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RESEARCH ARTICLE

Preparation of Cu^{2+} and Pb^{2+} spiked sediment for sediment toxicity tests: a case study from Soai Rap estuary in Sai Gon - Dong Nai river system

Chuẩn bị mẫu trầm tích kết hợp (Cu^{2+}, Pb^{2+}) cho thử nghiệm độc tính trầm tích: Nghiên cứu cụ thể từ cửa sông Soài Rạp trên hệ thống sông Sài Gòn-Đồng Nai

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Heavy metals contamination in river sediment is becoming more severe, as is also the case in Soai Rap estuary, Vietnam, where Cu and Pb polution is significant. The evironmental risks posed by heavy metals are usually assessed by toxicity tests using sediment spiked with contaminants in different concentrations. In order to recreate natural conditions, the preparation of sediment samples spiked with heave metals must be carried out following strict procedures. The objective of the study is therefore to determine the adsorption kinetic and equilibrium parameters of two heavy metals (Cu^{2+} and Pb^{2+}) on surface sediment collected from an intertidal mudflat in the Soai Rap estuary of Vietnam. The experiments were conducted with a liquid (Cu^{2+} and Pb^{2+} solutions) to solid (sediment) ratio of approximately 1:10. Elutriates were prepared by shaking the spiked sediment sample in artificial seawater at a ratio of 1:4 (wet sediment/water). The Cu^{2+} solution reached equilibrium after about 12 hours and the maximum adsorption capacity of 0.86 mg/g while the Pb^{2+} solution reached equilibrium after 10 hours, with the maximum adsorption capacity of 35.2 mg/g. The regression analysis of experimental data of Cu^{2+} and Pb^{2+} adsorption on sediment has shown good consistency with both Langmuir and Freundlich models, whereas the Langmuir model was found to be more appropriate. The adsorption kinetic of both heavy metals was well described by the pseudo second-order adsorption kinetic model and the desorption processes were characterised using the Langmuir and Freundlich models (both models were suitable for Cu^{2+} desorption but only Freundlich for Pb^{2+}). Using the present methodology, the concentrations of heavy metals spiked on sediment could be calculated, however the maximum adsorption capacity for both substances was not yet achieved. Further findings include the determination of the equilibrium time for adsorption, very relevant when spiking sediments for toxicity tests to evaluate the environmental risks of polution with heavy metals in the Soai Rap estuary, Vietnam.

Ô nhiễm kim loại nặng trong trầm tích cửa sông ngày càng trầm trọng, như trường hợp ở cửa sông Soài Rạp, Việt Nam, nơi mà ô nhiễm Cu, Pb là đáng kể. Rủi ro môi trường do kim loại nặng gây ra thường được đánh giá bằng các thử nghiệm độc tính sử dụng trầm tích kết hợp với các chất gây ô nhiễm ở các nồng độ khác nhau. Để tái tạo các điều kiện tự nhiên, việc chuẩn bị các mẫu trầm tích kết hợp với kim loại nặng phải được thực hiện theo những quy trình nghiêm ngặt. Do đó, mục tiêu của nghiên cứu là xác định các thông số động học và cân bằng hấp phụ của hai kim loại nặng (Cu^{2+} và Pb^{2+}) lên trầm tích mặt được thu thập từ một bãi bồi tại cửa sông Soài Rạp, Việt Nam. Các thí nghiệm được thực hiện với tỷ lệ chất lỏng (dung dịch Cu^{2+} và Pb^{2+}) và chất rắn (trầm tích) xấp xỉ 1:10. Dung dịch rửa giải được chuẩn bị bằng cách lắc mẫu trầm tích đã kết hợp trong nước biển nhân tạo theo tỷ lệ 1: 4 (trầm tích ướt/nước). Dung dịch Cu^{2+} đạt trạng thái cân bằng sau khoảng 12 giờ và dung lượng hấp phụ tối đa 0,86 mg/g trong khi dung dịch Pb^{2+} đạt trạng thái cân bằng sau 10 giờ, với dung lượng hấp phụ tối đa 35,2 mg/g. Phân tích hồi quy dữ liệu thực nghiệm của quá trình hấp phụ Cu^{2+} và Pb^{2+} lên trầm tích đã cho thấy phù hợp với cả hai mô hình Langmuir và Freundlich, nhưng mô hình Langmuir được tìm thấy là phù hợp hơn. Động học hấp phụ của cả hai kim loại nặng được mô tả là phù hợp với mô hình động học hấp phụ bậc hai giả và các quá trình giải hấp được đặc trưng bằng mô hình Langmuir và Freundlich (cả hai mô hình đều phù hợp với giải hấp Cu^{2+} nhưng chỉ Freundlich cho Pb^{2+}). Sử dụng phương pháp hiện tại, nồng độ kim loại nặng kết hợp lên trầm tích có thể được tính toán, tuy nhiên khả năng hấp phụ tối đa của cả hai chất vẫn chưa đạt được. Hơn nữa, việc xác định thời gian cân bằng cho hấp phụ, rất phù hợp khi sử dụng trầm tích kết hợp cho thử nghiệm độc tính để đánh giá rủi ro môi trường ô nhiễm kim loại nặng ở cửa sông Soài Rạp, Việt Nam.

Keywords: spiked sediment; heavy metals; adsorption; desorption; Soai Rap

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1. Introduction

Recently, industrial activities and urbanization in estuary regions have led to an increased pollution, especially with heavy metals, which can impact the ecosystem due to their toxicity and adsorptive behaviors (Jain, 2001; Zhang et al., 2012; Costa-Böddeker et al., 2017). This includes physical and chemical processes such as the adsorption on sediments, the precipitation with ferrous and manganese oxides, with carbonate and the adsorption by organic matters or by covalent bonds in minerals (Wijaya et al., 2017).

Soai Rap estuary belongs to the Sai Gon – Dong Nai river system, a major river system in Vietnam. It is located at the intersection of Can Gio district (Ho Chi Minh City), Can Giuoc district (Long An province), and Go Cong Dong district (Tien Giang province). Studies on heavy metal pollutions showed that Cu and Pb were the most common pollutions in Soai Rap estuary (Nguyen et al., 2018). Sediment toxicity tests are employed for evaluating the environmental risks of pollutants. A common technique used in toxic experiments is artificially "spiking" the sediments with known amounts of contaminants (Fathallah, 2014).

Equilibrium and kinetic of preparing spiked sediment can affect the bioavailability of chemicals in sediment (ASTM E1706-05). Consequently, the experimentation and explanation of the sensitivity of organisms to the toxins in the sediments will not be accurate (Simpson et al., 2004). Therefore, it is essential to survey the metal adsorption properties of sediments in the estuary and develop a reliable process to create sediments containing specific metal concentrations, in which the metals will act as the natural adsorbed substance to the surface of the sediments in a polluted environment (Lu et al., 2008).

The studying toxicology of estuary sediment is necessary, but put less attention of heavy metal adsorption character in sediment of the Soai Rap estuary. Therefore, batch and kinetic sorption experiments of Cu^{2+} and Pb^{2+} on sediment were conducted to explore the sorption characteristics of Soai Rap estuarine sediments. The Langmuir, Freundlich sorption and first and second-order kinetic models are used to describe the sorption characteristics of Cu^{2+} and Pb^{2+}. This information will be useful in studying spiked sediment toxicology.

2. Materials and methods

2.1 Sediment sampling

2.1.1 Sampling location and collection

After preliminary surveys, sediment samples were taken during low tides in March 2018. The location of the sampling site (10°24′58.46″ N, 106°48′30.871″ E) is an intertidal mudflat in the Soai Rap estuary with a low pollution level based on the results obtained from previous studies (Nguyen et al., 2018). Sediments were collected at a location 15-25 m from the river bank at a depth of 0-10 cm (EPA, 2001). Sampling tools were made of plastic (Lu et al., 2008) and each sample is 20 dm^3 in volume (Baran & Tarnawski, 2013).

2.1.2 Sample processing

Sediment samples were passed through a plastic sieve with 1 mm pore size (press sieving). Samples were made homogeneous and preserved separately in polyethylene (PE) container, then kept in the dark at 4°C prior to analysis and experiment (Atkinson et al., 2007; Fathallah, 2014).

2.1.3 Sample analysis

The humidity of the sediments was determined as described in the ASTM D2216-10 method; the pH of the overlying water was measured with HP 9010 pH meter equipment (Trans Instruments) according to ASTM D1293-18; salinity was measured with DYS DMT-10 (Korea) equipment and total organic carbon (TOC) was analyzed as described in the Walkley Black method (TCVN 8941, 2011).

Sediment samples were digested as guided in TCVN 6649 (TCVN 6649, 2000). The sediment sample of 1-2 g (wet weight) was treated with HNO_3 and H_2O_2. The sample was then filtered via a filter (0.45 µm, Whatman) and a measured volume of 100 mL with HNO_3 5%. Heavy metals' concentrations (Cu, Pb) were determined using a spectroscope ICP-OES (TCVN 6665, 2011).

2.2 Analysis

2.2.1 Preparations of chemicals

All chemicals used in the study were of analytical grade (Merck). Aqueous solutions of Cu and Pb were prepared from $CuCl_2$ $2H_2O$; $Pb(NO_3)_2$ respectively. All glassware and other containers were thoroughly cleaned by soaking in detergent followed by soaking in 10% nitric acid for at least 24 hours and finally rinsed with deionized water several times prior to use. Artificial saline water was created by mixing deionized distilled water with salt (PA) 35 ± 2 ‰ (Kester et al., 1967).

2.2.2 Adsorption of Cu^{2+} and Pb^{2+} solution in sediments

Wet sediments were washed with artificial saline water three times and then left to settle. This increases the adsorption sites on the sediments so that metal ions can penetrate the sediments easier (Benamer, 2014). The experiment procedure is described elsewhere (Lu et al., 2008; Noegrohati, 2005; Fan et al., 2017). Wet sediment after the washing process was used in the spiking experiment, because dried sediment would change the characteristics of the sediment and, therefore, reduce the representativeness of the sample. Adsorption experiments were designed with a liquid-to-solid volumetric ratio of approximately 1:10. The solutions (150 mL) were prepared by serial dilution of stock solutions (1,000 mg/L for Cu^{2+} and 10 g/L for Pb^{2+}). The range of concentrations of prepared Cu^{2+} and Pb^{2+} solutions varied from 0.0 to 80.7 mg/L, and 0.0 to 5,000 mg/L, respectively. The solutions were transferred into 250 mL polypropylene conical flasks containing 15 g of sediment. The contents of the conical flasks were sealed and shaken by GFL3015 shaker at around 150 rpm for 24 hours, which is more than sufficient time to reach equilibrium at room temperature based on preliminary experiments. The pH level was kept constant during the experiment. The concentration of free metal ions in the supernatant liquid was determined using ICP-OES. The settled fraction was centrifuged (Centrifuge DLAB DM0636) at 1,200 rpm for 15 minutes (Thain, 1992; Costa et al., 2016), then samples from the solid fraction were taken for metal-spiked sediment desorption equilibrium tests.

2.2.3 Adsorption kinetic of Cu^{2+} and Pb^{2+} solutions in sediments

Kinetic experiments were carried out by mixing 15 g of sediment with 150 ml of solution of constant Cu^{2+} and Pb^{2+} concentration (66.7 mg/L and 3,333 mg/L, respectively) and shaking them at around 150 rpm at room temperature. Samples were withdrawn at suitable time intervals, centrifuged at 1,200 rpm for 15 minutes and then metals concentrations were analyzed by the ICP-OES.

2.2.4 Desorption equilibrium of Cu^{2+} and Pb^{2+} solutions in spiked sediments

The solid fractions obtained from section 2.2.2 were shaken (GFL3015 shaker, 150 rpm) in artificial saline water in glass beakers at a ratio of 1:4 (wet sediment/water) for 12 h and centrifuged at 1,200 rpm for 15 minutes. After centrifugation, liquid samples were taken for metal analyses.

2.3 Data processing

2.3.1 Calculation of the adsorption capacity at equilibrium

Adsorption capacity (eq. 1) was calculated according to Jain (2001), Lu et al. (2008), Sangiumsak and Punrattanasin (2014):

$$q_i = \frac{(C_0 - C_i)}{M} \cdot V \cdot 1000 \qquad \text{(eq. 1)}$$

where:

- q_i = adsorption capacity at equilibrium (mg/g);
- C_o = initial aqueous concentration (mg/L);
- C_i = aqeous concentration at equilibrium (mg/L);
- M = mass of sediment (g)
- V = volume of solution (mL)

The adsorption capacity was calculated using the most common adsorption isotherms: Langmuir model – eq. 2 (Langmuir, 1906) and Freundlich model – eq. 3 (Freundlich, 1909):

Langmuir adsorption isotherm:

$$q_i = q_m \frac{K_L \cdot C_i}{1 + K_L \cdot C_i} \qquad \text{(eq. 2)}$$

where:

- q_m = maximum adsorption capacity at equilibrium (mg/g);
- K_L = Langmuir adsorption constant (L/mg).

Freundlich adsorption isotherm:

$$q_i = K_F . C_i^{1/nF} \qquad \text{(eq. 3)}$$

where:

- K_F (L/mg) and $1/n_F$ (-) = Freundlich adsorption constants.

To easily obtain the adsorption constants, the Langmuir and Freundlich adsorption isotherm models have been written in the following liniarized form by plotting $1/q_i$ vs. $1/C_i$ (eq. 4) and log (q_i) vs log (C_i) (eq. 5), respectively:

$$\text{Langmuir: } \frac{1}{q_i} = \frac{1}{K_L q_m} \frac{1}{C_i} + \frac{1}{q_m} \qquad \text{(eq. 4)}$$

$$\text{Freundlich: } \log(q_i) = \frac{1}{n_F} \log(C_i) + \log(K_F) \qquad \text{(eq. 5)}$$

2.3.2 Calculating adsorption kinetics

First and second-order kinetic modeling is often used to analyze and calculate the kinetic adsorption data (Sun and Wang, 2016; Jain, 2001).

Pseudo first-order kinetic equation:

$$\text{Ln}\left(q_e - q_t\right) - \text{Ln}q_e = -k_1 t \qquad \text{(eq. 6)}$$

$$\text{or: } \text{Ln}\left(q_e - q_t\right) = -k_1 t + \text{Ln}q_e \qquad \text{(eq. 7)}$$

with $\text{Ln}\left(q_e - q_t\right)$ plotted against *t;*

Pseudo second-order kinetic equation:

$$\frac{1}{q_t} = \frac{1}{t} \frac{1}{k_2 q_e^2} + \frac{1}{q_e} \qquad \text{(eq. 8)}$$

with 1/*q* plotted against 1/*t*.

where:

- q_e = the adsorption capacity Cu^{2+} (or Pb^{2+}) at equilibrium time (mg/g);
- q_t = the adsorption capacity Cu^{2+} (or Pb^{2+}) at time t (mg/g);
- k_1 and k_2 = constants of pseudo first-order and pseudo second-order kinetic.

2.3.3 Calculating desorption equilibrium

Survey of the metallic desorption parameters in the spiked sediment by which it is possible to determine the equilibrium conditions in the preparation of the eluent solution for the purpose of studying the metal toxicity in sediment. The Freundlich and Langmuir desorption equations are often used to determine the parameters in the desorption equilibrium (Aşçı et al., 2010).

Desorption equilibrium according to Freundlich:

$$\log(q_d) = \frac{1}{n_{Fdesorp}} \log(C_d) + \log(K_{Fdesorp}) \qquad \text{(eq. 9)}$$

where:

- $K_{Fdesorp}$ and $1/n_{Fdesorp}$ = Freundlich desorption constants;
- C_d = the equilibrium metal concentrations in solution (mg/L);
- q_d = the amounts of metal remained in the sediment after desorption.

Desorption equilibrium according to Langmuir:

$$\frac{1}{q_d} = \frac{1}{K_{Ldesorp} q_0} \frac{1}{C_d} + \frac{1}{q_0} \qquad \text{(eq. 10)}$$

where:

- $K_{Ldesorp}$ = Langmuir desorption constant.
- q_0 is the maximum remaining Cu^{2+} (or Pb^{2+}) concentration in the sediment (mg/g).

2.3.4 Data analysis

Control and replicate samples (n = 3) were employed in the analysis in order to minimize error sources and to evaluate accuracy and precision. The statistical analysis software SPSS 20.0 was used for determining the fitness of data through correlation test and constructing the regression equation. In addition, homogeneity was evaluated by Levene's test, Tukey's test post hoc (Sig > 0.05) and Tamhane's T2 (Sig < 0.05). These tests determined the deviation of averages in different experiments with the factor p < 0.05.

3. Results and discussions

Adsorption characteristics for the studied sediment should first be investigated, and the spiking conditions can then be determined. The main recommendations for this procedure are as follows.

3.1 Physical and chemical properties of sediments

The ranges and mean values of Cu, Pb, salinity, pH, and TOC in the sediment are listed in Table 1. The values obtained in this study are consistent with the results from Nguyen et al. (2018). Although the site selected for sampling was the same as in Nguyen et al. (2018), the content of Cu measured in the sediment was higher (21.4 mg/kg in comparison to 16.4 mg/kg in previous study) while Pb did not fluctuate. The different results may be explained by changes in coastal activity affecting the surface sediment at the sampling location. Nevertheless, the mean concentrations of Cu and Pb determined in this study are below the ERL guideline values of 34.0 and 46.7 mg/kg (Long et al., 1995) and way below the values mentioned by the QCVN 43:2012/BTNMT standard of 108 and 112 mg/kg, respectively (MONRE, 2012). For this reason, the sediment samples collected at the Soai Rap estuary can be considered as belonging to an unpolluted site and therefore used as reference sediment (ASTM E1706-05).

Table 1. Mean values and standard deviation (SD) of Cu, Pb, TOC, salinity concentrations and pH value in the sediment of the Soai Rap estuary

	pH	Cu	Pb	TOC	Salinity
	(-)	(mg/kg)	(mg/kg)	(%)	(‰)
Mean	7.1	21.41	28.62	2.78	20
SD	0.1	0.02	0.02	0.02	2

3.2 Kinetics and equilibriums adsorption of Cu^{2+} on sediment

3.2.1 Equilibrium adsorption of Cu^{2+} on sediment

Figure 1 shows the results of the variation in Cu^{2+} adsorption onto the sediments with initial concentrations C_0. It is possible to observe the increase of adsorption capacity with increasing Cu^{2+} concentration in the range from 0.00 to 80 mg/L. Figure 1 also clearly evidenced that the maximum adsorption capacity of the sediment has not been reached within the experimental conditions.

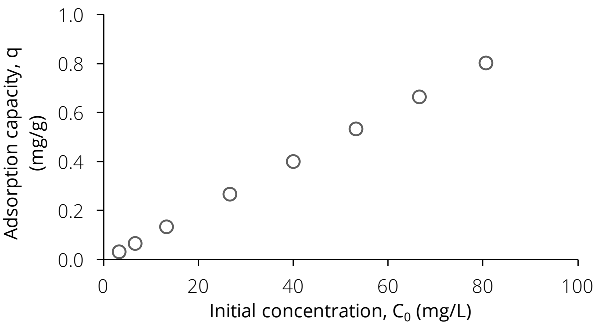


Figure 1. Relationship between the adsorption capacity *q* (mg/g) and initial concentration *C_0* (mg/L) of Cu^{2+}

To quantify the adsorption efficiency, the Langmuir and Freundlich isotherms have been represented in linearized form (Figure 2), with the respective adsorption constants and correlation coefficients (R^2) summarized in Table 2. The correlation coefficients were high (R^2 = 0.94–0.99) in all cases and thus, both models were preliminarily considered suitable for interpretation of Cu^{2+} ion adsorption on sediment. Nevertheless, the Langmuir model fitted slightly better the experimental data than Freundlich (R^2 = 0.99 vs. 0.94), which provides evidence of monolayer coverage of homogeneous adsorbent surface (Hegedűsová et al., 2016). The results of the study are similar to previous studies which confirm that Cu^{2+} adsorption on sediments fits well both Langmuir and Freundlich models (Fan et al., 2017; Wu & Ren, 2011; Lu et al., 2008). The maximum adsorption capacity of 0.86 mg/g determined by this study (Table 2) was lower than the result obtained Wu and Ren (2011) of 12.6 - 28.7 mg/g, which could be explained by the different solid / liquid ratios used (1/10 vs. 1/300).

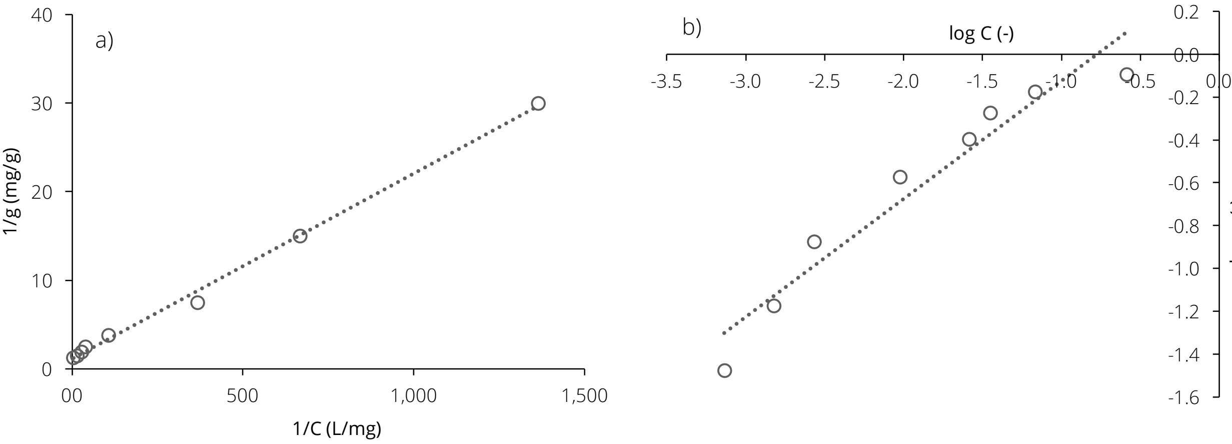


Figure 2. Adsorption equilibrium of Cu^{2+} onto sediments from spiking solutions: a) Langmuir model, b) Freundlich model

Table 2. Kinetic and equilibrium parameters of Cu2+ adsorption on sediment

Model	Parameter	Regression equation	R^2
Langmuir model	K_L = 56 L/mg; q_m = 0.86 mg/g	y = 0.0209x** + 1.1629**	0.9964
Freundlich model	K_F = 2.7 mg/g; n_F = 1.8	y = 0.551x** + 0.425**	0.9358
Pseudo first-order model	k_1 = 0.02 (1/min); q_e = 0.0005 mg/g	y = -0.0186x - 7.5334	0.7502
Pseudo second-order model	k_2 = 5,625 (g/(mg x min)); q_e = 0.67 mg/g	y = 0.0004x** + 1.5008**	0.9734

*** Significant with p<0.01*

3.2.2 Kinetics adsorption of Cu^{2+} on sediment

The kinetic data showed that adsorption increased rapidly in the first hour, increased further for the first 5 hours, then slowed down and after 12 hours reached the adsorption equilibrium (Figure 3). The initial rapid stage may be due to greater number of adsorption sites available for adsorption of Cu^{2+} (Anirudhan and Suchithra, 2010). This is consistent with previous studies where absorption equilibrium was reached in about 4-10 hours (Fan et al, 2017; Lu et al., 2008).

To evaluate the adsorption kinetics, pseudo first- and second-order kinetic models were used. The correlation coefficients and calculated adsorption capacity values (Table 2) indicate that the pseudo second-order model is suitable for interpretation of adsorption kinetics of Cu^{2+} on the sediment of Soai Rap estuary. The pseudo first-order model could not be used because the correlation coefficients were low (R^2 = 0.75) and the measured adsorption capacity q_e (0.0005 mg/g) was very different than the calculated value (0.667mg/g). That means that the rate of occupation of adsorption sites is proportional to the square number of unoccupied sites, because the pseudo second-order model is based on a second-order mechanism (Thajeel, 2013).

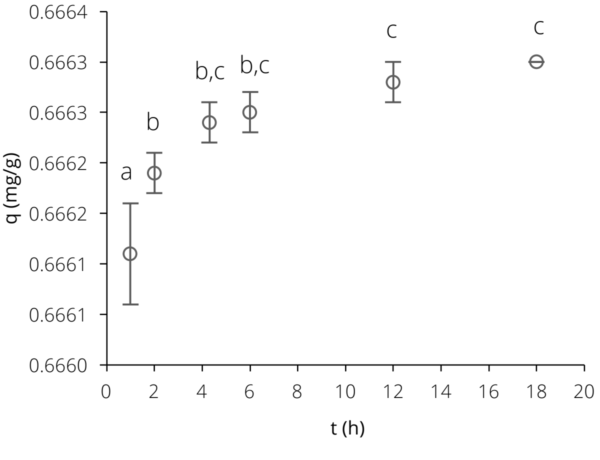


Figure 3. Relationship between the adsorption capacity of Cu^{2+} on sediment *q* (mg/g) and time *t* (h). Significant differences are indicated by different letters

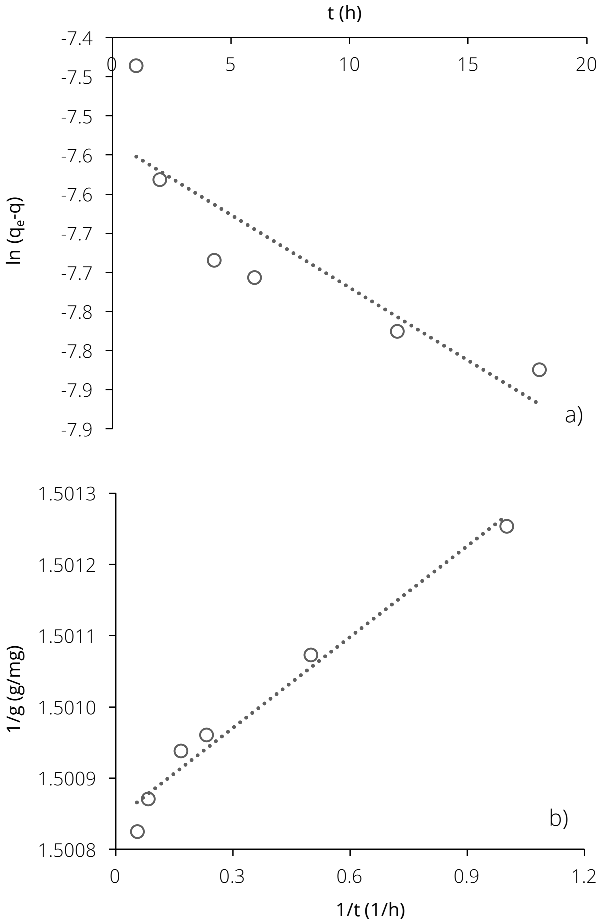


Figure 4. Adsorption kinetic of Cu^{2+} onto sediments from spiking solutions: a) pseudo first-order kinetic model, b) pseudo second-order kinetic model

The results of the correlation analysis ($p < 0.05$) of SPSS 20 showed that ln(q_e-q) and t were not correlated ($p = 0.06 > 0.05$) while 1/q and 1/t were correlated ($p < 0.01$).

3.3 Kinetics and equilibriums adsorption of Pb^{2+} on sediment

3.3.1 Equilibriums adsorption of Pb^{2+} on sediment

Figure 5 shows the variation in Pb^{2+} adsorption onto the sediments with initial concentrations C_0. The adsorption capacity increased linearly with increasing the Pb^{2+} concentration from 0.00 to 3,333 mg/L. Similar to Cu^{2+} adsorption, also in this case maximum adsorption capacity of the sediment was not reached under the experimental conditions.

The Langmuir and Freundlich isotherm models were fitted to the experimental data and the results obtained were similar to Hegedűsová et al. (2016) and Wu and Ren (2011).

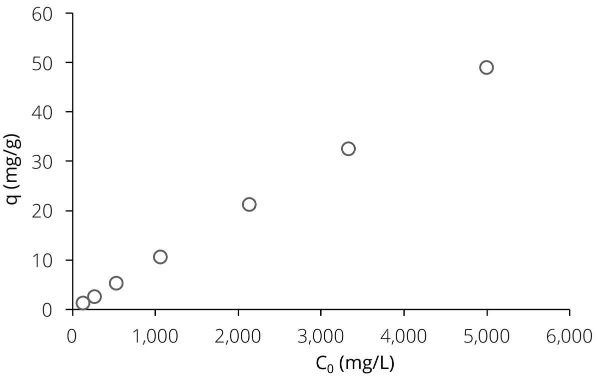


Figure 5. Relationship between the adsorption capacity *q* (mg/g) and the aqueous concentration *C_0* (mg/L) of Pb^{2+}

The Langmuir model proved to be more suitable (R^2 =0.99 vs. 0.90 for Freundlich), which illustrates the sediment adsorption of Pb^{2+} as chemical adsorption (Wu & Ren, 2011). The maximum adsorption capacity in this study (35.2 mg/g, see Table 3), was lower though than in the study of Hegedűsová et al. (2016) (65.36 mg/g).

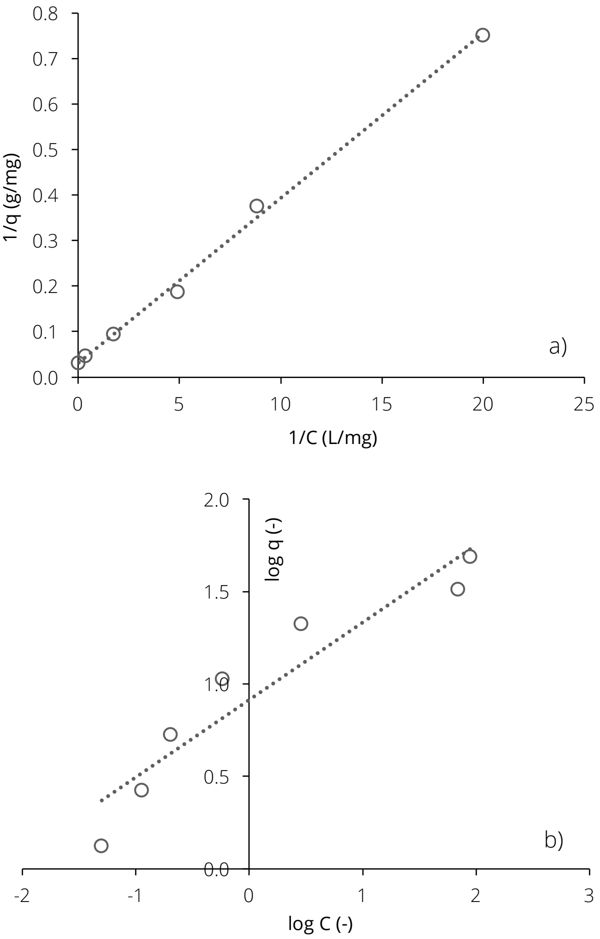


Figure 6. Adsorption equilibrium of Pb^{2+} onto sediments from spiking solutions: a) Langmuir model, b) Freundlich model

Table 3. Kinetic and equilibrium parameters of Pb^{2+} adsorption on sediment

Model	Parameter	Regression equation	R^2
Langmuir model	K_L = 0.78 L/mg; q_m = 35.2 mg/g	y = 0.0364x** + 0.0284*	0.9972
Freundlich model	K_F = 8.2 mg/g; n_F = 2.4	y = 0.4186x** + 0.9132**	0.8986
Pseudo first-order model	k_1 = 0.25 (1/min); q_e = 3.1 mg/g	y=-0.2518x + 1.1212	0.8632
Pseudo second-order model	k_2 = 0.2 (g/(mg x min)); q_e = 33 mg/g	y = 0.0046x** + 0.0304**	0.9787

*** Significant with p<0.01; * Significant with p<0.05*

The results of correlation analysis ($p < 0.05$) showed that 1/q and 1/C were correlated ($p < 0.01$), and similarly for log(q) and log(C).

3.3.2 Adsorption kinetics of Pb^{2+} on sediment

The sorption of Pb^{2+} to sediment was represented in Figures 7 at various times. These plots show that Pb^{2+} adsorption increased rapidly in the first 6 hours, then suddenly slowed down and almost reached the adsorption equilibrium. The time of Pb^{2+} adsorption equilibrium in this study was therefore considered to be 6 hours, slower than the 2 hours obtained by Wu and Ren (2011) in coastal sediment of the Yellow River Estuary, value obtained by using a different solid/liquid ratio (1:20 in comparison with 1:10 in this study).

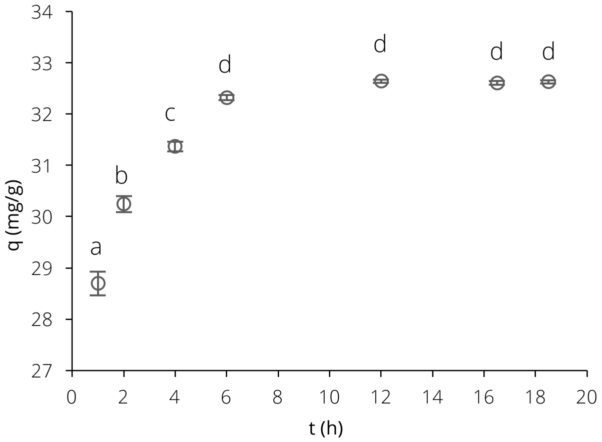
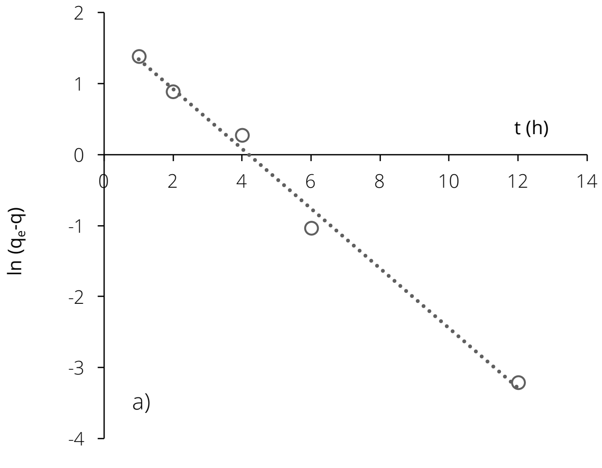


Figure 7. Relationship between the adsorption capacity of Pb^{2+} on sediment *q* (mg/g) and time *t* (h). Significant differences are indicated by different letters



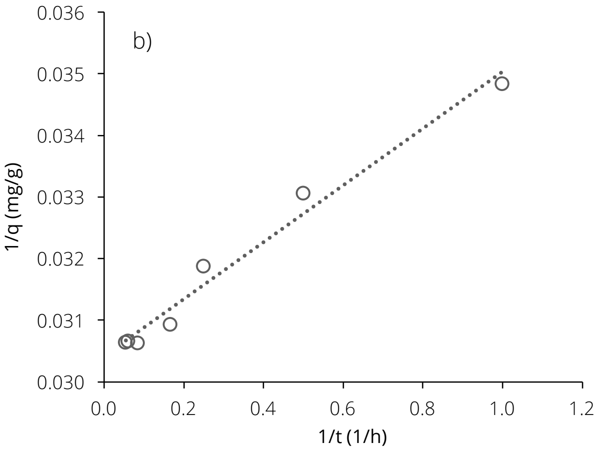


Figure 8. Adsorption kinetic of Pb^{2+} onto sediments from spiking solutions: a) pseudo first-order kinetic model, b) pseudo second-order kinetic model

The corresponding adsorption constants and adsorption capacity values were calculated and summarized in Table 3. The correlation coefficients R^2 indicate that the pseudo second-order model is slightly more suitable for the interpretation of adsorption kinetics of Pb^{2+} on the sediment of Soai Rap estuary (R^2=0.9787 vs. 0.8632). Similar results are also presented in the study of Hegedűsová et al. (2016) and the explanation is similar to the case of Cu^{2+} adsorption: the rate of occupation of adsorption sites is proportional to the square number of unoccupied sites (Thajeel, 2013).

3.4 Equilibrium desorption of Cu^{2+} and Pb^{2+} on sediment

The experimental data of Cu^{2+} desorption was described well using both Langmuir and Freundlich models, however the Langmuir model fitted better than the Langmuir (Table 4). The calculated maximum desorption capacity (q_0 = 0.91mg/g) approximated the experimental results (q_0 = 0.93 mg/g).

Also in case of Pb^{2+} desorption both models were fitted well the experimental, however, the maximum desorption capacity was 19.6 mg/kg while the adsorption capacity was 35.2 mg/g. This can be interpreted by the fact that Pb can be bound mainly as hydroxyl complexion to the sediment surfaces (hydrolytic condensation) and at high pH the Pb desorption process was disadvantaged (Rybicka et al., 1995).

Table 4. Equilibrium parameters of Cu^{2+} and Pb^{2+} desorption on sediment

Model	Parameter	Regression equation	R^2
Langmuir model for Cu^{2+}	K_L = 3.7 L/mg; q_0 = 0.901 mg/g	y = 0.298x** + 1.114**	0.9806
Freundlich model for Cu^{2+}	K_F = 1.3 mg/g; n_F = 1.3	y = 0.7692x** + 0.1079**	0.9465
Langmuir model for Pb^{2+}	K_L = 0.5 L/mg; q_0 = 19.6 mg/g	y = 0.1115x** + 0.0508**	0.9994
Freundlich model for Pb^{2+}	K_F = 0.13 mg/g; n_F = 0.66	y = 1.5147x** - 0.8852**	0.9689

*** Significant with p<0.01*

4. Conclusion

The adsorption of Cu^{2+} on sediment collected from the Soai Rap estuary reached equilibrium after about 12 hours and the maximum adsorption capacity was 0.86 mg/g. In case of Pb^{2+}, the equilibrium was reached after about 6 hours with the maximum absorbed capacity of 35.2 mg/g at a solid/liquid ratio of 1:10. The regression equation of adsorption of Cu^{2+} and Pb^{2+} on sediment was consistent with both Langmuir and Freundlich models, but the Langmuir model was found to be more suitable. The pseudo second-order adsorption kinetic model was appropriate for both Cu^{2+} and Pb^{2+}. The experimental data was used to calculate the spiking heavy metals' concentrations and the equilibrium time for toxicity testing of spiked sediment from Soai Rap estuary. To interpret the desorption (elution) process, the Langmuir and Freundlich models were tested. In case of Cu^{2+}, both models were found suitable but for Pb^{2+}, only the Freundlich model was appropriate.

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