Experimental and numerical study for the adsorption behavior of Cu(II) and Mn(II) in quartz sand

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Abstract

Heavy metals such as Cu(II) and Mn(II) are prevalent in the environment. The effect of heavy metals on the soils environment is based on the ability of soils to mobilize these contaminants. According to the soil decontamination perspective, examining the reaction technique between heavy metals and soil is indispensable. This study carried out experiments to investigate Cu(II) and Mn(II) adsorption behaviour in quartz sand. The isothermal adsorption results for Cu(II) and Mn(II) presented that the adsorption capacity reached the peak value when the initial concentration was about 10 mg/L. The declines of H^+ ions could uprise the adsorption rate activity for Cu(II) and Mn(II) and decrease the soil ability of the desorption for Cu(II) and Mn(II) ions. The adsorption rate of Cu(II) and Mn(II) is lower than the desorption rate under the situation of a low pH range with a solid acidic and low concentration of Cu(II) and Mn(II). The Freundlich and Langmuir adsorption isotherm models were applied to investigate the adsorption isotherm of Cu(II) and Mn(II). The study results confirmed that the Freundlich model synchronous the best with the observed experimental data compared with the Langmuir solution.

Keywords Heavy metals · Adsorption · Freundlich isotherm model · Langmuir isotherm model · Desorption

Introduction

Heavy metal contamination is an environmental issue that severely impacts aquatic and ecological organisms. These metals appeared in the environment through human activities like mining in mine tailings, pesticides industry, or effluents (Carolin et al. 2017). Heavy metals can react with minerals to form inorganic agents with unsteady solubility and acid or base stresses. Therefore, the remediation process from polluted soil is primary anxiety (Peligro et al. 2016).

Heavy metals growing up demonstrates a dangerous health issue for humans and animals (Xie et al. 2018). For example, exposure to Copper (Cu), specially Cu^{2+}, which is the most poisonous shape of copper (Awual et al. 2014), Copper (Cu) causes health issues, anemia, headache, kidney ruin and death (Tang et al. 2014). The toxicity of copper is related to the soil characteristics, soil pH and clay content which hold its reaction in the soil (Noll 2003). Manganese

(Mn) is a micronutrient to organisms. In plants, it engages in photosynthetic proteins and enzymes. However, the high Mn concentrations in plants affect tissues operations, such as enzymes, absorption, transportation, and other minerals (Ca, Mg, Fe and P) (Millaleo et al. 2010). Manganese biogeochemistry in soils is problematic because it is attended to many oxidation conditions (0, II, III, IV, VI and VII). Mn(II) is the most soluble kind of Mn in soil. In contrast, the solubility of Mn III and Mn IV is very low (Guest et al. 2002). pH and redox conditions impact Mn bioavailability in soils (Porter et al. 2004). However, high pH lets Mn adsorption in the soil particles (Fageria et al. 2002). Exposure to many Manganese (Mn) causes growth lag, infertility, fever, eye blindness and muscles (Ahmaruzzaman 2011).

The interchanges between metallic ions and mineral surfaces in any environment permit the adsorption of ions to the solid outspread, thereby detracting the concentration of ions in the aqueous stages lower than the solubility termination of the solid phase (Katz and Hayes 1995). Definition of partitioning heavy metals through the solid set and strictly forecasting their mobility in the natural environment seeks sufficient knowledge of the chemical procedure that predominates adsorption technicality (Fukushi 2017).

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Adsorption is usually the primary method for heavy metal accumulation in soils. However, desorption is a reversed process for adsorption to decontamination of the heavy metals from soil. The study of adsorption and desorption behaviour is necessary to explain the transport of heavy metals between the aqueous and solid phases. Heavy metals can be adsorbed in soils as ions and components or by exchangeable processes (Xie et al. 2018). Sorption is one of the most critical techniques that explain metals' transport in soil (Liu et al. 2006). According to the heterogeneous nature of soil sorption positions, mostly metal sorption is supposed to be nonlinear if metal concentrations are high (Tsang et al. 2007). Likewise, the fate and transport of many solutes, such as metals in soils, are sensitive to sorption nonlinearities (Serrano 2003). Nonlinearity in sorption positions may cause solutes to arrive at a monitoring point faster or slower than estimated by linear models. Bolt (1979) claimed that most soils are macroscopically heterogeneous. Thus, the transport and fate of metals in a natural system may be subjected to nonlinear equilibrium and non-equilibrium sorption.

Heavy metals in soils could be adsorbed as components such as ions and compounds or exchangeable styles (Huang et al. 1995). The most remarkable interfaces in soil heavy metal sorption are preponderantly inorganic components (Xie et al. 2018). Heavy metals such as Cu^{2+} and Mn^{2+} can be adsorbed into the soil and desorbed under specific statuses (Segura et al. 2006). The mobility of heavy metals is often influenced by soil features, such as pH, organic components quantities, temperature, and the kinds of ions. Mostly of Soils have a similar structural order, which can adsorb heavy metals via two various techniques: (1) outer sphere cation exchange, resulting from the interchanges between metal ions and persistent negative charge; and (2) inner sphere that formalization compounds through Si–O– and Al–O– groups at the soil particles borders (Tauqeer et al. 2022). Both techniques are conditional on the pH attached. Still, the last is significantly affected by pH because in acid stipulations (pH < 4), nearly all Silanol and Aluminol groups on the soil particle's borders will be protonated. For this reason, it is mandatory to upgrade the understanding of the effectiveness of pH on the adsorption capacity (Malandrino et al. 2006).

Therefore, studying the fate mechanisms of heavy metals is an essential research direction for the remediation process of heavy metals pollution at present and in the future. For this reason, this study investigates the adsorption and desorption mechanisms for copper (Cu^{2+}) and Manganese (Mn^{2+}) ions in quartz sand. Thence, groups of lab experiments were performed to realize the effectiveness of pH and the amount of concentration (different initial concentrations) on Cu^{2+} and Mn^{2+} adsorption and desorption.

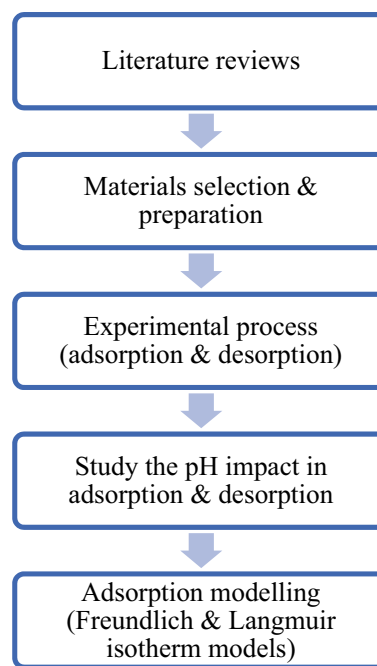This study has been carried on a straightforward methodology to describe the primary goal of this work. The

Fig. 1 Research methodology flow chart

Table 1 Quartz sand characteristics

Parameter	Value
Particle size (mm)	0.50–0.125
Bulk density (g/cm^3)	1.70
Porosity	0.42

methodology flow chart is presented in Fig. 1. Research work started with collecting and reviewing relative previous studies and research that related to the adsorption and desorption of heavy metals in various soil types. Quartz sand, Cu^{2+}, and Mn^{2+} were applied as experimental materials to investigate the adsorption and desorption process with linked pH factors explaining its impacts on adsorption and desorption. Finally, the equilibrium adsorption was modelled using the standard models (Freundlich and Langmuir isotherm models).

Materials and methods

Laboratory adsorption and desorption experiment

Adsorbent The quartz sand sample was air-dried. Some essential characteristics of the samples are listed in Table 1.

Chemicals $CuSO_4$ and $MnSO_4$ were used in adsorption/ desorption experiments with concentrations (10, 20, 50, 80, and 100) mg/L.

Instrumentation Microwave plasma atomic emission spectrometry (MP-AES) was utilized to measure the Copper Cu(II) and Manganese Mn(II) concentrations in the solutions.

Experiment procedure Experiments for the adsorption of copper Cu^{2+} and Manganese Mn^{2+} in quartz sand were executed in a batch of polyproline tubes (Selim et al. 2013). The Cu^{2+} and Mn^{2+} solutions were intended by dissolving $CuSO_4$ and $MnSO_4$ in desilted water to have the base concentration of 100 mg/L and diluted to the required initial concentrations. In the isothermal experiments, 30 mL of different initial Cu^{2+} and Mn^{2+} concentrations (10, 20, 50, 80, and 100 mg/L) solutions were put in a 50 mL centrifuge tube with a fixed quartz soil adsorbent dosage (3 g) and was shaking for 24 h at 25 °C, and the pH value of solutions was set to be 5.5. The adsorbent was unattached, and the adsorbed Cu^{2+} and Mn^{2+} were determined. The equilibrium adsorption investigations were carried out to define the maximum metal removal in experimental process terms. The impact of pH on metal's sorption was examined in solutions with one heavy metal ion. Equilibrium considerations were performed at pH 2, 4, and 5.5, with an initial concentration of 100 mg/L for each heavy metal and an equilibrium time of 24 h at 25 °C.

The amount of adsorption S (mg/kg) can be calculated as (Xie et al. 2018):

$$S = \frac{\left(C_{\text{init}} - C_{\text{eq}}\right) \times V}{M \times 1000}, \tag{1}$$

where: C_{init} and C_{eq} have presented the initial concentration and equilibrium concentration of Cu(II) and Mn(II), respectively (mg/L), V is the volume of the aqueous state (mL), and M (g) is the soil mass. The adsorption rate (%) can be measured using the following equation:

$$\text{Ads}(\%) = \frac{(C_{\text{init}} - C_{\text{eq}})}{C_{\text{init}}} \times 100. \tag{2}$$

Numerical model

The isothermal adsorption model examines the sorption mechanism and the average commanding procedures in a batch reaction. Studies in isothermal adsorption were carried out to change the initial concentration of adsorbate, temperature, reaction time, particle size, pH, and kinds of sorbent and sorbate (Zhao et al. 2010). It is a series of measurements of the experimental data until equilibrium is acquired. The results are examined using equilibrium equations to set the best fit, better perceiving the sorption mechanism. Based on the batch sorption experimental results, the copper and manganese sorption isotherms on the quartz sand were analyzed using two sorption models, the Freundlich and Langmuir

models (Twarakavi et al. 2008). The sorption process validation was described according to the correlation coefficient (r^2). The Origin Pro 2021 software is utilized in the analytical model to solve the issues dependent on the sorption isotherms.

The Freundlich model is mainly utilized to characterize the adsorption isotherm, which can be demonstrated as (Appel 1973):

$$S = K_{\text{f}} C^{1/N}. \tag{3}$$

The Langmuir model is generally utilized for the monolayer chemisorption of the gaseous stage, usable in the aqueous phase-in in most situations. This isotherm is fundamentally used when no sturdy adsorption is predictable and regular adsorption surface (Harter and Baker 1978). A generally applied form of the Langmuir adsorption isotherm is:

$$S = \frac{K_{\text{L}} \times S_{\text{max}} \times C}{1 + K_{\text{L}} \times C}, \tag{4}$$

where: S is the sorption amount (mg/kg), C is the solution concentration (mg/L), K_{F}, K_{L} is partitioning coefficients according to the Freundlich and Langmuir model (L/kg), which are used to measure the affinity of the heavy metal in soil, and N is a dimensionless reaction (Ugwu and Igbokwe 2019).

Results and discussions

Adsorption of Copper Cu²⁺ and Manganese Mn²⁺

Effects of different initial concentrations in adsorption The measurements of the adsorption rate with different Cu^{2+} and Mn^{2+} concentrations are shown in Fig. 2. We observed that the adsorptive rate of Cu^{2+} and Mn^{2+} rapidly grew up at the beginning stage and then gradually declined. The adsorption rate achieves the peak value at the low initial concentration of 10 mg/L and progressively decreases. This behaviour is related to the chemical characteristics of Cu^{2+} and Mn^{2+} and the number of adsorption sites of quartz sand. Due to the low concentration, there are a lot of adsorption sites, and these sites decrease with concentration increase. Many researchers emphasize this behaviour of Cu^{2+} and Mn^{2+} ions in soils. Xie et al. (2018) examined the behaviour of Cu^{2+} in silty clay soil that gave the same style of at low concentration of Cu^{2+} the soil will have the maximum adsorption capacity and the Cu^{2+} adsorptive rate swiftly increased at the beginning phase, then gently reduced. When the initial concentration of Cu^{2+} and Mn^{2+} is minimal, several adsorption sites are on the soil surface, so most Cu^{2+} and Mn^{2+} can be integrated with the high-energy adsorption sites (Reed and Cline 1994). As the equilibrium concentration grows, more
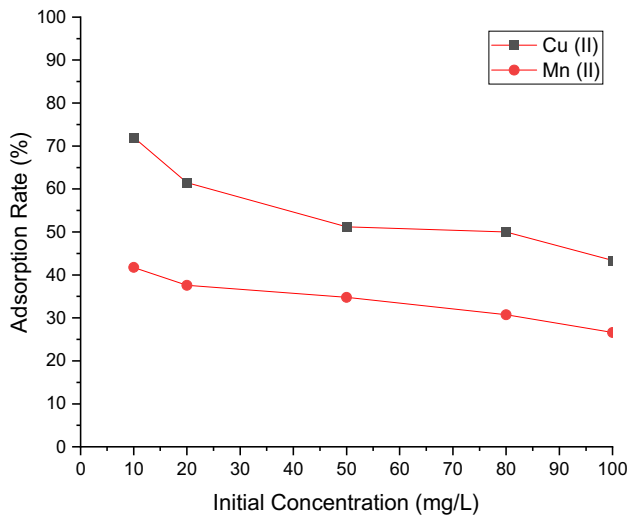
Fig. 2 The relationship between the initial concentration of Cu(II) and Mn(II) with adsorption rate in quartz sand

Cu^{2+} and Mn^{2+} attach to the competition to occupy adsorption areas. When the adsorption areas with a high binding energy oncoming the total capacity, the attribution of non-specific adsorption rises. Cu^{2+} and Mn^{2+} gently stretch out the adsorption equilibrium, and adsorption capacity declines posteriorly.

Effects of pH on adsorption To explore the impact of pH on isothermal adsorption, many experiments are performed at several pH values of 2.0, 4.0 and 5.5. The influence of pH on the adsorption rate for Cu^{2+} and Mn^{2+} is presented in Fig. 3, which shows the pH affected on the Cu^{2+} ions in Fig. 3a and the effect of pH on Mn^{2+} in Fig. 3b. It is concluded that the adsorption of Cu^{2+} and Mn^{2+} grows as the pH rises. This characteristic can be comprehended from a few features. At first, the concentration with acidity pH, the amount of H^+ ions will be at high concentration, which will be caused the dissolution of the soil mineral—also causing the release of ions like Mg^{2+}, Fe^{2+}, and Al^{3+} (Özdemir and Yapar 2009). These ions compete with Cu^{2+} and Mn^{2+} for adsorption areas. Secondly, the surface sets are protonated if the pH is strongly acidic. As a result, it will create a positive surface charge which might break the ability to generate compounds with Cu^{2+} and Mn^{2+} (Agbenin and Atin 2003). Thirdly, the ionic status might modify with upraised pH, and the hydroxylation of Cu^{2+} and Mn^{2+} produces Cu^{2+} and Mn^{2+} more convenient to the soil.

However, the upraised pH value caused a remarkable increase in the soil adsorption capacity for Cu^{2+} and Mn^{2+}, as shown in Fig. 4, which presents the effect of pH on the adsorption capacity in Cu^{2+} ions Fig. 4a, b which, indicates the increasing of pH increase the adsorption rate for soil.

When pH is higher than 4, the adsorption capacity of Cu^{2+} and Mn^{2+} resorts to be constant. This occurrence might be based on the variation of the soil point-of-zero charge, which is dominated by pH. H^+ ions create the soil particle's surface positive charges when the solution pH is smaller than the compatible value to the point-of-zero charges. Then the soil adsorption areas will be declined, causing a low Cu^{2+} and Mn^{2+} adsorption capacity. With upraised pH, the amount of H^+ ions will be reduced, causing a high number of the hydroxyl group to bond with soil particles; thus, adsorption capacity rises. After the negative charge groups of the soil surface hold out the equilibrium with Cu^{2+} and Mn^{2+}, the adsorption capacity will not grow anymore. It is illustrated that the adsorption capacity is based not only on the soiling charge but also on the soil's structure and characteristics.
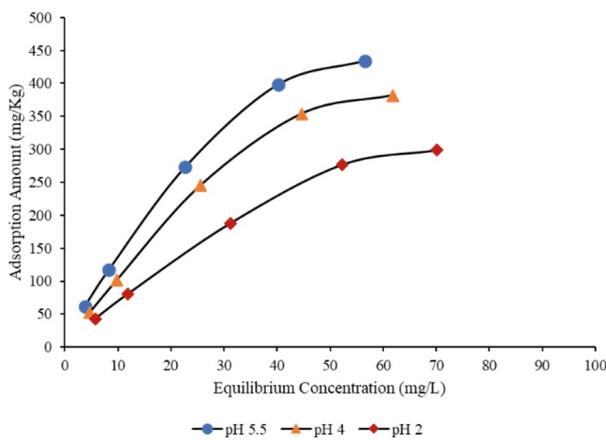
(a) Effect of pH in the Cu (II) adsorption Amount
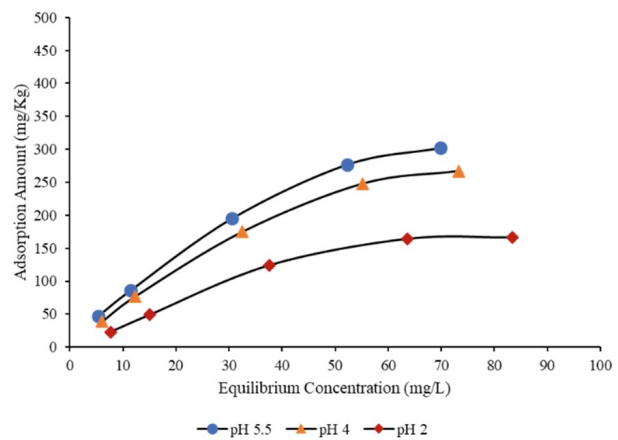
(b) Effect of pH in the Mn (II) Adsorption Amount

Fig. 3 The effect of pH on adsorption amount for Cu(II) and Mn(II)

(a)　Effect of pH in Cu (II) Adsorption
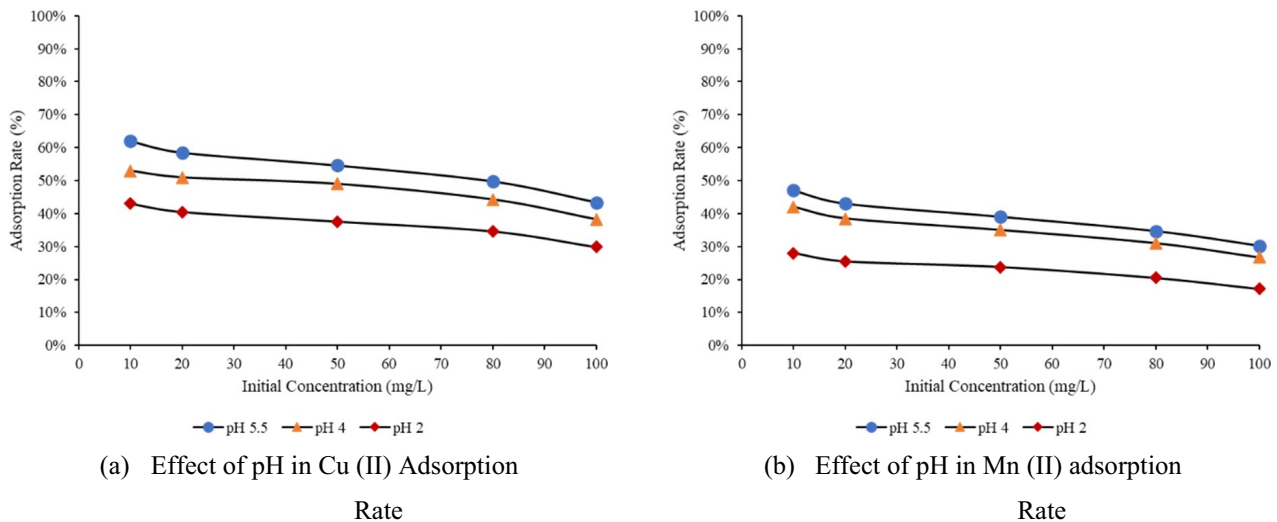Rate

(b)　Effect of pH in Mn (II) adsorption
Rate

Fig. 4 The effect of pH on adsorption capacity rate for Cu(II) and Mn(II)

The same heavy metals behaviours have been expressed by Agbenin and Atin (2003) and Xie et al. (2018). Generally, the adsorption behaviour of Cu^{2+} ions in quartz sand is more efficient than Mn^{2+} ions, and this behaviour of Cu^{2+} is based on the affinity power for Cu^{2+} ions and the strong ability of Cu^{2+} ions to adsorbed in quartz sand particles.

Adsorption isothermal modelling

The measurements of the adsorption isothermal and parameters which, based on the adsorption strength, two types of isotherm models involving the Freundlich and Langmuir models are utilized to measure the adsorption of Cu^{2+} and Mn^{2+}. These two equilibrium isotherm adsorption models are used to fit the experimental results and optimize the adsorption parameters that describe and explain the performance of quartz sand in heavy metals adsorption. Freundlich and Langmuir's models with the experimental results are presented in Figs. 5 for Cu^{2+} and 6 for Mn^{2+}. Freundlich and Langmuir's model parameters are present in Table 2 with a determining factor to indicate the accuracy and fitting of the model to experimental results.

Table 2 presents the adsorption modelling parameters for Freundlich and Langmuir at different pH ranges (5.5, 4, 2). Generally, the Freundlich model gives a more fitting performance than the Langmuir model to the experimental results, which appear from the determination factor (R^2). Freundlich portioning coefficient (K_F) provides the appropriate adsorption amount for Cu^{2+} and Mn^{2+} at different pH ranges, which gives the amount of Cu^{2+} ions adsorbed more effectively from Mn^{2+} ions with high-affinity factor values (N). also, in the Langmuir model, the Cu^{2+} ions adsorbed more than Mn^{2+} in quartz sand. This behaviour for Cu^{2+} ions

is related to the affinity energy, which is high in Cu^{2+} compering with Mn^{2+} ability. Many previous studies have the same adsorption behaviour for Cu^{2+}, like (Xie et al. 2018) and (Sandoval-Flores et al. 2018) investigated the Cu^{2+} ion's high-affinity energy comparing to Zn^{2+} ions. Figures 5 and 6 present the Freundlich and Langmuir isothermal adsorption models at different pH ranges (5.5, 4, 2), which gives the high adsorption capacity for Cu^{2+} and Mn^{2+} at pH 5.5 with high fitting from the Freundlich model to the experimental results, however, the adsorption performance decline with reducing the pH value. This characteristic can be understood by increasing the acidity pH. The amount of H^+ ions will be at a high concentration, which will be caused the dissolution of the soil mineral—also causing the release of ions like Mg^{2+}, Fe^{2+}, and Al^{3+} (Özdemir and Yapar 2009). These ions compete with Cu^{2+} for adsorption areas, reducing adsorption performance with increasing acidity. The fitted curves and model parameters indicate that the quartz sand adsorption performance for Cu^{2+} and Mn^{2+} ions is predominated by multilayer and heterogeneous adsorption depending on the pH scale.

Desorption of Copper Cu^{2+} and Manganese Mn^{2+}

Desorption experiments have also been performed to assess the efficiency of soil to emission heavy metals ions under specific terms. Figure 7 illustrates the relation between the concentration of Cu^{2+} and Mn^{2+} with the desorption capacity rates in quartz sand. Mn^{2+} gives more efficiency in desorption capacity than Cu^{2+}, which can relate to the affinity of ions with soil particles that Cu^{2+} ions have a stronger affinity with quartz sand from Mn^{2+} ions. In general, the maximum heavy metal desorption can happen at high concentration
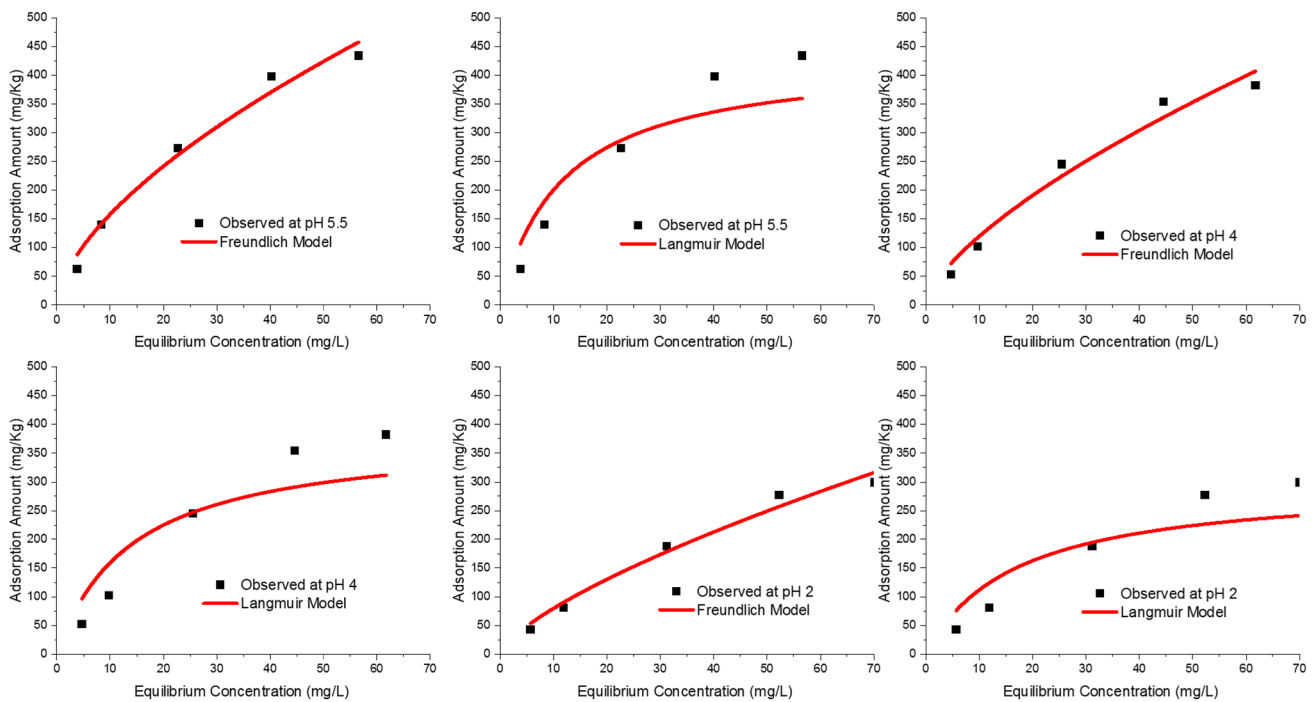
Fig. 5 Cu(II) Freundlich and Langmuir isothermal adsorption models at different pH range

Table 2 The Cu(II) and Mn(II) adsorption isotherms models parameters in quartz sand

Ion	pH	Freundlich model			Langmuir model	
		K_F (L/Kg)	N	R^2	K_L (L/Kg)	R^2
Cu(II)	5.5	3.25	0.88	0.96	0.017	0.80
	4	2.54	0.71	0.96	0.071	0.84
	2	1.56	0.51	0.97	0.064	0.83
Mn(II)	5.5	1.58	0.52	0.99	0.013	0.90
	4	1.19	0.46	0.98	0.061	0.84
	2	0.93	0.37	0.97	0.054	0.82

and the desorption capacity decrease at decreasing the concentration. A rise in initial concentration implies that additional metal ions are present in the mixture. Hence, more ions are attached to the same quantity of soil, which results in saturation of the soil adsorbent, causing a decrease in desorption capacity rate (Igberase et al. 2017).

pH effects on desorption Desorption experiments with pHs 2, 4 and 5.5. The results show that the Cu^{2+} and Mn^{2+} desorbed rate is reduced when pH increases, as presented in Fig. 8a, b. This occurrence could be demonstrated based on the surface charge. The positive surface charge declines with the uprise of pH; thus, the combination of Cu^{2+} and Mn^{2+} with soil will be more stabilized. In addition, the impact of pH on the desorption capacity is characterized in Fig. 7a, b. Cu^{2+} and Mn^{2+} desorption capacity have a high rate at pH 2. Heavy metals are desorbed because of high amounts of H^+ ions at pH 2. The adsorption rate of Cu^{2+} and Mn^{2+} is lower than the desorption rate at strongly acidic and low concentrations of Cu^{2+} and Mn^{2+} in quartz sand.

Generally, pH affects the adsorption and desorption of Cu^{2+} and Mn^{2+} in quartz sand. These two processes have opposite behaviour to each other. At adsorption procedures, the uprising of pH range will improve and increase the adsorption capacity, but the opposite trend will happen when you deal with desorption; the reduction of pH scale will enrich the soil's ability to desorbed the Cu^{2+} and Mn^{2+}. Figure 9a, b shows the relationship between adsorption and desorption amounts of Cu^{2+} and Mn^{2+} based on the pH range.
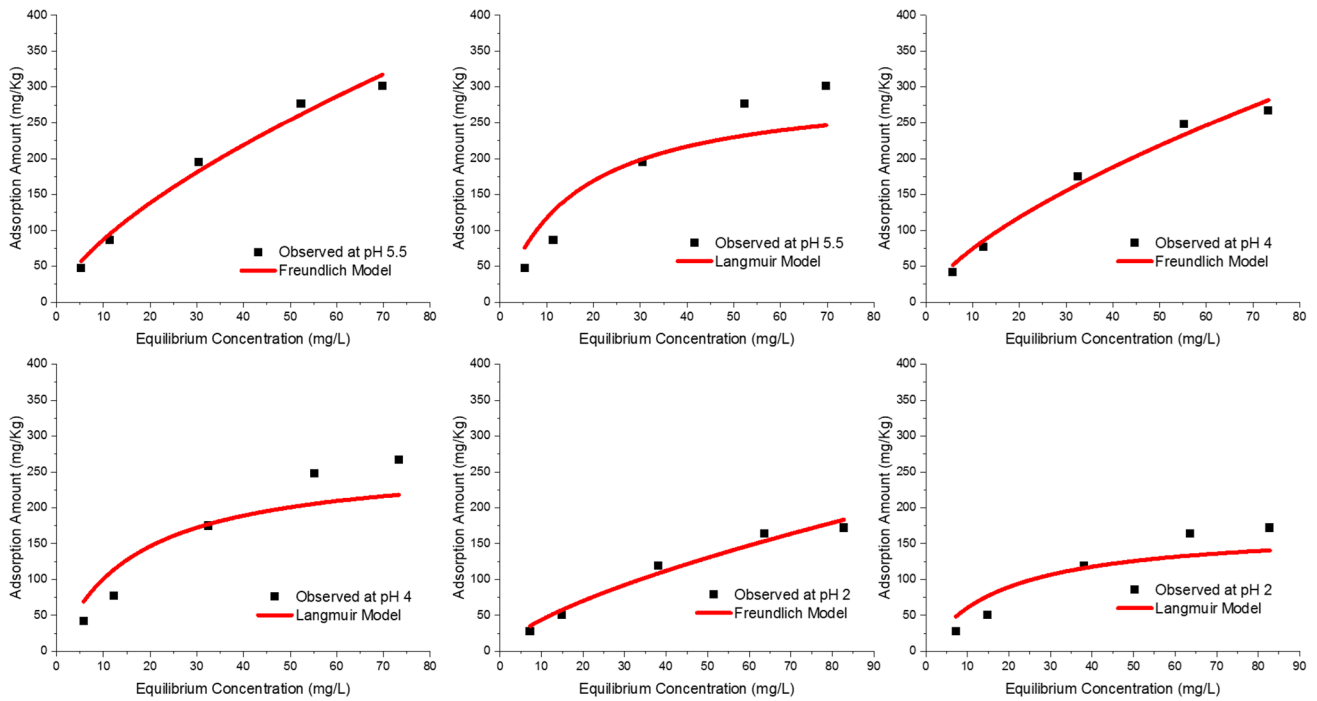
Fig. 6 Mn(II) Freundlich and Langmuir isothermal adsorption models at different pH range

(a) Effect of pH in Cu (II) Desorption Rate
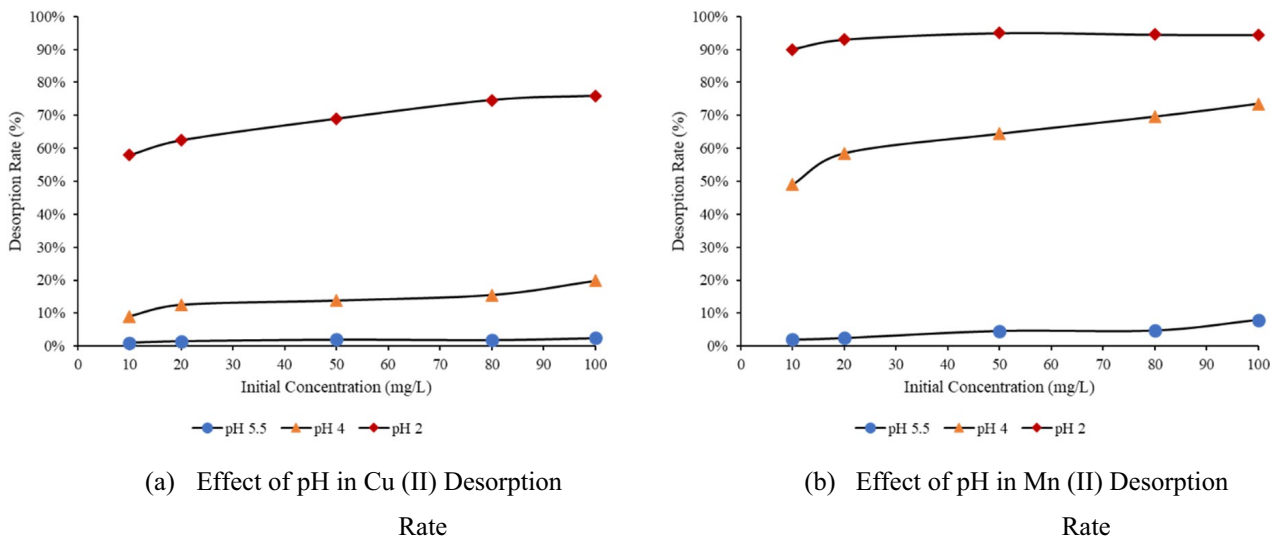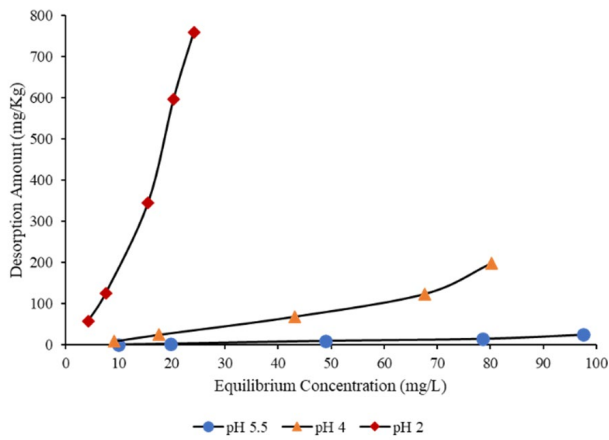
(b) Effect of pH in Mn (II) Desorption Rate

Fig. 7 The relationship between the initial concentration of Cu(II) and Mn(II) with the desorption rate (%)

Conclusion

In this study, the Isothermal adsorption experiment is carried out in a batch of tubes, performed at 25 °C and pH 5.5 with different initial Cu^{2+} and Mn^{2+} concentrations (10, 20, 50, 80, 100 mg/L). pH and initial concentration as impacted factors are considered in this study. The main results obtained in this study can be summarized as follows: The isothermal adsorption results detect that the adsorption rate for Cu^{2+} and Mn^{2+} reached the peak value when the initial concentration was about 10 mg/L. The isothermal adsorption could be fitted by the Freundlich model with high accuracy correlation factor. The pH amounts are considered an essential function in adsorption and desorption procedures. The high concentration of H^+
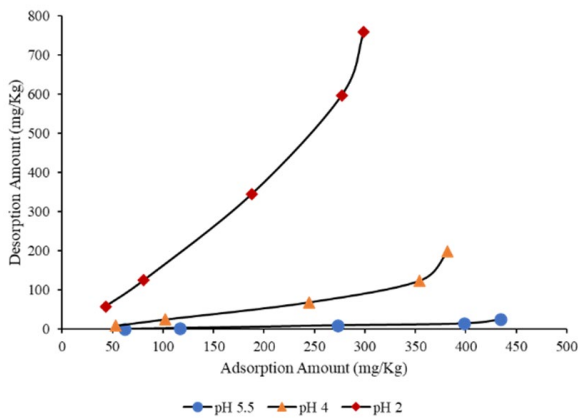
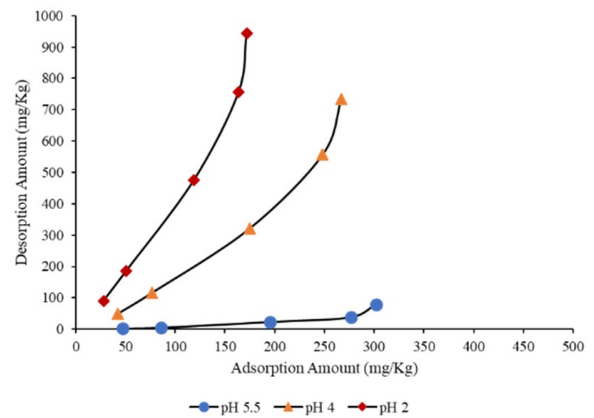(a) Effect of pH in Cu (II) Desorption Amount
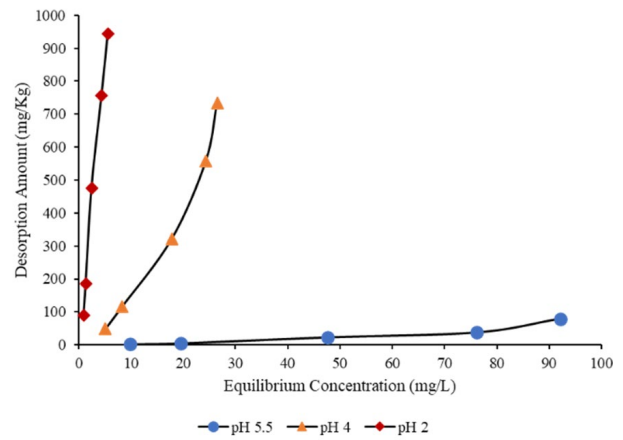
(b) Effect of pH in Mn (II) Desorption Amount

Fig. 8 The effect of pH on desorption amount for Cu(II) and Mn(II)

(a) Effect of pH in Cu (II) Adsorption and Desorption Amount

(b) Effect of pH in Mn (II) Adsorption and Desorption Amount

Fig. 9 The relationship between adsorption and desorption of Cu(II) and Mn(II) based on pH

can upgrade the mobility of Cu^{2+} and Mn^{2+} ions in quartz sand and decrease the intensity of Cu^{2+} and Mn^{2+} adsorption. Also, the adsorption rate of Cu^{2+} and Mn^{2+} ions is lower than the desorption rate beneath using sturdy acidity and a minor concentration of Cu^{2+} and Mn^{2+}. Desorption experiments are conducted under the same conditions using $CaCL_2$ solution (0.01 mol/L). The results illustrate that the integration of Cu^{2+}, Mn^{2+} and quartz sand are comparatively stabilized. The conversion and mobility of Cu^{2+} and Mn^{2+} are hard to happen under particular terms like pH of 5.5 and temperature of 25 °C.

Declarations

Conflict of interest All authors declare that they have no conflict of interest.

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