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In situ Concentration and Adsorption Characteristics of Cu(II) and Pb(II) in Bed Sediments of River Niger in Lokoja Area, Nigeria

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In this present study, concentrations of copper and lead were investigated in natural sediment at three locations along the Niger River in Lokoja, Nigeria. In addition, the ability of bed sediment to control metal ion contamination in aquatic systems through absorption as a sink process was also evaluated. Parameters and models that control the behaviour of metals in solution, such as pHzpc, pH of the sediment, kinetics, and equilibrium isotherms were interpreted. The pH value of sediment in water and calcium chloride ($CaCl_2$) was in 4.6-7.2 range, indicating that the sediment is moderately acidic and indicating the slow movement of metal ions to overlying water column. The tolerance of River Niger to metal adsorption in the sediment was in the order of Cu<Pb. According to thermodynamic adsorption data, equilibrium isotherms and kinetic studies, the adsorption behaviour of Cu(II) and Pb(II) ions in aqueous solutions occurs spontaneously, and follows Langmuir and Freundlich isotherms, and has a pseudo-first-kinetic order. The current copper (18.81-34.68 mg/kg) and Lead (14.81-38.36 mg/kg) content in Niger River sediment samples are relatively low compared to other river sediments an indication of low anthropogenic activities in the study area.

Keywords: sediment; River Niger; heavy metals; adsorption; isotherm; kinetics

I. INTRODUCTION

Heavy metals have a tendency to bioaccumulate and biomagnify along the food chain, and persist in the aquatic environment (Yam *et al.,* 2020), and toxic to humans, so they are considered serious pollutants. Due to industrial production (Lu *et. al.,* 2019; Worakhunpiset, 2018), surface runoff, sewage discharge, (Lu *et al.,* 2019) and agricultural activities (Shen *et al.,* 2019), sediments on the bottom of rivers, estuaries, bays and some offshore oil fields are frequently polluted by heavy metals.

Thus, in the aquatic ecosystem, sediment is considered to be the sink and convergence of heavy metals, and the main transportation and storage of potentially toxic metals (Zhang *et al.,* 2014). Once heavy metals enter the water body, their fate can be defined through a series of physical, chemical and biological reactions, including adsorption-desorption (Duncan *et. al.,* 2018; Fan *et al.,* 2017), precipitation and dissolution (Duncan *et al.,* 2018), bioaccumulation, ion exchanges, complexation, and oxidation-reduction (Fan *et al.,* 2017). In addition, the above mentioned processes are affected by temperature, dissolve oxygen concentration, disturbance of water and pH (Duncan *et al.,* 2018).

The metal discharged into the water precipitates and accumulates in the bottom sediment, where the metal can be released due to changes in the physical/chemical and biological conditions of the bottom water (Wojtkowska, 2013). Because of the dynamic nature of the aquatic environment, physical processes such as tides, wind currents and wind waves (Lu *et al.,* 2019), saturation vis-a-vis the overlying water column, and the chemical nature of the water, may cause sediments to resuspend or be desorbed. In the process of sediment resuspension or desorption, the adsorbed metal

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*Corresponding author's e-mail: aloysius.pam@fulokoja.edu.ng ions will be released into the river system, causing harm to the aquatic ecosystem, and entering the food chain through benthic organisms. With the increase in population and human activities, the river sediments are becoming more enriched with heavy metals making the water unfit for drinking, fishing, agriculture, etc., additionally causing the biological wellbeing and biodiversity of the river system to be further threatened by the quality of the sediments. Pollutants in surface water are frequently transported to the bottom sediments through the adsorption and precipitation process of suspended particulates(Lin & Chen, 1998). The high sorption of heavy metals onto suspended and riverbed sediments can reduce their concentration in aquatic systems. Adsorption remains the main process in the mobility of metals in the river (Jain & Ram, 2009) and because of the accumulative and persistence tendencies of metals, concentration of metals in the sediments could be higher than the underlying surface water in 1-3 orders of magnitude (Lin & Chen, 1998). According to the US Environmental Protection Agency (EPA) research, copper, and lead are both priority pollutants (Huang *et al.,* 2020).

The metal content of the sediment produced during the long-term precipitation process makes it possible to obtain a comprehensive depiction of reservoir pollution (Wojtkowska, 2013). In a bid to determine the concentration of copper and lead in sediment and ascertain the risk posed to the aquatic communities, many researchers have attempted to evaluate the level of buildup of these metals in of sediment, with little or no attention on the tolerance of the river to heavy metal adsorption in sediment. For instance, Duncan *et al.* (2018) assessed heavy metal pollution in the sediments of the Pra River and its tributaries. Singh *et al.* (2017) analysed the bottom sediments of the Ghaghara River and found that the concentrations of Pb and Cu(II) in the sediments were 10.71, 14.26 mg/kg, 2.76, and 11.74 mg/kg, respectively. In another study, the accumulation of Cu(II) and Pb(II) in the Tiser river sediments were reported by Sakan *et al.* (2009). In addition, allowing the sediment to adsorb heavy metal ions as a sink process is a reliable way to reduce the risks associated with metal ions in the river system. However, existing literature reports on copper and lead adsorption are specifically used for wastewater treatment, and many activated carbons (Imamoglu & Tekir, 2008; Onundi *et al.,* 2010), mineral rocks (Cao *et al.,* 2004), and Clay (Pyrgaki *et al.,* 2018) have has been used to explore adsorption properties and reduce the concentration of copper and lead in the polluted media. Only a few studies have been dedicated to the adsorption of Cu(II) and Pb(II) on sediments. Although there are preliminary literature reports on the content of Cu(II) and Pb(II) in the River Niger sediments, there is little data on the adsorption behaviour of these metals in River Niger sediments. In the current investigation, we appraised the Cu(II) and Pb content in the sediment of river Niger. Batch adsorption experiments of Pb(II) and Cu(II) were conducted to appraise the adsorption characteristics of the sediment and evaluate its adsorption capacity. In addition, isotherm and kinetic models are used to describe the uptake behaviour of Cu(II) and Pb(II) in aqueous systems. To our understanding, no study has reported literature data from the river Niger on adsorption of metals on sediments, thus the study represents a significant contribution to the current state of knowledge of the study area and will be helpful in understanding the environmental behaviour of Cu(II) and Pb(II) and supporting strategies to control water pollution.

II. MATERIALS AND METHODS

A. Study Area and Sediments Sampling

The study area Lokoja is located between longitude 6° 39 E and 7° 00 E and latitude 7° 45 N and 8° 12 N at the confluence of River Niger and River Benue (Figure 1). The area has two seasons: the dry season (November/December to March/April) and the rainy season (April to November), with an average annual rainfall of 1,000 mm. Open-air slaughterhouses, markets, metal processing, industrial activities and busy roads along the river constitute point-sources and non-point sources of pollution in the area. Three locations (Kabawa, Guji & Marine) along the river were designated for sediment sampling. The river sediments were collected by manual dredging in shallow waters near the riverbanks using plastic scoop, transferred into plastic bags, and transported to the laboratory. The sediments were allowed to air dry under room temperature and screened with a 0.85 mm sieve for further analysis. The method used in sampling is similar to the method reported in (Duncan *et al.,* 2018).

B. Adsorption Procedure

Two hundred (200) mL of various concentrations of Pb (10, 20, 50, 80 and 100 mg/L) and Cu(II) (10, 20, 30, 40 and 60 mg/L) were added to a flask containing 0.2 g/L of sediment, respectively. The study was conducted within the temperature range of 25-40 °C. To investigate the time-dependent uptake of Cu(II) and Pb(II) on the sediments, 200 mL of 20 mg/L of Cu(II) and 50 mg/L of Pb(II) were mixed with 0.2 mg/L of sediments in a 250-mL flask and stirred continuously at 25 °C, with the pH of resulting solution approximately equal to 5. After the equilibration time (2h) has passed, the adsorption experiment is terminated. At different time interval, aliquots were taken and filtered and the residual concentration of Cu(II) and Pb(II) in the solution were determined, and the adsorption amount q_e was calculated using Equation (1):

$$q_e = \frac{(C_o - C_e)V}{M} \tag{1}$$

Where qe is the adsorption amount, C_o and C_e are initial concentration and equilibrium concentration of Cu(II) and Pb(II) in solution(mg/L), *M* is the mass of the sediment used in g, and *V* is the volume of the adsorbate in solution in L.

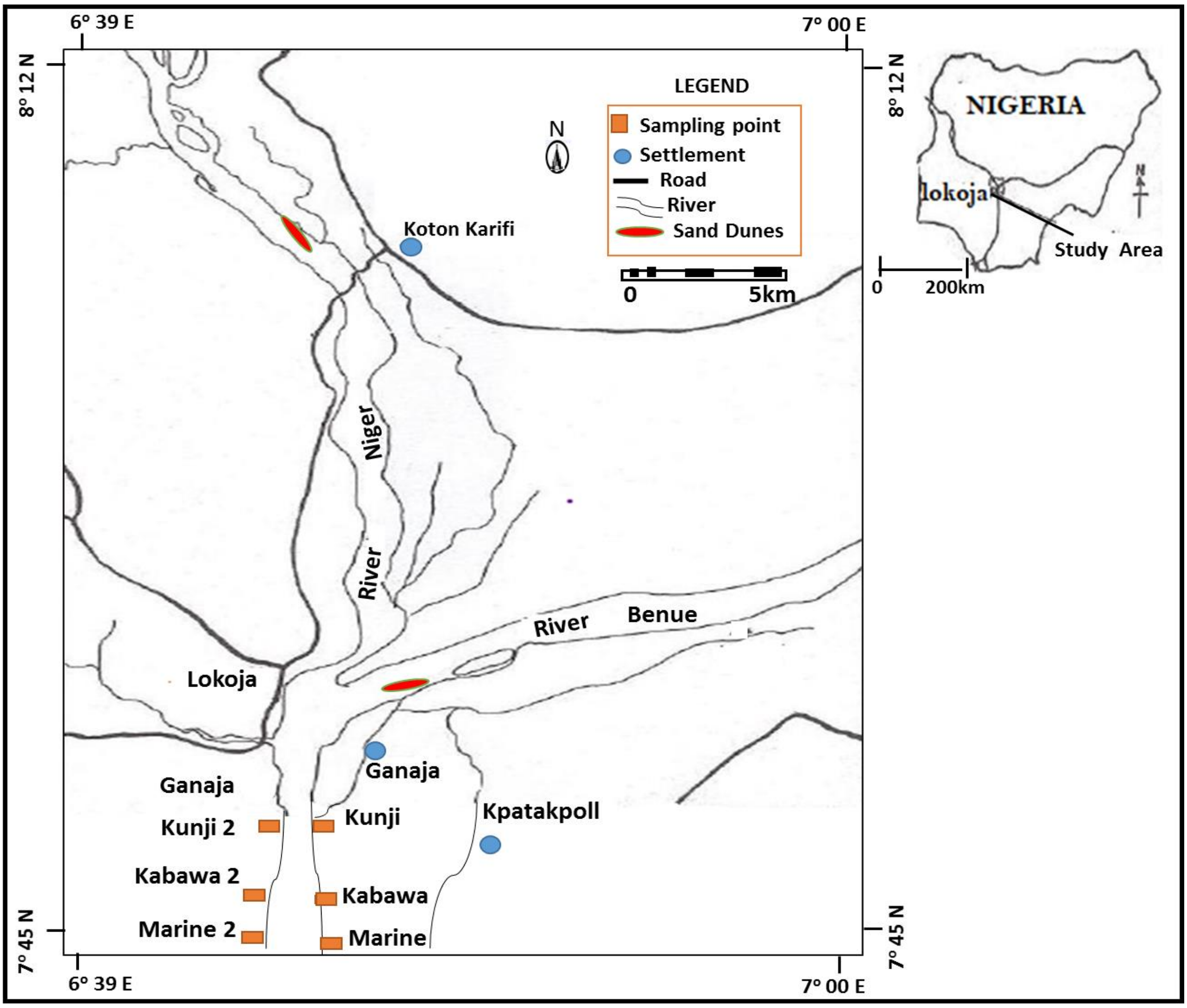

Figure 1. Map of the River Niger showing the study area and sampling point

C. Reagent and Analysis of Sediments

All chemicals used are of analytical grade. Standard solutions of lead and copper are prepared from lead nitrate and copper nitrate in deionised water. After pretreatment (air drying, homogenisation and grinding) of the sediment, some physical/chemical properties were determined. The sediment samples were analysed for pH value in water (pHw) and $CaCl_2$ (pHCa) using method reported in Minasny *et al.* (2011). The point of zero charge (pH_{ZPC}) was determined using the pH drift method using NaCl as the background solution, one hundred (100) mL of 0.1 M NaCl was introduced into the flask, and the pH value is changed between 1-7 by adding dilute NaOH or HNO_3. Then 1 g of sediment was added to the flask and stirred for 24 hours. To obtain pH_{ZPC}, we measured the stable final pH and plotted it against the initial pH. At that point, the resulting curve cuts the initial pH ($pH_{initial}$) = The final pH (pH_{final}) is considered the pH_{ZPC} of the sediment.

Using triacid mixture method (HNO_3/HCl/ $HClO_4$:1:3:1) (Pandey & Singh, 2017), the content of copper and lead in the sediments were examined. The mixture was heated on a digestion mantle placed in a fume hood at a fixed temperature of 200 ^oC for 5 hours until the fumes of $HClO_4$ disappeared. The element concentrations of copper and lead are determined by atomic absorption spectroscopy (Thermo Scientific-S series, USA). The quantification is based on the calibration curve of the metal standard solution.

III. RESULTS AND DISCUSSION

A. PH, pH_{zpc} and Metal Concentration in Sediments

Figure 1(a) reports the results of pH in water and in $CaCl_2$. The pH_{Ca} was lower than pHw. This is to be expected, because $CaCl_2$ causes the exchange of Ca with Al^{3+} and H^+ on the soil surface, therefore, the pH is reduced (Minasny *et al.,* 2011). The pH values of the river Niger sediments were in the range of 4.52 to 7.82. When compared with the pH values of other river sediments in the literature, including the 8.8 to 8.9 reported for Bodo creek sediments, Nigeria (Vincent-Akpu *et al.,* 2015), slightly alkaline (7.2-7.89) in Tajan river sediments, Iran (Ebadi & Hisoriev, 2018), 7.3-7.6 in Yangtze river sediments, China (Fan *et al.,* 2017), and 4.72 to 6.73 in Nwaja creek, Nigeria (Adesuyi *et al.,* 2016). The results of river Niger sediments showed a pH value that is moderately acidic to neutral, which indicates that the movement of the metal ions from the surface sediments to the underlying soil layer will be definite, however, at a slow rate.

pH_{PZC} is linked to the electrochemical physiognomies of the sediments, and represents the point where the surface charge density (net charge) is zero. pH_{PZC} plays a vital role in environmental chemistry because it defines the specificity of the matrix that may adsorb harmful ions (Mahmood *et al.,* 2011), especially in the case of adsorption of heavy metals from aqueous solutions (Kodama & Sekiguchi, 2006). The surface of the inorganic oxides on the surface of the soil could be represented as -YOH, where Y is the soil surface. When the active site on the sediment surface is protonated or deprotonated, it may lead to the surface charge of $-YOH_2^+$ or $-YO^-$, respectively. The –YOH point on the surface is neutral = the pH_{ZPC}.. The pH_{ZPC} of Guji, Marine and Kabawa are 5.5, 5.5 and 4.9, respectively. It is well known that when the pH value of the sediments solution is higher (Bradl, 2004) than pH_{PZC}, it will promote the surface adsorption of heavy metals. In this study, the reported pH_{ZPC} is low, in the range of 4.9-5.5. This means that when the pH is higher than 4.9 and 5.5, the adsorption of heavy metals will be higher (i.e the net charge of the sediment is positive when solution pH is lower than PZC but negative at higher pH; the metals will be adsorbed on YO^- and not on YOH_2^+). The result of pH_{PZC} correlated closely with the sedimentological pH, which is moderately acidic.

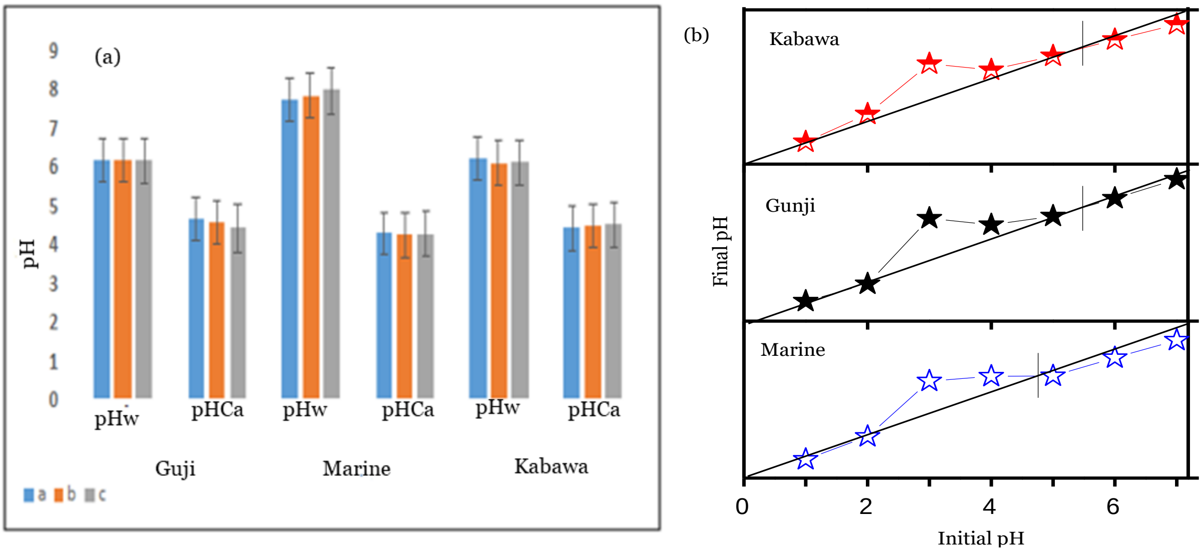

Figure 2. (a) pH determination in water and in $CaCl_2$, and (b) pH_{ZPC} for Kabawa, Guji and Marine

Industrial discharge, urban effluents, run off from agricultural activities can enrich sediment levels in the receiving river waters. The concentration of Cu(II) and Pb(II) at the different sites are summarised in Figure 3. The concentration range of Cu(II) (mg/kg) was 20.3 and 35.27 (Kabawa), 33.64 and 49.04 (Guji), 17.32 and 20.31(Marine), while the respective concentration range of Pb(II)(mg/kg) was 22.23 and 23.34(Kabawa), 12.38 and 17.38 (Guji), and 28.99 and 47.73 (Marine). The marine station is located upstream of the town and is affected by rural and suburban areas. The higher concentration of Pb(II) at marine station is due high vehicular traffic around this area and proximity to the market area. Kabawa and Gujji, which are downstream sites, have shown concentration higher than the Marine for Cu(II). This fact is expected because downstream of rivers, lakes and canals in urban areas are the most polluted (Nguyen *et al.,* 2016).

The overall trend in Cu(II) concentration was Guji>Kabawa>Marine. Cu(II) appeared the most abundant element in river Niger with a mean concentration ranging from 18.81-34.68 mg/kg. Similar or higher level Cu(II) concentrations in sediments as identified in our study region were detected in several sediments of river Ghaghara (2.76 - 11.74 mg/kg), India (Singh *et al.,* 2017), Alaro River (7.36), Nigeria (Ipeaiyeda *et al.,* 2018), Lishui river (22.84), China (Shen *et al.,* 2019); Kaohsiung Harbor, Taiwan (22.2-226) (Chen *et al.,* 2007). The relative shape increase and highest concentration of Cu(II) at Kabawa and Marine seem to be caused by domestic and agricultural causation, and Cu(II) is an important ingredient of pesticide. The Cu(II) abundance in this river Niger has been attributed to anthropogenic actives, including pesticide entering to the river through agricultural runoff, urban-industrial release and municipal solid waste. Nigeria does not have precise legislative restrictions on heavy metal pollution in sediments. Therefore, the copper content in the Niger River was compared with the Toxicity Reference Value (TRV) (Martin & Meybeck, 1979) and (USEPA, 1999) threshold values. The thresholds of TVR and USEPA are 45 mg/kg and 31.6 mg/kg, respectively, indicating that the river system with this concentration is considered to have low anthropogenic activities relative to the TRV threshold, however polluted according to USEPA standard. Copper is widely used in electrical wiring, roofing, and production of alloys, pigments, cooking utensils, and piping. Further, input of pesticides enhances copper from urban and agricultural areas.

Domestic sewage, pesticides and fertilisers, industrial effluents, paints and dyes, and vehicular emissions are the major anthropogenic sources of Pb(II) (Rout *et al.,* 2013). Metals in airborne particles can be reached directly through atmospheric deposition, or indirectly through surface runoff (National Research Council, 2000). The mean concentration of Pb(II) is 14.81-38.36 mg/kg. The concentrations are lower than those reported for sediment of River Pra, Ghana (135.863- 335.381) (Duncan *et al.,* 2018). However, the concentrations were higher than 5.86 to 5.98 mg/kg reported for kienké and Tchangué watersheds, southern Cameron (Mandeng *et al.,* 2019), and Alaro River, Nigeria (7.76 mg/kg)

(Ipeaiyeda *et al.,* 2018). The Pb(II) average in this work is higher than the average shale (Singh *et al.,* 2017), the USEPA threshold (USEPA, 1999), and the toxicity reference value (Martin & Meybeck, 1979) of 20 mg/kg, 35.8 mg/kg and 31mg/kg, respectively. The concentration of heavy metals in Niger River sediments is outside the guideline but within background levels. The high presents of copper in all the study location compared to lead may be is attributed to the incorporation of lead into source rocks and agricultural soil through various sources of pollution (Mandeng *et al.,* 2019) in addition to comparably low anthropogenic activities in the study area.

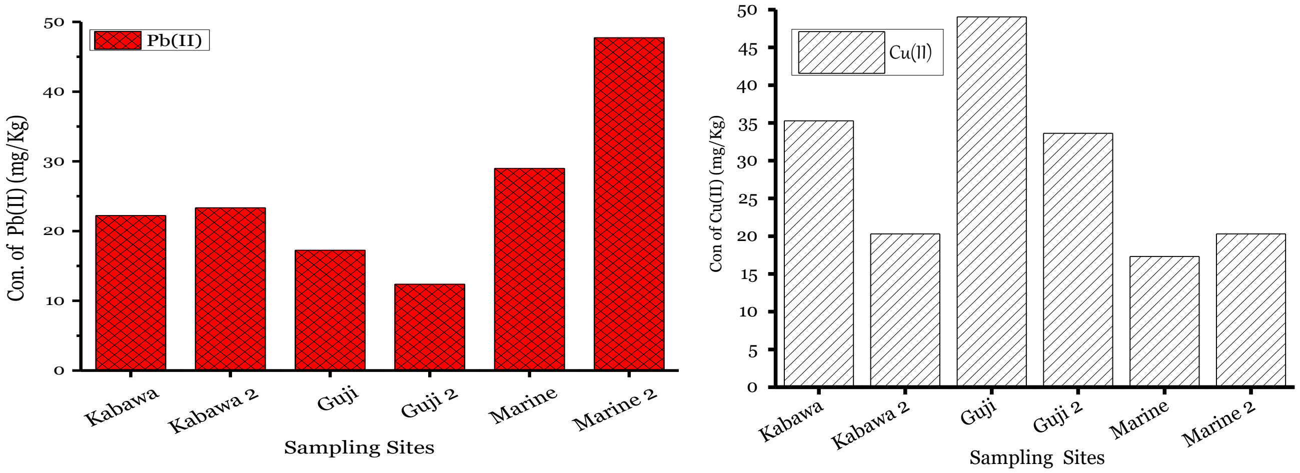

Figure 3. Results of heavy metal concentration in sediment (mg/kg)

B. Dynamic Adsorption, Equilibrium Isotherm, and Thermodynamic Parameters

In order to explain the mechanism of the adsorption process, the kinetic data was fitted to the pseudo-first-order kinetic equation and the pseudo-second-order kinetic equation. The linear form of the pseudo first and second order equations is shown in Equation (2) and (3):

$$\ln(q_e - q_t) = \ln q_e - k_1 t \qquad (2)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \qquad (3)$$

where k_1 and k_2 are the rate constant for the pseudo-first and pseudo-second –order equations respectively, q_e and q_t represent the amount of Cu(II) and Pb(II) ions adsorbed at equilibrium and at any given time t, correspondingly.

The correlation coefficient (R^2) of the kinetic models is presented in Table 2. Going by the result, the pseudo-second kinetic model is the best fitting model for the sorption of Cu(II) and Pb(II) on the sediment (i.e., R^2 is close to unity and the Qexp (Q experimental) is close to the calculated Q (Qcal)). This indicates that the adsorption process is controlled by the accessible active sites on the sediment, rather than the concentration of Cu(II) and Pb(II). in the bulk solution.

The intra-particle diffusion model was also used to examine the adsorption and diffusion mechanism of Cu(II) and Pb(II) on river sediments. The linearises form of the intraparticle diffusion model is expressed in Eq.4 as a function of $t^{1/2}$.

$$Q_t = K_d t^{1/2} + C \qquad (4)$$

where C is the intercept and K_d is the intraparticle diffusion rate constant (mg/g min$^{1/2}$).

Figure 4 (c-d) shows the profile of the intra-particle diffusion model of Cu(II) and Pb(II). This profile examines a two-step curve involving surface adsorption and intraparticle diffusion. The first stage covering the time range between 10-50 min, describes the faster migration of Cu(II) and Pb(II), respectively, towards the sediment surfaces through film diffusion (mass transfer, i.e. surface phenomenon attributed to diffusion of the metal ions via the film solution to the external surface of sediments). The second stage is a process is a gradual uptake of metal ions through diffusion within the particles (intraparticle diffusion), and involves a process of slow adsorption, which is limited by the diffusion of solutes in the pores of the sediment and in the liquid next to the pore walls. In the process of removing Cu(II) and Pb(II) on the sediment, since the straight line does not pass through the origin of the figure, film diffusion and intra-particle diffusion will occur simultaneously.

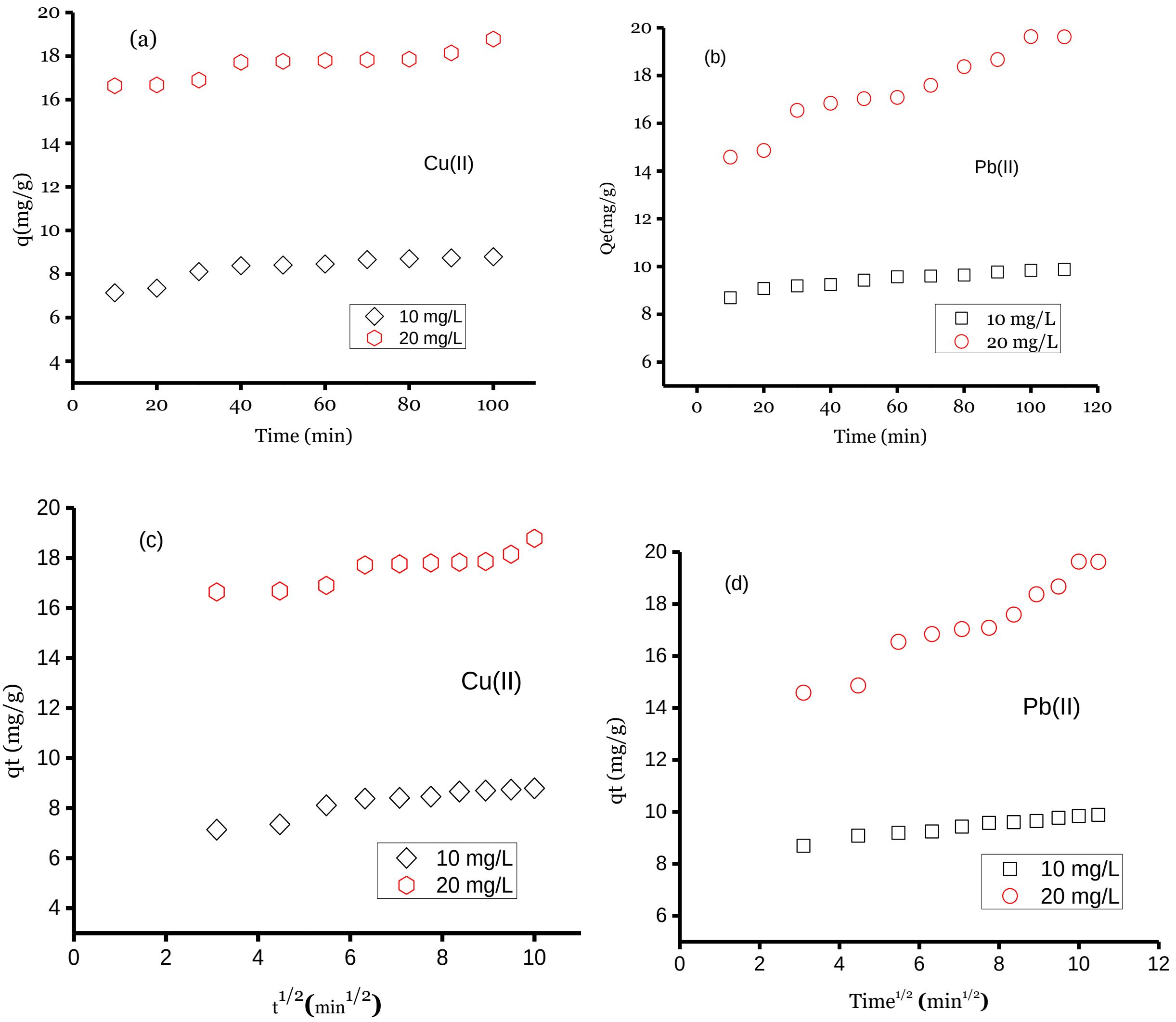

Figure 4. Adsorption Kinetic of Cu(II) and Pb(II) by sediment (a-b), plots of intraparticle kinetic model for Cu(II), and Pb(II) (c-d)(pH=5.0, dosage = 0.2 g/L)

Table 1. Estimated kinetic and isotherm model parameters and their correspond correlation coefficients

	Pseudo-First -order				Pseudo-second -order		
	Q_e Cal. (mg/g)	Q_e exp (mg/g)	k_1 (min^{-1})	R^2	$Q_e$exp (mg/g)	k_2 (g $mg^{-1}min^{-1}$)	R^2
Cu(II)	18.78	3.28	0.0282	0.8664	16.7	0.0528	0.9934
Pb(II)	18.80	2.131	0.0156	0.9584	18.5	0.00068	0.9434

To examine the interaction between the amount of Cu(II) and Pb(II) Ion adsorption on the sediment surface and its residual concentration in the water phase, adsorption studies were conducted at equilibrium condition. Freundlich and Langmuir, the most common isotherms used to explain adsorption characteristics are deployed based on the date generated during the adsorption process (Figure 5). The Langmuir isotherm assumes that there is a single layer of adsorption of metal ions on the surface of the sediment, and the linear form is represented by the following Equation:

$$\frac{C_e}{q_e} = \frac{1}{Q_m b} + \left(\frac{1}{Q_m}\right) C_e \tag{5}$$

where C_e is the concentration of the metal ions adsorbed on sediment at equilibrium (mg/L), q_e is the adsorption capacity of the sediment at equilibrium (mg/g), Q_m is the maximum monolayer capacity of metal ions adsorbed in mg/g, and b equilibrium constant describing the bonding energy of adsorption (L/mg).

On the other hand, the Freundlich isotherm model was used to explain sorption on both multilayer and heterogeneous sediment surfaces. It remains largely empirical and does not predict sediment surface saturation. The linear form of the Freundlich equation is given by following expression.

$$\mathrm{In} q_e = \mathrm{In} k_F + \frac{1}{n} \mathrm{InC_e} \tag{6}$$

where C_e is the concentration of metal ions adsorbed on the sediment at equilibrium (mg/L), and qe is the adsorption capacity of sediments in equilibrium (mg/g). kF and n represent the Freundlich constant, kF is a good indicator of the relative retention affinity of metal and sediment (Lin & Chen, 1998), and n is related to the adsorption strength and changes with the unevenness of the surface of the sediment. The larger the value of n, the better the absorption of metal ions.

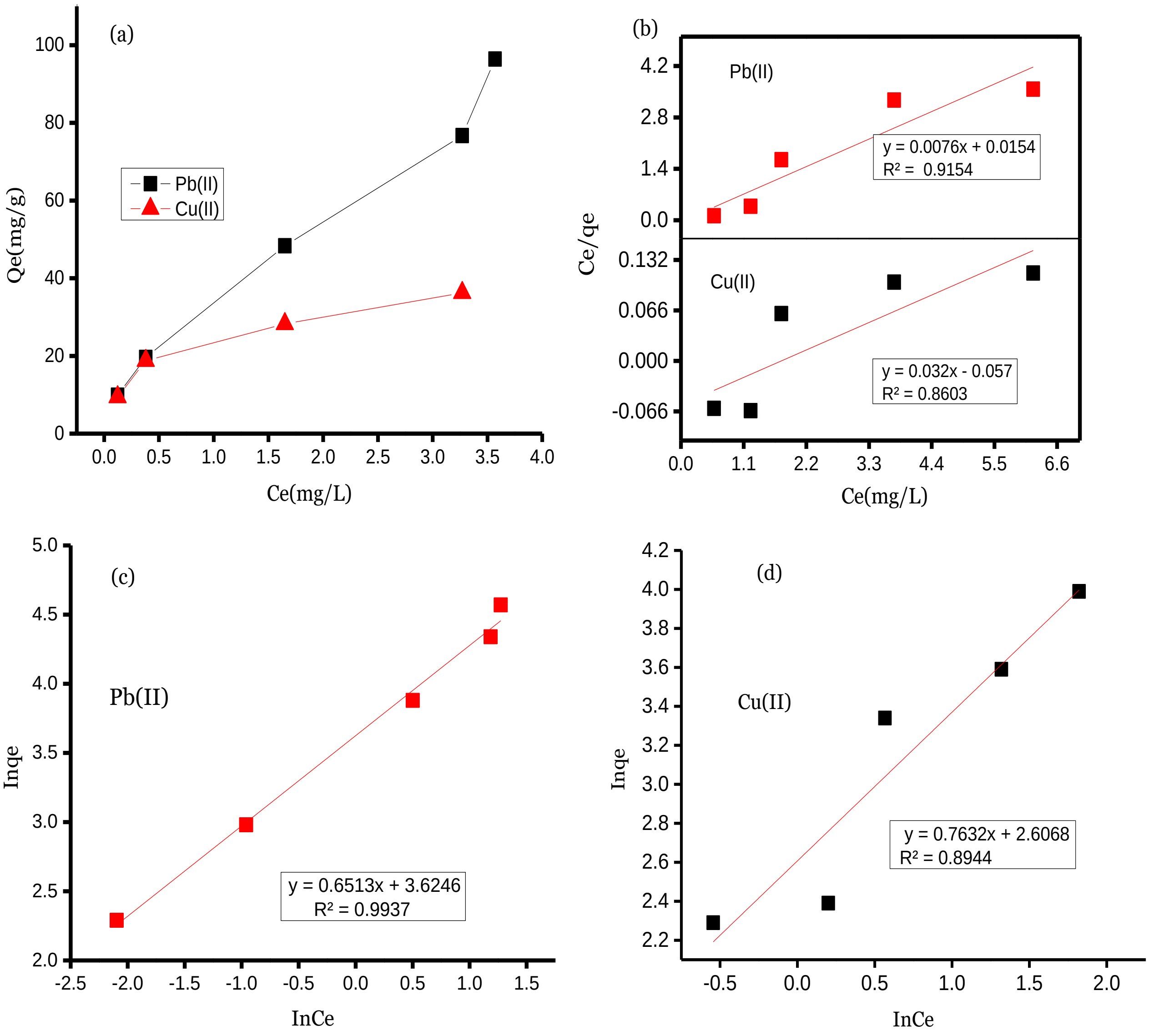

Figure 5. (a) Experimental adsorption isotherm for Pb(II) ions and Cu(II) ions on marine sediments, (b) linearised Langmuir isotherm, and (c) linearised Freundlich isotherm (pH=5, dosage = 0.2 g/L)

As seen in Table 2, the results according to the value of R^2, both isotherms can describe the adsorption of Cu(II) and Pb(II) in the sediments fairly well. Langmuir and Freundlich constants indicate that the adsorption of Pb(II) on the sediments is more favourable than Cu(II). Using the Langmuir model, the equilibrium constants of Pb(II) and Cu(II) were higher than that of Freundlich, it is probable that the range of concentration used in the current work (10—100 mg/L) is in the monolayer regime (Unob *et al.,* 2007). This may be correct because the value of 1/n is less than unity and indicates that adsorption was less significant within the range of concentration investigated, and the amount adsorbed could increase significantly at higher concentrations (i.e., higher concentrations could distinguish both models more clearly). However, the Freundlich isotherm show more conformism regarding the R^2 value, so adsorption on the heterogeneous surface occurs, and the interaction between the adsorbed molecules causes the adsorption heat to be unevenly distributed on the surface. In addition, monolayer coverage of Cu(II) and Pb(II) ions on the surface of the sediments may be formed according to Langmuir model. The metal affinity order was Pb(II)> Cu(II) of the two adsorption model was consistent with trend of hydrated radii. Saeedi *et al.* (2011) observed similar metal affinity order of Pb(II)>Cu(II) for Jajrood River sediments.

Table 2. Thermodynamic parameters of Cu(II) and Pb(II) adsorption in sediments

	Qmax (mg/)	**Langmuir Isotherm**			**Freundlich Isotherm**		
		K_L	R_L	R^2	K_F	*1/n*	R^2
Pb(II)	131.57	0.490	0.019	0.9154	37.5	1.535	0.9937
Cu(II)	31.25	0.204	0.058	0.8603	13.56	1.310	0.8944

The thermodynamic parameters are listed in Table 3. Free energy (ΔG^o), entropy (ΔS^o) and enthalpy (ΔH^o) provide detailed information on energetic changes related to Cu(II) and Pb(II) adsorptions processes and were calculated from Equation (7)-(8).

$$\Delta G^o = - RT \ln K_C \tag{7}$$

$$\ln K_C = \left(\frac{\Delta S}{R}\right) - \left(\frac{\Delta H}{R}\right)\frac{1}{T} \tag{8}$$

$$K_C = C_{Ae}/C_{Se} \tag{9}$$

where K_C is the equilibrium constant, C_{Ae} is the amount of adsorbate on the sediment (mg/L), C_{Se} is the equilibrium concentration of Cu(II) and Pb(II) in the solution (mg/L), and R is the general gas constant (8.314 J/mol K). The amount of Cu(II) and Pb(II) Ions increase with increasing temperature, which indicates that the removal process of these metals is endothermic. The values of ΔH^o and ΔS^o were obtained from the slop and intercept of liner plot of In K_C versus 1/T. As the temperature increases, the ΔG^o value becomes more negative, indicating that the surface reaction is spontaneous. This result is attributable to the increased movement and diffusion of Cu(II) and Pb(II) ions to the pore locations of the sediment. The endothermic characteristics of the adsorption process are determined by the positive value of ΔH^o.

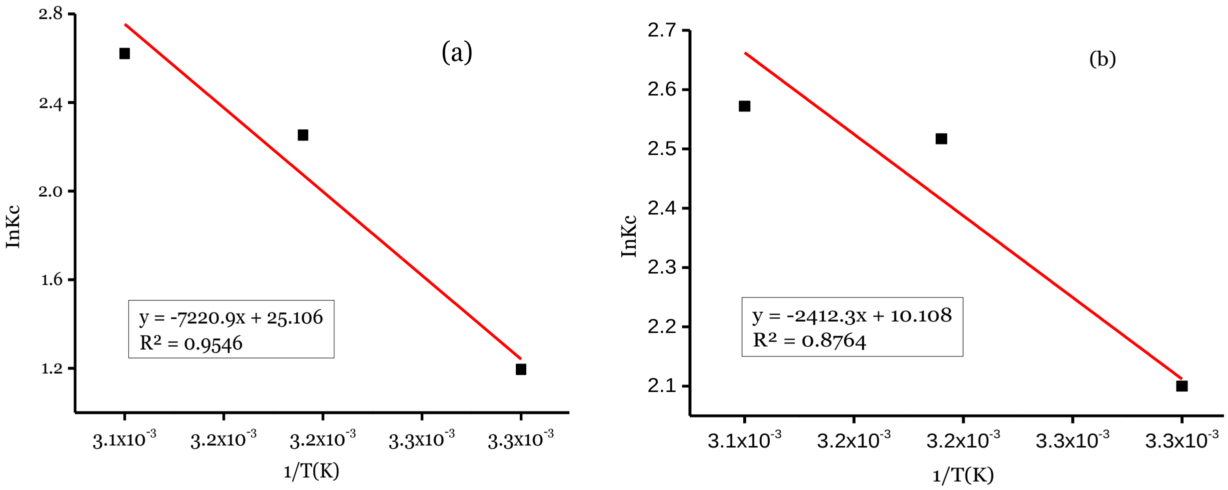

Figure 6. Van't Hoff's plot for Pb(II) and Cu(II)) adsorption on sediment (pH = 5; sediments dosage = 0.2 g/200 L; Pb(II) and Cu(II), Conc.= 50 mg/L, pH=5)

Table 3. Thermodynamic parameters for the adsorption of Cu(II) and Pb(II) onto sediments

	Pb(II)					**Cu(II)**				
Temp (K)	Qe (mg/g)	InK	ΔG^{o} kJ/mol	ΔS^{o} J/Kmol	ΔH_{o} kJ/mol	Qe (mg/g)	InK	ΔG^{o} kJ/mol	ΔS^{o} J/Kmol	ΔH^{o} kJ/mol
298	44.9	1.195	-3.010			44.5	2.100	-5.290		
308	45.2	2.253	-5.863	83.20	23.93	46.3	2.517	-6.550	84.03	20.05
313	46.6	2.621	-7.038			46.5	2.572	-9.523		

C. Comparative Study

The adsorption capacity of Niger River sediments was compared with the adsorption capacity of some other sediments previously reported (Table 4). The data shows that the river sediments can be used to adsorb Cu(II) and Pb(II), which demonstrate the potential of the river sediments to control metal pollution that may enter the aquatic system through different sources.

Table 4. Comparison of Cu(II) and Pb(II) maximum adsorption capacities

River sediment	**Maximum Adsorption Capacity, Q_m (mg/g)**		**References**
	Cu(II)	**Pb(II)**	
River Niger	31.25	131.57	This study
Yangtze River	62.3	-	Fan *et al.,* 2017
Nile River	3630	22	Soltan *et al.,* 2006
Lan-Che River	6.20	9.30	Lin & Chen, 1998

IV. CONCLUSION

The finding in the present work has demonstrated the potential of river sediments to control metal pollution that may enter the aquatic system through different sources. The result of pH of the sediments in both water and $CaCl_2$, showed moderately acidic sediments and indication of slow movement of the metal ions to the underlying. Among the probed metal ions, the rivers sediments has strong affinity for Pb(II) ions compared to Cu(II) ions. Both Langmuir and Freundlich isotherms described the uptake of copper and lead in the sediments reasonably well. Though the current Cu(II) and Pb(II) content in Niger River sediment samples are relatively low when compared to other river sediments, this situation could change as the concentration of copper and lead in the sediments increases over time. In this regard, it is recommended to continuously monitor the sediment collected from the area for heavy metal content, and it is recommended to adopt regulatory measures to reduce pollution.

V. REFERENCES

Adesuyi, AA, Ngwoke, MO, Akinola, MO, Njoku, KL & AO Jolaoso 2016, 'Assessment of physicochemical characteristics of sediment from Nwaja Creek, Niger Delta, Nigeria', Journal of Geoscience and Environment Protection, vol. 4, no. 1, p. 16.

Ali, MM, Ali, ML, Islam, MS & MZ, Rahman 2016, 'Preliminary assessment of heavy metals in water and sediment of Karnaphuli River, Bangladesh', Environmental Nanotechnology, Monitoring & Management, vol. 5, pp. 27-35. doi: 10.1016/j.enmm.2016.01.002.

Bradl, HB 2004, 'Adsorption of heavy metal ions on soils and soils constituents', Journal of Colloid and Interface Science, vol. 277, no. 1, pp. 1–18. doi: 10.1016/j.jcis.2004.04.005.

Buyang, S, Yi, Q, Cui, H, Wan, K & S Zhang 2019', 'Distribution and adsorption of metals on different particle size fractions of sediments in a hydrodynamically disturbed canal', Science of the Total Environment, vol. 670, pp. 654-661. doi: 10.1016/j.scitotenv.2019.03.276.

Cao, X, Ma, LQ, Rhue, DR & CS, Appel 2004, 'Mechanisms of lead, copper, and zinc retention by phosphate rock', Environmental Pollution, vol. 131, no. 3, pp. 435-444. doi: 10.1016/j.envpol.2004.03.003.

Chen, CW, Kao, CM, Chen, CF & CD, Dong 2007, 'Distribution and accumulation of heavy metals in the sediments of Kaohsiung Harbor, Taiwan', Chemosphere, vol. 66, no. 8, pp. 1431-1440. doi: 10.1016/j.chemosphere.2006.09.030.

Duncan, AE, de Vries, N & KB, Nyarko 2018, 'Assessment of heavy metal pollution in the sediments of the River Pra and its tributaries', Water, Air, & Soil Pollution, vol. 229, no. 8, p. 272.

Ebadi, AG & H Hisoriev 2018, 'Physicochemical characterisation of sediments from Tajan river basin in the northern Iran', Toxicological & Environmental Chemistry, vol. 100, no. 5-7, pp. 540-549. doi: 10.1080/02772248.2018.1460929.

Fan, J, Zhao, G & J, Sun 2017, 'Binary component sorption of cadmium, and copper ions onto Yangtze River sediments with different particle sizes', Sustainability, vol. 9, no. 11, pp. 2089. doi: 10.3390/su9112089.

Huang, L, Rad, S, Xu, L, Gui, L, Song, X, Li, Y, Wu, Z & Z Chen 2020, 'Heavy metals distribution, sources, and ecological risk assessment in Huixian Wetland, South China', Water, vol. 12, no. 2, pp. 431.

Imamoglu, M & O, Tekir 2008, 'Removal of copper (II) and lead (II) ions from aqueous solutions by adsorption on activated carbon from a new precursor hazelnut husks', Desalination, vol. 228, pp. 108-113. doi: 10.1016/j.desal.2007.08.011.

Jain, CK & D Ram 1997, 'Adsorption of metal ions on bed sediments', Hydrological Sciences Journal, vol. 42, no. 5, pp. 713-723. doi: 10.1080/02626669709492068.

Kodama, S & H, Sekiguchi 2006, 'Estimation of point of zero charge for activated carbon treated with atmospheric pressure non-thermal oxygen plasmas', Thin Solid Films, vol. 506, pp. 327-330. doi: 10.1016/j.tsf.2005.08.137.

Lin, JG & SY, Chen 1998, 'The relationship between adsorption of heavy metal and organic matter in river sediments', Environment International, vol. 24, no. 3, pp. 345-352.

Lu, F, Zhang, H, Jia, Y, Liu, W & H, Wang 2019, 'Migration and diffusion of heavy metal Cu from the interior of sediment during wave-induced sediment liquefaction process', Journal of Marine Science and Engineering, vol. 7, no. 12, p. 449.

Mahmood, T, Saddique, MT, Naeem, A, Westerhoff, P, Mustafa, S & A, Alum 2011, 'Comparison of different methods for the point of zero charge determination of NiO', Industrial & Engineering Chemistry Research, vol. 50, no. 17, pp. 10017-10023.

Mandeng, EPB, Bidjeck, LMB, Bessa, AZE, Ntomb, YD, Wadjou, JW, Doumo, EPE & LB, Dieudonné 2019, 'Contamination and risk assessment of heavy metals, and uranium of sediments in two watersheds in Abiete-Toko gold district, Southern Cameroon', Heliyon, vol. 5, no. 10, p. e02591. doi: 10.1016/j.heliyon.2019.e02591.

Martin, JM & M, Meybeck 1979, 'Elemental mass-balance of material carried by major world rivers', Marine Chemistry, vol. 7, no. 3, pp. 173-206.

Minasny, B, McBratney, AB, Brough, DM & D, Jacquier 2011, 'Models relating soil pH measurements in water and calcium chloride that incorporate electrolyte concentration', European Journal of Soil Science, vol. 62, no. 5, pp. 728-732. doi: 10.1111/j.1365-2389.2011.01386.x.

Oh, S, Shin, WS & HT Kim 2016, 'Effects of pH, dissolved organic matter, and salinity on ibuprofen sorption on sediment', Environmental Science and Pollution Research, vol. 23, no. 22, pp. 22882-22889. doi: 10.1007/s11356-016-7503-6.

Onundi, YB, Mamun, AA, Al Khatib, MF & YM, Ahmed 2010, 'Adsorption of copper, nickel and lead ions from synthetic semiconductor industrial wastewater by palm shell activated carbon', International Journal of Environmental Science & Technology, vol. 7, no. 4, pp. 751-758. doi: 10.1007/BF03326184.

Ipeaiyeda, AR & PC, Onianwa 2018, 'Monitoring and assessment of sediment contamination with toxic heavy metals: case study of industrial effluent dispersion in Alaro River, Nigeria', Applied Water Science, vol. 8, no. 6, pp. 1–10. doi: 10.1007/s13201-018-0815-6.

Pandey, J & R, Singh 2017, 'Heavy metals in sediments of Ganga River: up-and downstream urban influences', Appl Water Sci., vol. 7, pp. 1669–1678. doi: 10.1007/s13201-015-0334-7.

Pyrgaki, K, Messini, P & V, Zotiadis 2018, 'Adsorption of Pb and Cu from aqueous solutions by raw and heat-treated attapulgite clay', Geosciences, vol. 8, no. 5, p. 157. doi: 10.3390/geosciences8050157.

Rout, TK, Masto, RE, Ram, LC, George, J & Padhy, PK 2013, 'Assessment of human health risks from heavy metals in outdoor dust samples in a coal mining area', Environmental Geochemistry and Health, vol. 35, no. 3, pp. 347-356.

Saeedi, M, Hosseinzadeh, M & M, Rajabzadeh 2011, 'Competitive heavy metals adsorption on natural bed sediments of Jajrood River, Iran', Environmental Earth Sciences, vol. 62, no. 3, pp. 519-527. doi: 10.1007/s12665-010-0544-0.

Sakan, SM, Đorđević, DS, Manojlović, DD & PS, Predrag 2009, 'Assessment of heavy metal pollutants accumulation in the Tisza river sediments', Journal of Environmental Management, vol. 90, no. 11, pp. 3382-3390.

Shen, F, Mao, L, Sun, R, Du, J, Tan, Z & M, Ding 2019, 'Contamination evaluation and source identification of heavy metals in the sediments from the Lishui River Watershed, Southern China', International Journal of Environmental Research and Public Health, vol. 16, no. 3, pp. 3361–14. doi: 10.3390/ijerph16030336.

Singh, H, Pandey, R, Singh, SK & DN, Shukla 2017, 'Assessment of heavy metal contamination in the sediment of the River Ghaghara, a major tributary of the River Ganga in Northern India', Applied Water Science, vol. 7, no. 7, pp. 4133-4149. doi: 10.1007/s13201-017-0572-y.

Soltan, ME, Rashed, MN & GM, Taha 2001, 'Heavy metal levels and adsorption capacity of Nile river sediments', International Journal of Environmental Analytical Chemistry, vol. 80, no. 3, pp. 167-186. doi: 10.1080/03067310108044368.

National Research Council 2000, Environmental transport and exposure pathways of substances emitted from incineration facilities, in Waste Incineration & Public Health, National Academies Press (US).

Nguyen, TTH, Zhang, W, Li, Z, Li, J, Ge, C, Liu, J, Bai, X, Feng, H & L, Yu 2016, 'Assessment of heavy metal pollution in Red River surface sediments, Vietnam', Marine Pollution Bulletin, vol. 113, no. 1-2, pp. 513-519. doi: 10.1016/j.marpolbul.2016.08.030.

Unob, F, Wongsiri, B, Phaeon, N, Puanngam, M & J, Shiowatana 2007, 'Reuse of waste silica as adsorbent for metal removal by iron oxide modification', Journal of Hazardous Materials, vol. 142, pp. 455–462. doi: 10.1016/j.jhazmat.2006.08.049.

USEPA 1999, National Recommended Water Quality Criteria, in National recommended water quality criteria-correction-United State Environmental Protection Agency EPA 822-Z-99-001, (http://www.epa.gov./ostwater/pci/revcom). p. 25.

Vincent-Akpu, IF, Tyler, AN, Wilson, C & G, Mackinnon 2015, 'Assessment of physico-chemical properties and metal contents of water and sediments of Bodo Creek, Niger Delta, Nigeria', Toxicological & Environmental Chemistry, vol. 97, no. 2, pp. 135-144. doi.org/10.1080/02772248.2015.1041526.

Wojtkowska, M 2013, 'Migration and forms of metals in bottom sediments of Czerniakowskie Lake', Bull Environ Contam Toxicol., vol. 90, pp. 165–169. doi: 10.1007/s00128-012-0881-7.

Worakhunpiset, S 2018 'Trace elements in marine sediment and organisms in the Gulf of Thailand', International Journal of Environmental Research and Public Health, vol. 15, no. 4, pp. 1-15. doi: 10.3390/ijerph15040810.

Yam, RSW, Fan, Y, Tan, Z, Wang, T & Chiu, C 2020, 'Assessing impacts of metallic contamination along the tidal gradient of a riverine mangrove : multi-metal bioaccumulation and biomagnification of filter-feeding bivalves', Forests, vol. 11(5), pp. 1–15.

Zhang C, Yu, ZG, Zeng, GM, Jiang, M, Yang, ZZ, Cui, F, Zhu MY, Shen, LQ & L, Hu 2014, 'Effects of sediment geochemical properties on heavy metal bioavailability', Environment International, vol. 73, pp. 270-81. doi: 10.1016/j.envint.2014.08.010.