 9) at different pH values (adsorbate concentration = 100 mg/L; adsorbent dose = 40 g/L)

Metals pH	Pb	Cu	Zn	Cd	Mn
7	98.14	99.94	52.50	59	24.70
8	98.95	99.80	98.15	82.50	33.20
9	98.88	99.55	98.60	92.27	66.90

The difference of sorption efficiency for different metals is due to the variation of solubility product of their hydroxides (Table IV). These results indicate that the pH of river Nile (water and sediment) is the most important factor in the control of metal ions sorption on the sediments. The pH of river Nile water in the range 7.18 – 8.77 [8,23] lead to minimize the pollution effect of metals by sorption mechanism on the bed sediments, where their pH ranged from 6.89 to 7.63 (Table I).

Statistical analysis of data

The statistical analysis of the database shows negative significant correlation between pH values and the percent adsorption of Pb ($r = -0.850$), Cu ($r = -0.831$), and Zn ($r = -0.786$). These correlations indicate the similar adsorption behaviour for these metals, whereas, high adsorption capacity were obtained at $pH < 6$, but when the pH value increases, it causes hydrolysis and sedimenting of metals. Good positive correlation between pH and Cd ($r = 0.712$), was attributed to the increase of Cd adsorption with increasing pH of solution until pH 8. No obvious correlation between pH and Mn ($r = 0.251$) indicate that the adsorption of Mn is weakly pH – dependent. Close positive significant correlation between the percent adsorption of Pb and Cu ($r = 0.999$) demonstrate the strong similarity in their adsorption behaviour at different pH and different adsorbate concentrations. In addition, they showed similar solubility products as hydroxides. These relations reflect their correlation with zinc, as Zn strongly correlated with Pb ($r = 0.988$), and Cu ($r = 0.988$). Negative correlation coefficients were found between the percent adsorption of Cd and Pb ($r = -0.825$), Cd and Cu ($r = -0.814$), and Cd and Zn ($r = -0.774$). On other hand, positive correlation coefficient was observed between Cd and Mn ($r = 0.688$). These relations reflect the difference of behaviour between Cd and Pb, Cu and Zn and the similarity between Cd and Mn.

CONCLUSION

Most sediment samples studied have high concentrations of Pb and Cd followed by moderate concentrations of Zn and little concentrations of Mn and Cu according to the index of geoaccumulation.

The present study has shown the ability of sediments to adsorb metal ions even in acidic conditions. The adsorption values of Pb are the higher, then in descending order are Cu, Zn, Cd, and Mn. When pH is less than 6, the main activity is sediment adsorbing heavy metal ions, but when the pH more than 6, the main activity is hydrolysis and sedimenting of heavy metal ions. The adsorption of metal ions followed the Langmuir and Freundlich isotherm models. The adsorption of Pb, Cu, Cd, Mn, and Zn was significantly correlated with the maximum adsorption capacity and adsorption intensity constants. According to Langmuir and Freundlich equations, the Nile sediments have a high adsorption capacity for Pb, Cu, Cd, Mn and Zn, being about 22, 3630, 446, 9, and 42 time that of their mean intrinsic concentrations, respectively. The sediments of the river Nile have greater potential for the removal of heavy metals in acidic and basic medium by adsorption and sorption mechanisms.

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