

## Adsorption and Leaching Behavior of Copper, Zinc and Lead Ions by Three Different River Nile Sediments at Aswan, Egypt

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**ABSTRACT:** The present study was carried out to investigate the adsorption and leaching behavior of  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{Pb}^{2+}$  by sediments collected from the western banks of three different sectors along River Nile at Aswan governorate, Egypt. The feasibility of sediments for the removal of  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{Pb}^{2+}$  from aqueous solutions was tested under the effect of three conditions (pH, initial metal concentration and contact time). By increasing pH, the adsorption of  $\text{Cu}^{2+}$  and  $\text{Pb}^{2+}$  by sediments decreased while that of  $\text{Zn}^{2+}$  increased. The optimum pH values for  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{Pb}^{2+}$  removal were determined as 5, 8.5 and 5, respectively. The adsorption capacities of sediments for metal ions were in the order of  $\text{Pb}^{2+} > \text{Cu}^{2+} > \text{Zn}^{2+}$ . The maximum uptake for  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{Pb}^{2+}$  by sediments occurred at contact times of 48 h, 24 h and 72 h, respectively. Adsorption data were fitted well by Freundlich, Dubinin–Radushkevich and Temkin isotherms. The experimental results obtained were analyzed using two adsorption kinetic models, pseudo-first-order and pseudo-second-order, in which pseudo-second-order equation described the data more than pseudo-first-order one. The average leaching percentages of  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{Pb}^{2+}$  from sediments were 0.77%, 2.72% and 0.38%, respectively, with respect to pH, 0.83%, 2.49% and 0.38%, respectively, with respect to temperature, and also 0.79%, 2.34% and 0.38%, respectively with respect to contact time. The leaching percentages of metal ions from sediments were in the order of  $\text{Zn}^{2+} > \text{Cu}^{2+} > \text{Pb}^{2+}$ .

**Keywords:** Heavy metals, adsorption, sediments, River Nile, pollution

### INTRODUCTION

Some heavy metal ions (Pb, Cd and Hg) in waters are toxic to human and aquatic animals even at low concentrations. They are usually stable and non-biodegradable, and so they tend to bioaccumulate in living tissues causing some serious health concerns (Lukman et al., 2013). Heavy metals are found in wastewater of many industries such as pigments, paints, batteries, metal products,

ammunition production, and ceramic glazes (Amer et al., 2010).

Toxic heavy metal ions have been removed from polluted water by different methods such as adsorption, ion exchange, reverse osmosis, chemical precipitation, etc. Adsorption is considered as one of the most preferred methods for the removal of toxic heavy metals from polluted water as it has been found to be very simple, effective and economical method (Bhattacharyya and Gupta, 2008).

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Adsorption has additional advantages of removing both inorganic and organic pollutants, as suitability for using batch and continuous processes, possibility of reactivation and reuse the adsorbent, safety of operation, less sludge generation, and low costs (Mohanty et al., 2006).

Several studies have been investigated for the removal of toxic heavy metals from polluted water and wastewater using soils and sediments in riverbeds and in suspension (Veli and Alyüz, 2007; Jiang et al., 2010; Chaari et al., 2011; Abat et al., 2012; Jelodar et al. 2012; Sangiumsak and Punrattanasin, 2014; Lim and Lee, 2015).

The qualifications of River Nile (Egypt) sediments and the distribution of heavy metals were studied by Abdel-Satar (2005), Moalla et al. (2006) and El-Kammar et al. (2009).

In this study, adsorption and leaching behavior of  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{Pb}^{2+}$  ions by River Nile sediment from the water were investigated to achieve the pollution load of

these metals from the different input sources to the River Nile water. To achieve optimum conditions for adsorption and leaching processes, pH, initial metal concentration and contact time were studied. In order to determine the adsorption equilibrium of the studied heavy metals with River Nile sediments from River water, experiments were applied to Langmuir, Freundlich, Dubinin–Radushkevich and Temkin adsorption isotherms. Metal adsorption kinetics (first and second order reaction kinetics) were applied in order to determine the adsorption mechanism and adsorption characteristic constants.

## MATERIAL & METHODS

The adsorbents used in this study were three surface sediment samples collected from the western banks of three different sectors include Aswan, Gezira and Edfu (S1, S2 and S3, respectively) along River Nile at Aswan governorate, Egypt as shown in Fig. 1.

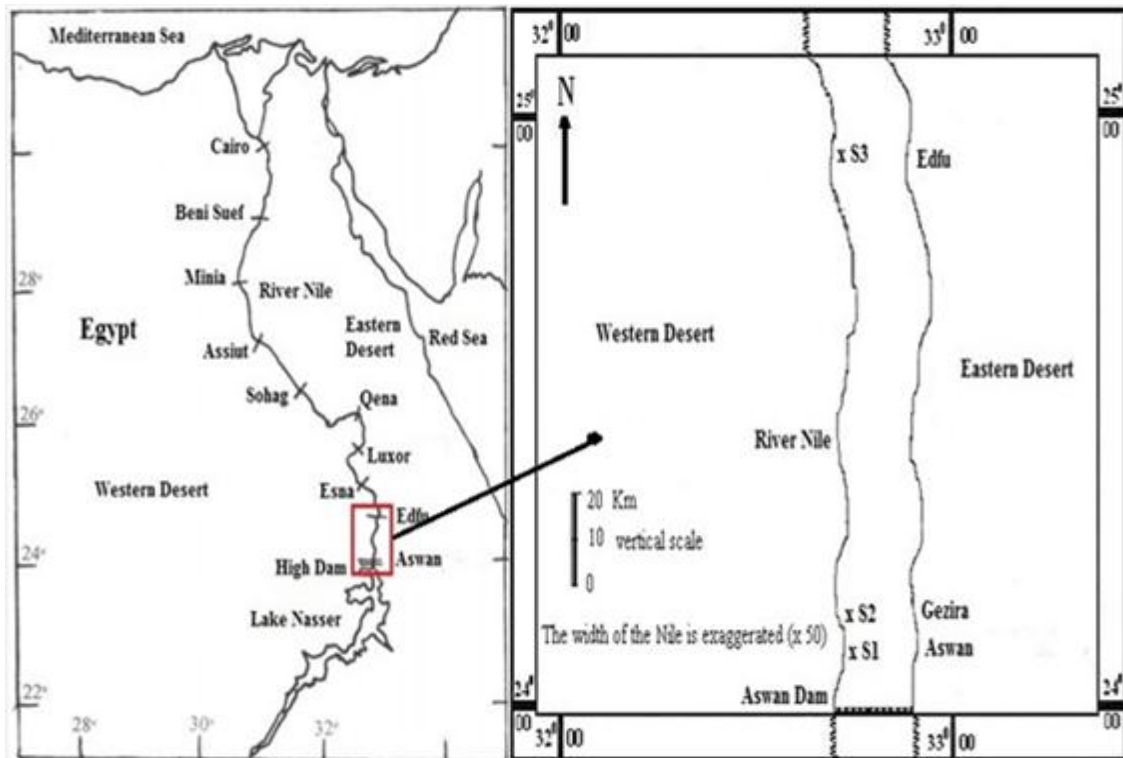


Fig. 1. Map shows the sampling locations of sediments along River Nile

Sediment samples were collected during spring 2015 by standard Ekman grab sampler (Wildco 196-B12, USA), packed in airtight polyethylene bags to minimize oxidation, and stored at approximately 4°C until returning to the laboratory. Upon reaching the laboratory, samples were air-dried at room temperature. Later subsamples of the sediments were sieved through a 500 µm sieve (W.S. TYLER ASTM E-11 NO. 35, USA) to be of regular particle sizes and to remove non-sediment particles and oven-dried (FALC STF-N 240, Italy) at 105 °C for 24 h. The dried samples were ground in an agate mortar up to 63 µm size. Then the samples were stored until analysis under normal room conditions with minimal temperature and humidity fluctuations and shielded from incident light (Pansu and Gautheyrou, 2007).

The reagents used in this study were of analytical reagent grade: potassium dichromate, concentrated sulfuric acid, 1,10-phenanthroline monohydrate, ferrous sulfate heptahydrate, ferrous ammonium sulfate hexahydrate, concentrated hydrochloric acid, sodium carbonate, methyl orange, concentrated nitric acid,  $\text{KH}_2\text{PO}_4$ , and NaOH. Stock standard solutions (1000 mg/L) of  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{Pb}^{2+}$ . Working standard solutions were prepared by diluting their respective stock solutions. The pH was adjusted to the desired values with a portable meter (Martini Mi805, Romania) using 0.05 M NaOH or 0.1 M HCl.

The pH and electrical conductivity (EC) of sediment samples were measured by using a portable meter (Martini Mi805, Romania). The pH was measured in the supernatant suspension of 1:5 sediment:water (w/v) mixtures (Pansu and Gautheyrou, 2007). The electrical conductivity (EC) was measured in 1:5 sediment:water (w/v) extracts (Carter and Gregorich, 2007; Pansu and Gautheyrou, 2007).

The organic matter content of sediments was indirectly estimated through the multiplication of the total organic carbon

concentration, determined by dichromate oxidation method, by conversion factor. Organic carbon present in sediment sample is oxidized completely by a known amount of excess potassium dichromate in the sulfuric acid medium and the remaining potassium dichromate is then titrated against ferrous ammonium sulfate (FAS) using ferroin as an indicator. The dichromate consumed by the sample is equivalent to all oxidizable organic carbon (Nelson and Sommers, 1982; Pansu and Gautheyrou, 2007).

The carbonates of sediments were determined by back titration method where calcium carbonate present in sediment sample is neutralized with a known amount of excess hydrochloric acid and the remaining hydrochloric acid is then titrated against sodium carbonate using methyl orange as an indicator. The hydrochloric acid consumed by the sample is equivalent to carbonate content (Pansu and Gautheyrou, 2007).

For heavy metals analysis, sediment samples were digested before determining total metals using nitric acid-hydrochloric acid digestion technique to reduce interference by organic matter and to convert metals associated with particulates to the form of free metals that can be determined by atomic absorption spectrometer (Pansu and Gautheyrou, 2007). Total Zn, Cu and Pb concentrations were analyzed in the digestion solution of sediment samples by flame atomic absorption spectrometer (Thermo Scientific iCE 3500, USA) at wavelengths of 213.9 nm, 324.7 nm and 217 nm, respectively.

Adsorption experiments were performed in a series of 600 ml beakers containing 5 g of oven-dried sediment adsorbents and 500 ml of metal ion solutions (10 g/L solid-solution ratio). 0.5 mL of orthophosphate phosphorus solution (50 mg  $\text{PO}_4^{3-}$ -P/L) was added to each beaker to enhance the adsorption of metal ions (Selim, 2015), where the adsorption of phosphate onto the oxide surfaces increased the negative charge on the oxide surface, thus enhancing the

adsorption of metal ions (McLean and Bledsoe, 1996). The pH was adjusted to the desired values, then the samples were covered with aluminum foil and equilibrated for a specific contact time at constant room temperature of 25 °C. After the equilibration period, the sediment adsorbents were separated by filtration through GF/C filters (Macherey-Nagel MN GF-3, Germany) and the concentrations of Cu<sup>2+</sup>, Zn<sup>2+</sup> and Pb<sup>2+</sup> remained in the solutions were analyzed by flame atomic absorption spectrometer (Thermo Scientific iCE 3500, USA). The concentrations of Cu<sup>2+</sup>, Zn<sup>2+</sup> and Pb<sup>2+</sup> adsorbed were calculated from the concentration differences.

The adsorption percentage of metal ion by sediment and the adsorption capacity of sediment for metal ion were calculated using the following equations:

$$\text{Adsorption (\%)} = \frac{(C_o - C_e)100}{C_o} \quad (1)$$

$$q_e = \frac{(C_o - C_e)V}{1000M} \quad (2)$$

where C<sub>o</sub> is the initial metal ion concentration in solution (µg/L), C<sub>e</sub> is the concentration of metal ion in solution at equilibrium (µg/L), q<sub>e</sub> is the adsorption capacity of sediment for metal ion or the amount of metal ion adsorbed on sediment (µg/g), V is the volume of metal ion solution used (mL), and M is the weight of sediment used (g).

The optimum conditions for metal adsorption were studied through pH, initial metal concentration and contact time. The effect of pH on the adsorption of Cu<sup>2+</sup>, Zn<sup>2+</sup> and Pb<sup>2+</sup> by sediments were conducted with initial metal ion concentrations of 70 µg/L, 90 µg/L and 40 µg/L for Cu<sup>2+</sup>, Zn<sup>2+</sup> and Pb<sup>2+</sup>, respectively at pH values ranging from 3.5 to 8.5, and contact time of 48 h. The effect of initial metal ion concentration on the adsorption of Cu<sup>2+</sup>, Zn<sup>2+</sup> and Pb<sup>2+</sup> by sediments was carried out using initial metal

ion concentrations ranging between 40-230 µg/L for Cu<sup>2+</sup>, 60-150 µg/L for Zn<sup>2+</sup>, and 50-450 µg/L for Pb<sup>2+</sup> at the optimum determined pH values and a contact time of 48 h. On the other hand, the effect of contact time on the adsorption of Cu<sup>2+</sup>, Zn<sup>2+</sup> and Pb<sup>2+</sup> by sediments were conducted using the optimum determined initial metal ion concentrations and pH values at contact time intervals ranging between 12-72 h.

Adsorption data were fitted using Langmuir, Freundlich, Dubinin–Radushkevich and Temkin isotherms, while adsorption kinetics were fitted using Pseudo-first-order kinetics, and Pseudo-second-order kinetics

Leaching experiments were performed in a series of 600 ml beakers containing 15 g of sediment samples and 500 mL distilled water (30 g/L solid-solution ratio), and the pH was adjusted to the desired values. The samples were covered with aluminum foil and contact time was employed at constant temperature. Thereafter, the sediment samples were separated by filtration through GF/C filters (Macherey-Nagel MN GF-3, Germany) and the concentrations of Cu<sup>2+</sup>, Zn<sup>2+</sup> and Pb<sup>2+</sup> leached in water were analyzed by flame atomic absorption spectrometer (Thermo Scientific iCE 3500, USA). The leaching percentage of metal ion in sediment was calculated from the concentration of metal ion leached from the sediment to the concentration of initial metal ion in sediment sample, which was determined by the HNO<sub>3</sub>-HCl digestion procedure.

The leaching behavior of Cu<sup>2+</sup>, Zn<sup>2+</sup> and Pb<sup>2+</sup> from sediments with respect to pH, temperature and contact time were studied at pH values (3.5-8.5), temperatures (25-45 °C), and contact times (12-72 h).

## RESULTS AND DISCUSSION

The physicochemical properties (pH, electrical conductivity, carbonates, and organic matter) of the River Nile sediment samples (S1, S2, and S3) are given in Table 1.

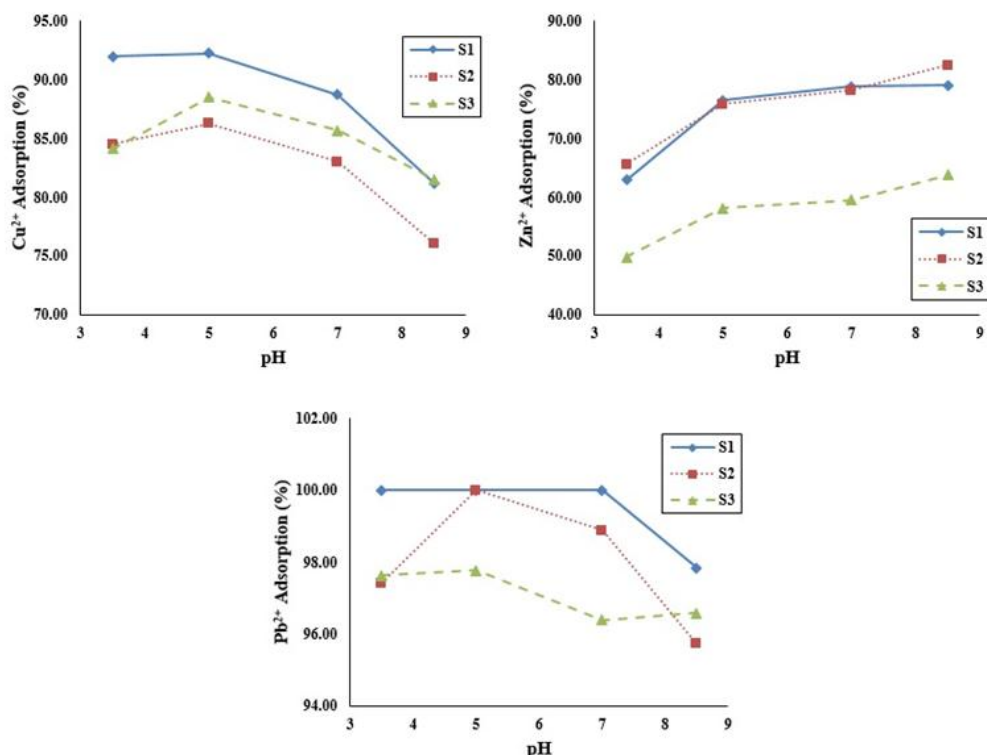
For adsorption studies, the effect of pH on the adsorption of  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{Pb}^{2+}$  by sediments were conducted with initial metal ion concentrations of 70  $\mu\text{g/L}$ , 90  $\mu\text{g/L}$  and 40  $\mu\text{g/L}$  for  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{Pb}^{2+}$ , respectively at pH values ranging from 3.5 to 8.5 and a contact time of 48 h.

As seen from Fig. 2, the adsorption of  $\text{Cu}^{2+}$  and  $\text{Pb}^{2+}$  by sediments decreased with increasing pH. The optimum pH value for maximum removal of  $\text{Cu}^{2+}$  and  $\text{Pb}^{2+}$  by S1, S2 and S3 sediments were pH 5

(92.23%, 86.28% and 88.50% for  $\text{Cu}^{2+}$  and 100%, 100% and 97.77% for  $\text{Pb}^{2+}$ , respectively). In contrast, the adsorption of  $\text{Zn}^{2+}$  by sediments increased with increasing pH. The optimum pH value for  $\text{Zn}^{2+}$  removal was 8.5 of which 79.02%, 82.40% and 63.82% of  $\text{Zn}^{2+}$  were removed by S1, S2 and S3 sediments, respectively. At higher pH values greater than 8.5 there is a possibility of the precipitation of the hydroxide species of the metal ions.

**Table 1. Some physical and chemical properties of the three sediment samples used in this study.**

Properties	Sediment sample		
	S1	S2	S3
Electrical conductivity ( $\mu\text{s/cm}$ )	183	236	689
pH	8.06	7.95	7.68
Organic matter (%)	1.48	1.13	0.95
Carbonate content (%)	3.16	3.48	3.68
Copper (mg/kg)	28.57	16.89	22.31
Zinc (mg/kg)	68.30	65.71	62.57
Lead (mg/kg)	9.42	37.98	9.25



**Fig. 2. Effect of pH on the adsorption of  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{Pb}^{2+}$  by sediments**

Similar results were observed by Lukman et al. (2013), who used natural clay for the adsorption of  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{Pb}^{2+}$  from single component solutions. They indicated that the adsorption of Cu and Pb ions in single component scenario became highest between pH values 4 and 6, while the adsorption of Zn ions increased with increasing pH up to (pH=8) at which all Zn ions were removed in single component scenario.

The basic mechanism that governs the adsorption characteristics of sediments at pH ranging between 3.5 and 8.5 is adsorption and ion exchange. The optimum adsorption of  $\text{Cu}^{2+}$  and  $\text{Pb}^{2+}$  at pH 5 may be attributed to the replacement of cations located on the exchangeable sites of sediments, i.e.  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  by  $\text{Cu}^{2+}$  and  $\text{Pb}^{2+}$  present in the aqueous solutions (Kaya and Ören, 2005; Eba et al., 2010). While the optimum adsorption of  $\text{Zn}^{2+}$  at pH 8.5 may be due to the electrostatic forces of attraction between the positively charged  $\text{Zn}^{2+}$  and the negatively charged surface of sediments (Akpomie et al., 2015; Khalfa et al., 2016).

**Effect of initial metal ion concentration.** The adsorption of  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{Pb}^{2+}$  by sediments increased with increasing their initial concentrations in solutions (Fig. 3). The highest adsorption of  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{Pb}^{2+}$  by sediments occurred at initial concentrations of 230  $\mu\text{g/L}$ , 150  $\mu\text{g/L}$  and 450  $\mu\text{g/L}$ , respectively at which 95.23%, 91.18% and 91.75% of  $\text{Cu}^{2+}$ , 75.56%, 76.20% and 75.49% of  $\text{Zn}^{2+}$ , and 97.58%, 96.63% and 97.60% of  $\text{Pb}^{2+}$  were adsorbed on S1, S2 and S3 sediments, respectively. This may be due to increasing driving force of the metal ions towards the active sites on sediments (Adebowale et al., 2006).

Similar results were observed by Adebowale et al. (2006) for the adsorption of Pb and Cd ions using both phosphate-modified and unmodified kaolinite clay,

Amer et al. (2010) for the adsorption of Pb (II), Zn (II) and Cd (II) using sodium polyphosphate-kaolinite clay, and Dawodu et al. (2012) for the adsorption of lead (II) using Agbani Clay. They all reported that increasing initial metal ions concentration resulted in an increase in the metal ions removed by adsorbents.

The average adsorption capacities of sediments for  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{Pb}^{2+}$  were 12.79  $\mu\text{g/g}$ , 7.85  $\mu\text{g/g}$  and 25.27  $\mu\text{g/g}$ , respectively as illustrated in Table 2.

The adsorption capacities of sediments for metal ions were in the order of  $\text{Pb}^{2+} > \text{Cu}^{2+} > \text{Zn}^{2+}$ . This was similar to the results obtained by Adebowale et al. (2005) when phosphate-modified, sulfate-modified and unmodified kaolin were used for the adsorption of  $\text{Pb}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{Cu}^{2+}$ , and Lim and Lee (2015) when soil was used for the adsorption of  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{Pb}^{2+}$ .

**Effect of contact time.** As shown in Fig. 4, the initial adsorption of metal ions at the initial contact time was very fast and the maximum uptake for  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{Pb}^{2+}$  by sediments occurred at contact times of 48 h, 24 h and 72 h, respectively at which 95.23%, 91.18% and 91.75% of  $\text{Cu}^{2+}$ , 79.46%, 78.27% and 77.35% of  $\text{Zn}^{2+}$ , and 99.60%, 98.72% and 99.75% of  $\text{Pb}^{2+}$  were adsorbed on S1, S2 and S3 sediments, respectively. Thereafter, the adsorption remained almost constant due to the decrease of adsorption sites on the sediments which gradually interacted with the metal ions. The contact time needed to reach the maximum removal of metal by sediments is dependent on the type of heavy metal (Taamneh and Sharadqah, 2016). The adsorption rate depends on the metal ions transported from the bulk liquid phase to the actual adsorption sites (Jiang et al., 2010; Sangiunsak and Punrattanasin, 2014).

Table 2. Average adsorption capacities of sediments for  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{Pb}^{2+}$ .

Sediment	$q_e$ ( $\mu\text{g/g}$ )			Adsorption capacities sequence
	$\text{Cu}^{2+}$	$\text{Zn}^{2+}$	$\text{Pb}^{2+}$	
S1	13.16	7.83	25.36	$\text{Pb}^{2+} > \text{Cu}^{2+} > \text{Zn}^{2+}$
S2	12.54	7.91	25.09	$\text{Pb}^{2+} > \text{Cu}^{2+} > \text{Zn}^{2+}$
S3	12.66	7.79	25.37	$\text{Pb}^{2+} > \text{Cu}^{2+} > \text{Zn}^{2+}$
Total average	12.79	7.85	25.27	$\text{Pb}^{2+} > \text{Cu}^{2+} > \text{Zn}^{2+}$

$q_e$  ( $\mu\text{g/g}$ ) = adsorption capacity of sediment for metal ion.

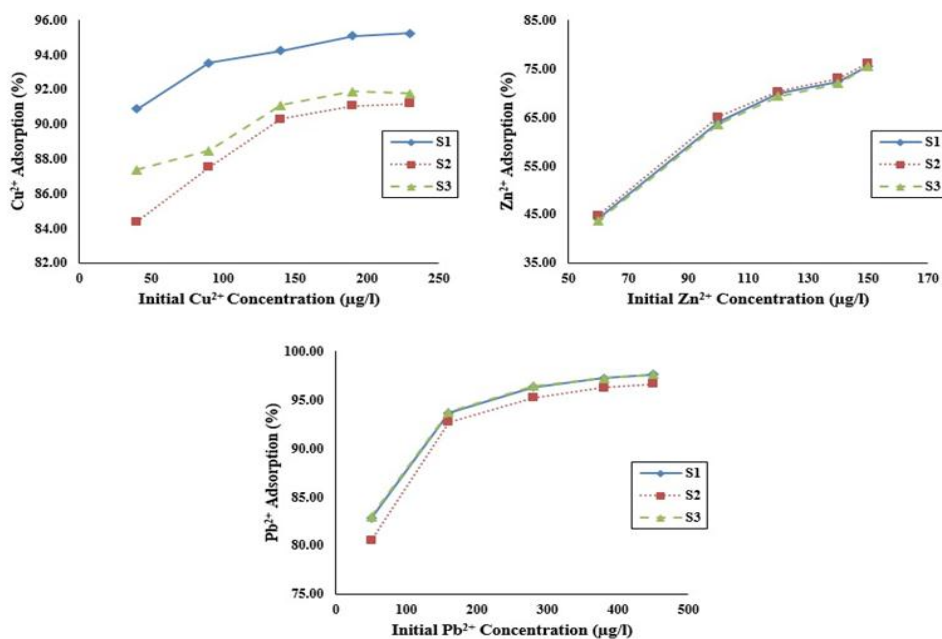


Fig. 3. Effect of initial metal ion concentrations on the adsorption of  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{Pb}^{2+}$  by sediments.

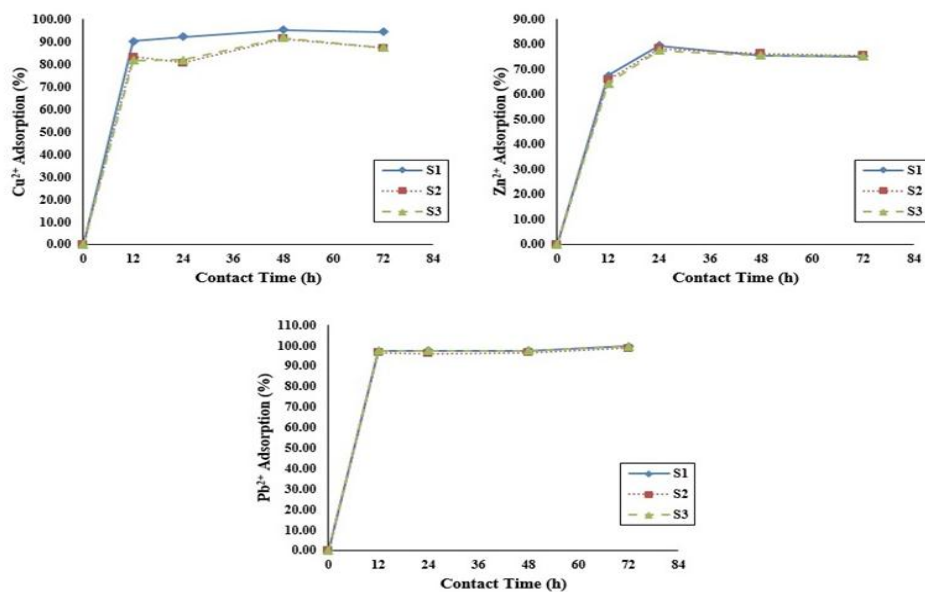


Fig. 4. Effect of contact time on the adsorption of  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{Pb}^{2+}$  by sediments

In summary, the optimum conditions for the maximum adsorption of  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{Pb}^{2+}$  by sediments were determined as pH values of 5, 8.5 and 5, respectively, initial metal concentrations of 230  $\mu\text{g/L}$ , 150  $\mu\text{g/L}$  and 450  $\mu\text{g/L}$ , respectively, and contact times of 48 h, 24 h and 72, respectively.

The experimental data are best described by Langmuir adsorption isotherm, a plot of  $C_e/q_e$  versus  $C_e$  will give a straight line with slope of  $1/Q_0$  and intercept of  $1/bQ_0$ . Such plot is used to find the Langmuir parameters. Langmuir plots for the adsorption of  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{Pb}^{2+}$  by sediments are depicted in Fig. 5.

It is clear from the deviation of the graph from linearity and the lower correlation coefficient values  $R^2$  (0.653-0.923) that the experimental data are not better fitted to Langmuir isotherm. Therefore, we further tested the data with other common adsorption models. This is a

strong evidence that the adsorption of  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{Pb}^{2+}$  by sediments doesn't strictly follow a monolayer coverage and that chemical adsorption is not the predominant process that occurs between the metal ions and sediments (Jamhour et al., 2016). The Freundlich isotherm constants were deduced by plotting  $\log q_e$  versus  $\log C_e$  (Fig. 6). Table 3 lists the values of the calculated Freundlich constants  $K_f$  and  $1/n$ .

Since the values of  $R^2$  ranged from 0.926 to 0.996 for the adsorption of metal ions ( $\text{Cu}^{2+}$  and  $\text{Pb}^{2+}$ ) with an exception of  $\text{Zn}^{2+}$ , which supported that these adsorption events followed the Freundlich isotherm well. The Freundlich isotherm was more appropriate to explain the adsorption of  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{Pb}^{2+}$  onto sediments when compared with Langmuir isotherm. This suggests that the adsorption of  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{Pb}^{2+}$  by sediments is a physical multilayer adsorption.

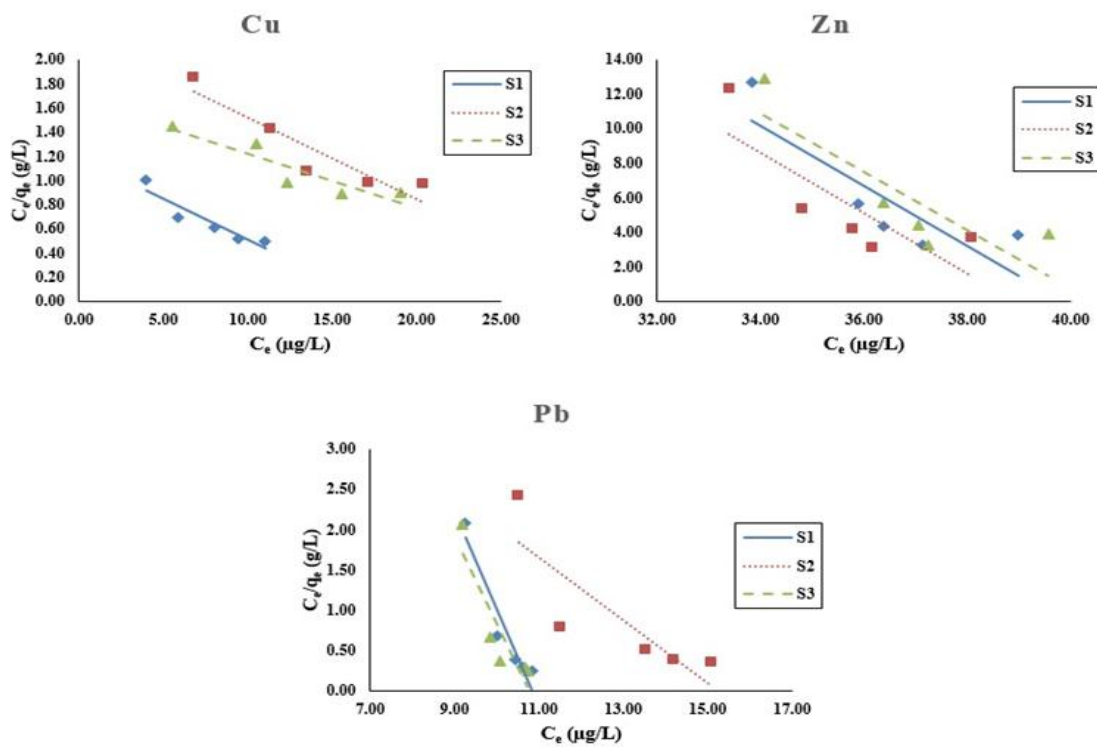


Fig. 5. Langmuir isotherm for  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{Pb}^{2+}$  adsorption by sediments



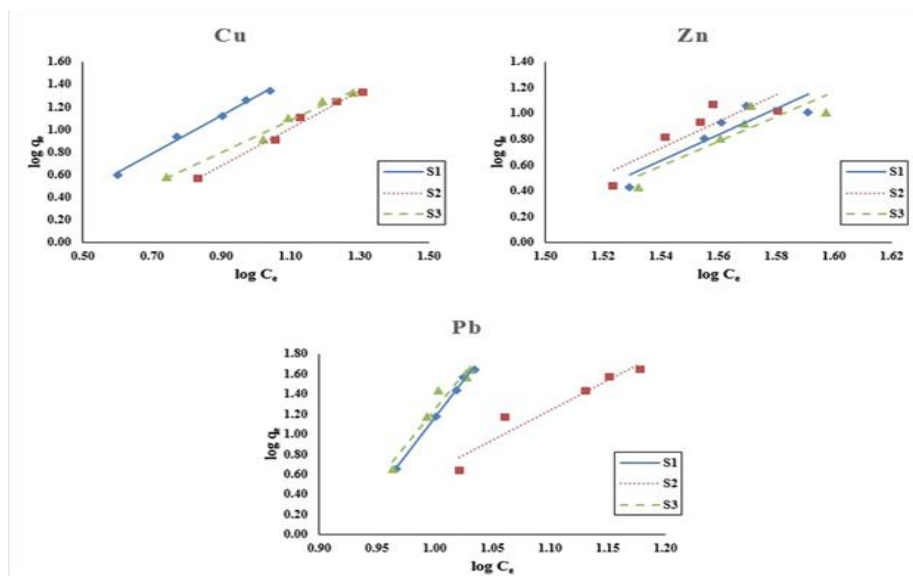


Fig. 6. Freundlich isotherm for  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{Pb}^{2+}$  adsorption by sediments

The D-R isotherm parameters were determined by plotting  $\ln q_e$  versus  $\epsilon^2$  (Fig. 7) and the values are provided in Table 3. The data listed in Table 3 show that the adsorption of  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{Pb}^{2+}$  onto sediments fit the D-R isotherm well based on the values of  $R^2$  at 0.786-0.996. The mean adsorption energies (E) for  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{Pb}^{2+}$  are less than 8 KJ/mol, which are not within the energy range of ion-exchange reactions 8–16 kJ/mol,

corresponding to physical adsorption (Rieman and Walton, 1970).

For Temkin isotherm, when  $q_e$  was plotted against  $\ln C_e$ , a straight line was obtained (Fig. 8) from which the Temkin isotherm parameters were calculated and the values are shown in Table 3. From Table 3, the  $R^2$  values obtained (0.724-0.981) shows that the Temkin isotherm provided a quite good fit to the experimental data of the adsorption of  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{Pb}^{2+}$  onto sediments.

Table 3. Langmuir, Freundlich, D-R and Temkin isotherm parameters for  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{Pb}^{2+}$  adsorption by sediments.

Isotherm model	S1			S2			S3		
	$\text{Cu}^{2+}$	$\text{Zn}^{2+}$	$\text{Pb}^{2+}$	$\text{Cu}^{2+}$	$\text{Zn}^{2+}$	$\text{Pb}^{2+}$	$\text{Cu}^{2+}$	$\text{Zn}^{2+}$	$\text{Pb}^{2+}$
<b>Langmuir isotherm</b>									
$R^2$	0.867	0.717	0.923	0.856	0.653	0.709	0.831	0.711	0.803
<b>Freundlich isotherm</b>									
$K_f$ ( $\mu\text{g/g}$ )	0.40	1.4E-15	1.7E-14	0.16	5.9E-16	5.0E-06	0.32	7.4E-15	1.3E-13
$1/n$	1.69	10.05	14.91	1.64	10.36	5.94	1.43	9.56	14.13
$n$ (g/L)	0.59	0.10	0.07	0.61	0.10	0.17	0.70	0.10	0.07
$R^2$	0.995	0.797	0.996	0.990	0.750	0.926	0.982	0.771	0.947
<b>D-R isotherm</b>									
$q_m$ ( $\mu\text{g/g}$ )	25.41	1235.08	35148.49	22.15	1558.03	403.98	19.71	953.22	29178.63
$K$ ( $\text{mol}^2/\text{J}^2$ )	6.3E-06	1.1E-03	1.4E-04	1.6E-05	1.1E-03	8.5E-05	1.0E-05	1.1E-03	1.3E-04
E (KJ/mol)	0.28	0.02	0.06	0.17	0.02	0.08	0.22	0.02	0.06
$R^2$	0.962	0.832	0.996	0.925	0.786	0.956	0.879	0.808	0.962
<b>Temkin isotherm</b>									
B (J/mol)	17.53	59.28	247.29	16.12	62.47	103.97	14.11	54.91	245.59
A (L/g)	0.29	0.03	0.11	0.17	0.03	0.10	0.21	0.03	0.11
$R^2$	0.959	0.782	0.918	0.947	0.753	0.981	0.914	0.724	0.958

Adsorption kinetics were carried out using Pseudo-first-order kinetics and Pseudo-second-order kinetics. For Pseudo-first-order kinetics, the values of  $q_e$  and  $k_1$  were deduced by plotting  $\ln(q_e - q_t)$  versus  $t$  (Fig. 9, Table 4). For Pseudo-second-order kinetics plotting  $t/q_t$  against  $t$  gave a straight line (Fig. 10) from which the values of  $q_e$  and  $k_2$  were deduced (Table 4).

The results from Table 4 show that the adsorption of  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{Pb}^{2+}$  by sediments was better described by the pseudo-second-order model with correlation coefficients,  $R^2 > 0.997$  and the difference between calculated  $q_e$  and experimental  $q_e$  values is slight. Similar results were observed by Veli and Alyüz (2007), who used natural clay (Cankırı bentonite) for the adsorption of  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$ .

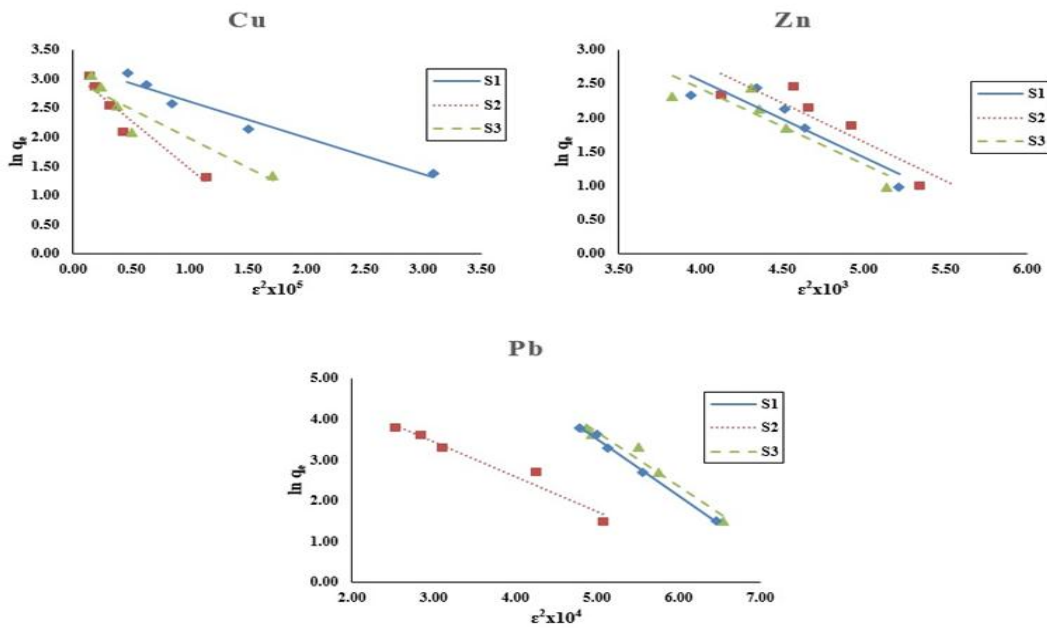


Fig. 7. D-R isotherm for  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{Pb}^{2+}$  adsorption by sediments

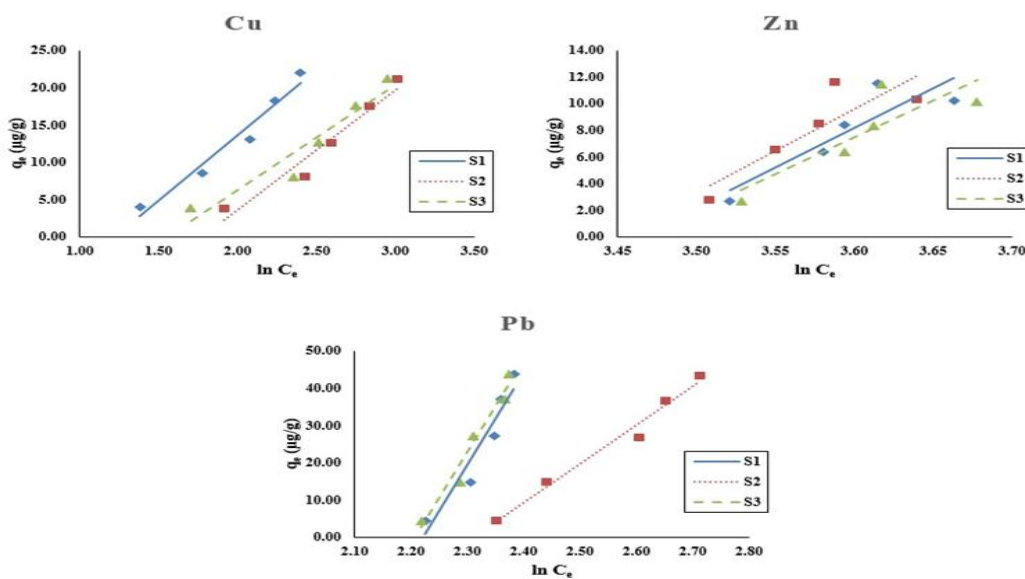


Fig. 8. Temkin isotherm for  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{Pb}^{2+}$  adsorption by sediments

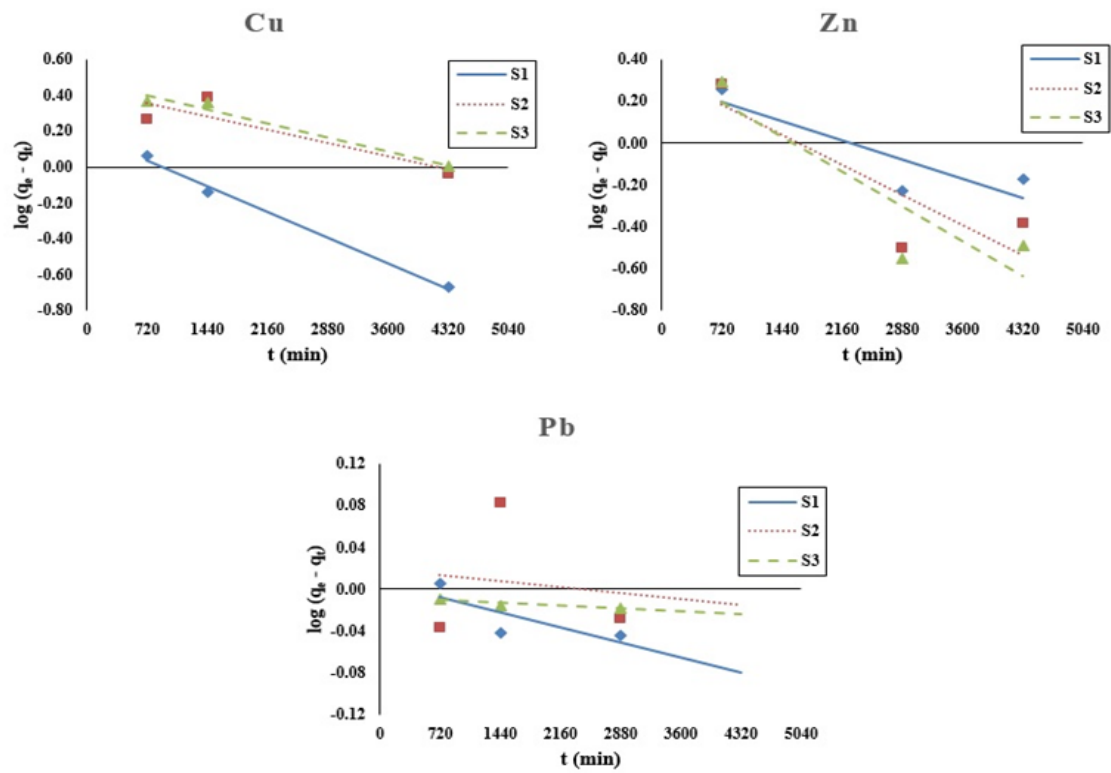


Fig. 9. Pseudo-first-order reaction kinetics for the adsorption of  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{Pb}^{2+}$  by sediments

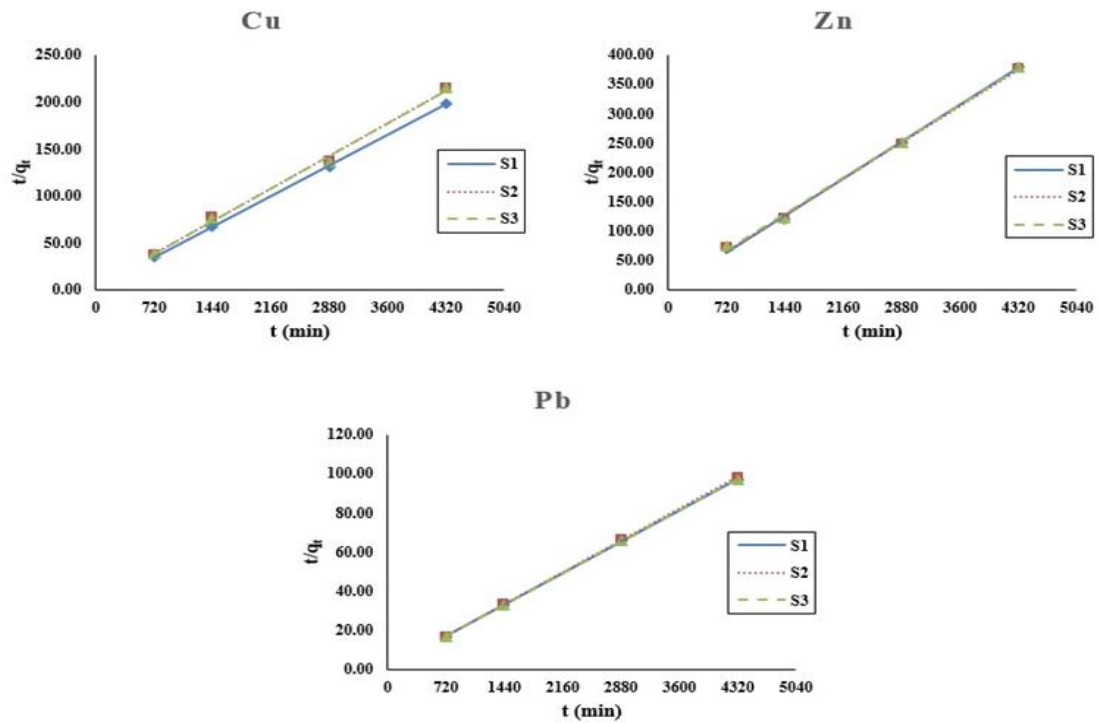


Fig. 10. Pseudo-second-order reaction kinetics for the adsorption of  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{Pb}^{2+}$  by sediments

**Table 4. Pseudo-first-order and pseudo-second-order kinetic parameters for Cu<sup>2+</sup>, Zn<sup>2+</sup> and Pb<sup>2+</sup> adsorption by sediments.**

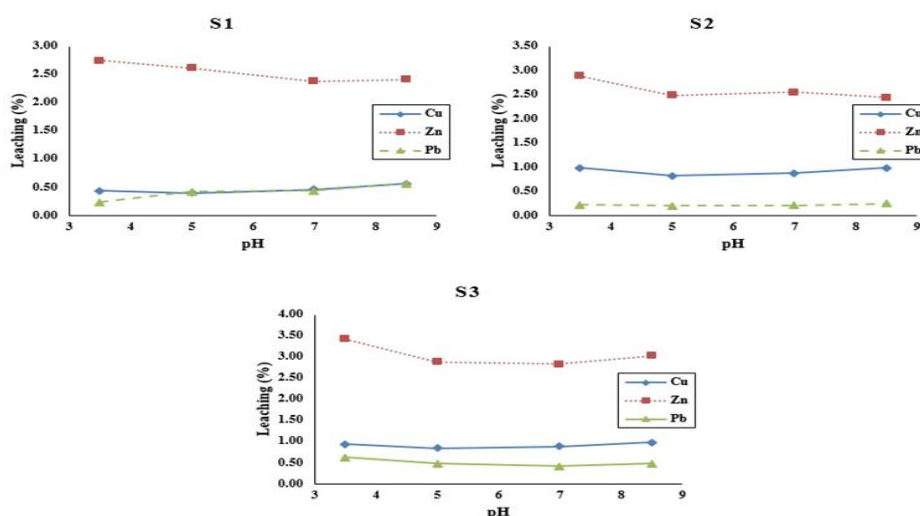
Sediment	Metal	q <sub>e,exp</sub> (µg/g)	Pseudo-first-order kinetic			Pseudo-second-order kinetic		
			q <sub>e,cal</sub> (µg/g)	k <sub>1</sub> (min <sup>-1</sup> )	R <sup>2</sup>	q <sub>e,cal</sub> (µg/g)	k <sub>2</sub> (g/µg.min)	R <sup>2</sup>
S1	Cu <sup>2+</sup>	21.99	1.51	4.57E-04	0.995	22.06	1.12E-03	1.000
	Zn <sup>2+</sup>	12.07	1.95	2.96E-04	0.763	11.51	5.31E-03	0.998
	Pb <sup>2+</sup>	44.57	1.02	4.59E-05	0.609	44.70	6.70E-04	1.000
S2	Cu <sup>2+</sup>	21.06	2.67	2.36E-04	0.800	20.76	6.08E-04	0.997
	Zn <sup>2+</sup>	11.89	2.11	4.58E-04	0.725	11.70	1.60E-03	0.998
	Pb <sup>2+</sup>	44.18	1.04	1.77E-05	0.016	44.34	5.92E-04	1.000
S3	Cu <sup>2+</sup>	21.19	2.99	2.48E-04	0.970	20.85	6.01E-04	0.997
	Zn <sup>2+</sup>	11.75	2.31	5.33E-04	0.793	11.68	1.22E-03	0.998
	Pb <sup>2+</sup>	44.64	0.98	8.81E-06	0.838	44.76	6.53E-04	1.000

As represented in Fig. 11, the leaching of Cu<sup>2+</sup> and Pb<sup>2+</sup> from sediments was independent to pH and almost constant, while the leaching of Zn<sup>2+</sup> from sediments decreased with increasing pH. The leaching percentages of the studied metal ions from sediments with respect to pH ranged between 0.4-0.99% for Cu<sup>2+</sup>, 2.38-3.43% for Zn<sup>2+</sup>, and 0.2-0.63% for Pb<sup>2+</sup>.

Szarek-Gwiazda (2014) deduced that the leaching of heavy metals (Cd, Pb, Cu, Zn, Mn and Fe) from the sediments of the Dobczycki, Czorsztyński and Rożnowski Reservoirs was pH-dependent. The reservoir sediments had a variable ability to release heavy metals with increasing

acidity (lowering pH). At pH 5 and pH 3, the considerable leaching of Mn (up to 60% and 85% of the total amount, respectively), Cd (up to 35% and 56%, respectively) and Pb (up to 25% and 39%, respectively), the lower leaching of Cu (up to 18% and 30%, respectively) and Zn (up to 14% and 20%), and the lowest leaching of Fe (below 5%) were found.

The leaching of Cu<sup>2+</sup>, Zn<sup>2+</sup> and Pb<sup>2+</sup> from sediments wasn't temperature-dependent and almost constant (Fig. 12). The leaching percentages of the studied metal ions from sediments with respect to temperature varied between 0.6-1.07% for Cu<sup>2+</sup>, 2.35-2.65% for Zn<sup>2+</sup>, and 0.23-0.49% for Pb<sup>2+</sup>.



**Fig. 11. Effect of pH on the leaching of Cu<sup>2+</sup>, Zn<sup>2+</sup> and Pb<sup>2+</sup> from sediments.**

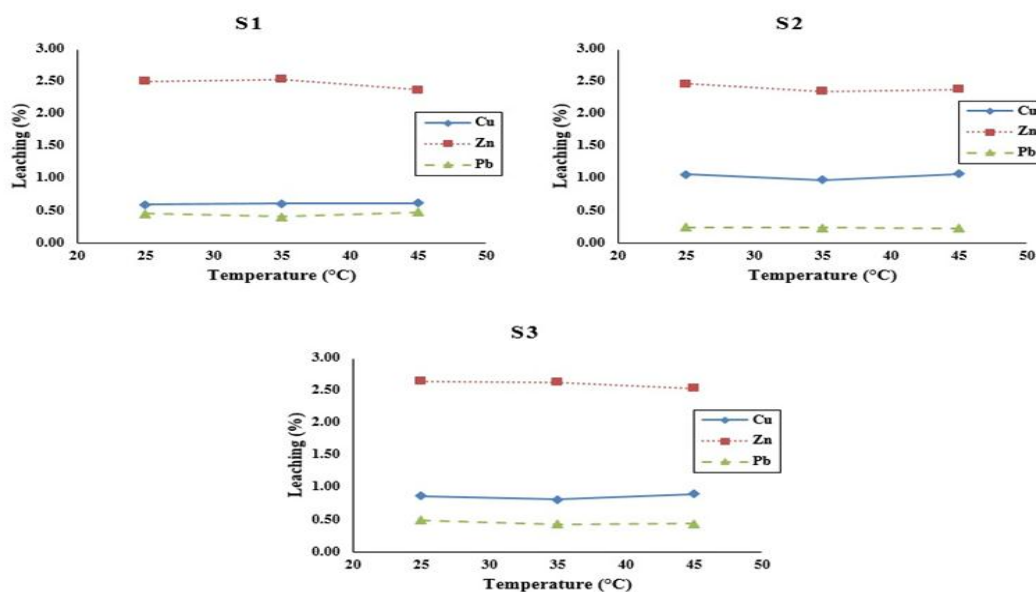


Fig. 12. Effect of temperature on the leaching of  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{Pb}^{2+}$  from sediments

As indicated in Fig. 13, the leaching of  $\text{Cu}^{2+}$  and  $\text{Pb}^{2+}$  from sediments was independent to contact time and almost constant, while the leaching of  $\text{Zn}^{2+}$  from sediments increased with increasing contact time and the highest leaching for  $\text{Zn}^{2+}$  occurred at contact time of 72 h at which 3.09%, 2.76% and 3.35% of  $\text{Zn}^{2+}$  were leached from S1, S2 and S3 sediments, respectively. The leaching percentages of the studied metal ions from

sediments with respect to contact time varied between 0.56-1.06% for  $\text{Cu}^{2+}$ , 0.73-3.35% for  $\text{Zn}^{2+}$ , and 0.2-0.5% for  $\text{Pb}^{2+}$ .

Baran et al. (2015) reported that the leaching of heavy metals in relation to their total content in dredged bottom sediments fluctuated from 1 to 5.5% for Zn, 0.9 to 9.4% for Cu, 3.3 to 4.5% for Ni, 1.6 to 6.9% for Pb, 0.9 to 19.2% for Cd, and 0.8 to 6.3% for Cr.

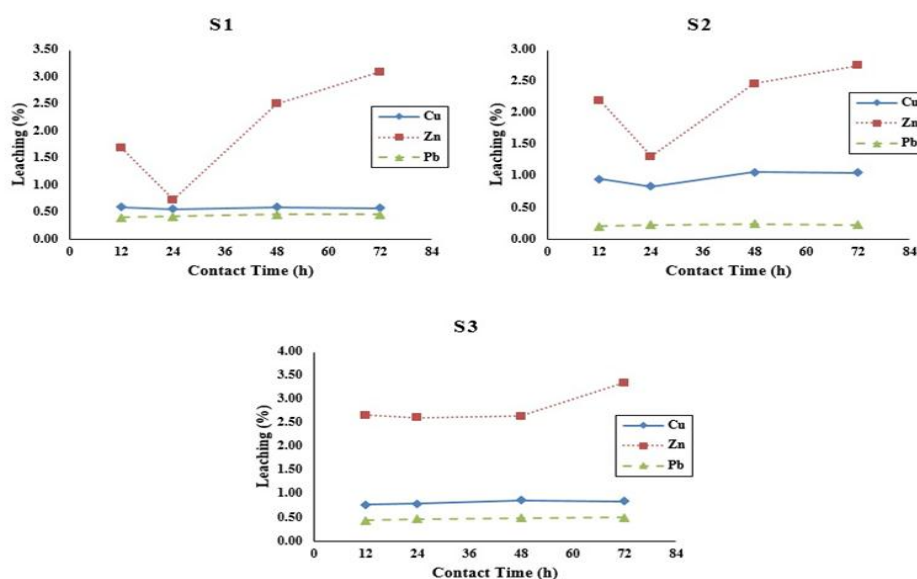


Fig. 13. Effect of contact time on the leaching of  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{Pb}^{2+}$  from sediments

**Table 5. Average leaching percentages of Cu<sup>2+</sup>, Zn<sup>2+</sup> and Pb<sup>2+</sup> from sediments with respect to pH, temperature and contact time.**

Sediment	Leaching (%) with respect to pH			Leaching (%) with respect to temperature			Leaching (%) with respect to contact time		
	Cu <sup>2+</sup>	Zn <sup>2+</sup>	Pb <sup>2+</sup>	Cu <sup>2+</sup>	Zn <sup>2+</sup>	Pb <sup>2+</sup>	Cu <sup>2+</sup>	Zn <sup>2+</sup>	Pb <sup>2+</sup>
S1	0.47	2.54	0.42	0.61	2.47	0.45	0.58	2.00	0.43
S2	0.92	2.59	0.22	1.04	2.40	0.24	0.97	2.19	0.23
S3	0.91	3.04	0.50	0.86	2.60	0.45	0.82	2.82	0.48
Total average	0.77	2.72	0.38	0.83	2.49	0.38	0.79	2.34	0.38

The average leaching percentages of Cu<sup>2+</sup>, Zn<sup>2+</sup> and Pb<sup>2+</sup> from sediments were 0.77%, 2.72% and 0.38%, respectively with respect to pH, 0.83%, 2.49% and 0.38%, respectively with respect to temperature, and also 0.79%, 2.34% and 0.38%, respectively with respect to contact time as indicated in Table 5. The differences in the leaching percentages of Cu<sup>2+</sup>, Zn<sup>2+</sup> and Pb<sup>2+</sup> from sediments may be due to their geochemical associations with individual sediment components (Szarek-Gwiazda, 2014).

The leaching percentages of the studied metal ions from sediments were in the order of Zn<sup>2+</sup> > Cu<sup>2+</sup> > Pb<sup>2+</sup>. It can be observed that Zn<sup>2+</sup> ions were the most leached from sediments and this enhanced the adsorption study results of why Zn<sup>2+</sup> ions were the least adsorbed by sediments.

## CONCLUSION

The adsorption behavior of Cu<sup>2+</sup>, Zn<sup>2+</sup> and Pb<sup>2+</sup> onto sediments can be affected by pH, initial metal ion concentration and contact time. The adsorption of Cu<sup>2+</sup> and Pb<sup>2+</sup> by sediments was inversely proportional to pH and the optimum pH value for Cu<sup>2+</sup> and Pb<sup>2+</sup> removal was 5. In contrast, the adsorption of Zn<sup>2+</sup> by sediments was directly proportional to pH and the optimum pH value for Zn<sup>2+</sup> removal was 8.5. The adsorption of Cu<sup>2+</sup>, Zn<sup>2+</sup> and Pb<sup>2+</sup> by sediments was directly proportional to their initial concentrations in solutions. The maximum adsorption for Cu<sup>2+</sup>, Zn<sup>2+</sup> and Pb<sup>2+</sup> by sediments occurred at contact

times of 48 h, 24 h and 72 h, respectively. The adsorption selectivity sequence of these metal ions was in the order of Pb<sup>2+</sup> > Cu<sup>2+</sup> > Zn<sup>2+</sup>. In contrast, the leaching study revealed a selectivity sequence in the order of Zn<sup>2+</sup> > Cu<sup>2+</sup> > Pb<sup>2+</sup>. The adsorption of Cu<sup>2+</sup>, Zn<sup>2+</sup> and Pb<sup>2+</sup> onto sediments was fitted to Freundlich, D-R and Temkin isotherms well, but the experimental data were not better fitted to Langmuir isotherm supporting that the adsorption has a physical nature. The adsorption of Cu<sup>2+</sup>, Zn<sup>2+</sup> and Pb<sup>2+</sup> by sediments was better fitted by the pseudo-second-order model.

As a result of this study, it may be concluded that sediments can play an important role in heavy metals cycling in the aquatic environment and mediate the uptake, storage, release and transfer of it between environmental compartments. Also, sediments can capture heavy metals entering water bodies and slowly releasing them back into the water column, and so input pollution with heavy metals to the River Nile water can be controlled.

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