Heavy metals sorption onto alluvial soil under various operational conditions

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Abstract

The removal of lead Pb^{+2}, copper Cu^{+2} and cadmium Cd^{+2} from aqueous solutions by alluvial soil (AL) as adsorbent has been investigated in a series of laboratory scale experiments under various operational conditions (solution pH, adsorbent dose, ions concentration and contact time). Characterization of AL has been carried out using infrared spectroscopy (FTIR) and scanning electron microscopy (SEM). The surface of AL beads is irregular with many spaces, channels and holes, which are helpful for mass transfer of metal ions into AL soil. The optimum ions removal can be achieved in alkaline solutions. Ions removal efficiency is directly related to contact time and adsorbant dose and inversely related to the initial ions concentration. Ion selectivity on AL followed the order of $Pb^{+2} > Cu^{+2} > Cd^{+2}$. The results confirm that AL can remove heavy metals from wastewater efficiently, which is a cheap and environmentally friendly adsorbent. Langmuir and Freundlich isotherms fit the experimental data perfectly. The results indicate that the adsorption of pb^{+2}, Cu^{+2} and Cd^{+2} ions is well fitted by the pseudo second-order kinetic model.

Key words: adsorption, alluvial soil, heavy metals, operational parameters, selectivity

SYMBOLS

C_i	Initial ion concentration (mg/l).
C_e	equilibrium ion concentration (mg/l).
V	Volume of solution (L).
m	mass of alluvial soil (g).
q_{eq}	adsorption capacity at equilibrium (mg/g).
q_{max}	max adsorption capacity (mg/g).
K_L	Langmuir constant (l/mg).
K_f	Freundlich constant (mg/g).
n	Adsorption intensity of adsorbent.
q_t	Amount of metal ions removal at time t(mg/g).
K_1	pseudo-first order rate constant (min^{-1}).
t	Contact time (min).
K_2	Pseudo-scond order rate constant of adsorption (g/mg/min).

INTRODUCTION

Many countries in the world are facing water scarcity (Kotsilkova *et al.* 2018). The use of treated wastewater and the recycling of industrial wastewater are available approaches for solving this problem. The vast majority of industries discharge effluents containing heavy metals that are in most cases toxic (Mesli & Belkhouche 2018). Heavy metals such as lead, copper and cadmium are severe pollutants which have many negative impacts on the environment, and harmful effects on

human physiology and other biological systems, even at very low concentrations (Pettinato *et al.* 2015a, 2015b). These toxic metals can cause accumulative poisoning, cancer and brain damage. Therefore the removal of heavy metal ions from their leaching solutions before being discharge to water streams is of a great importance to protect the environment (Mousa *et al.* 2016).

Industries such as manufacturers of vehicle batteries, printing and photographic materials lead to the release of enormous amounts of lead in wastewater. Lead can have a serious impact on the nervous system and disrupt the normal functioning of internal organs (Bou Kheir *et al.* 2019). Copper is discharged from many industries such as electronics manufacturing, metal plating, automotive industry, battery products, mining industries, chemical manufacturing and steel industries. The presence of copper in water streams may cause serious health problems for human beings, affecting their internal organs such as the heart, kidneys, liver, pancreas and brain, leading to intestinal distress and anemia. Cadmium has a prime role in many manufacturing industries such as plating, cadmium-nickel battery, phosphate fertilizer, stabilizers and alloys. It is regarded as one of the most poisonous heavy metals present in industrial wastes. Despite its appearance in low concentration, cadmium compounds are massively dangerous and are found at significant levels in the ecosystem. Additionally, they also cause hepatic toxicity and lung cancer. The permissible levels for lead, copper and cadmium in the environment are 0.05, 0.01 and 0.043 (mg/L), respectively (WHO 1996). Therefore, heavy metals concentrations must be below the permissible limits according to environmental regulations before being discharged to water streams.

Many techniques for metals ion removal from industrial wastewater have been developed and used, such as chemical precipitation (Oncel *et al.* 2013), filtration (Al-Qahtani 2016), adsorption electrochemical processes (Ghiloufi *et al.* 2016), membrane processes (Yurekli 2016), oxidation and chemical reduction (Yirsaw *et al.* 2016), evaporation (Lima *et al.* 2014), ion exchange and reverse osmosis (Ricci *et al.* 2015). Most of these techniques may be ineffective for heavy metal removal due to technical economic and environmental reasons (Mesli & Belkhouche 2018). Adsorption process is one of the most effective methods for heavy metal removal from industrial effluents (Kamar *et al.* 2016). The adsorption process offers flexibility in design and operation and in many cases will produce high-quality treated effluent (Kosa *et al.* 2012). Consequently, developing new economic adsorbents with high specific surface area and sorption capacity becomes a hot spot research subject (Sun *et al.* 2016). Researchers have utilized various adsorbent materials in order to remove heavy metals found in water and wastewater streams. Adsorbents like binary compounds, hazelnut hush, steel slag, maghnite caly, eggshell, olive stone activated carbon, rubber wood saw dust and alluvial soil (AL) of Indian origin have been used for heavy metals removal (Pettinato *et al.* 2015a, 2015b; Bohli *et al.* 2017). AL seems to be a promising low cost adsorbent; therefore more research is required to clarify the effect of operational conditions on the sorption capacity of AL and its selectivity for different ions.

The current study aimed to assess the adsorption behavior of AL for the treatment of water streams containing various concentrations of lead(II), copper(II) and cadmium(II) ions. The effect of operational parameters such as initial pH, initial metal concentration, adsorbent dose and contact time on the sorption performance was investigated. The selectivity of AL was identified. Langmuir and Freundlich models were utilized to explain the sorption isotherms. Pseudo first order and second order kinetic models were utilized to define the sorption kinetics of the used adsorbent.

MATERIALS AND METHODS

Materials

Lead nitrate, copper nitrate and cadmium nitrate were all purchased from Loba Chemie (India). All chemicals were not purified prior to usage. Distilled water was used to prepare the solutions.

Preparation of alluvial soil

AL was collected from the River Nile shore in Mansoura, Egypt. AL samples were initially dried by the sun for 5 days, and then heated at 500 °C for 7 hours. The dry soil was then ground to provide partial size by mesh screen of 200 μm, and afterwards put in storage to be used as an adsorbent.

Batch adsorption procedure

The adsorption of adsorbates (Pb, Cu and Cd) was carried out in batch experiments as shown in Figure 1. Solutions with various heavy metals concentrations were shacked in Stoppard bottles of 100 m with AL for 2 h. The concentration of heavy metal ions was determined before and after adsorption by using fast sequential atomic absorption spectrometry (model-VarianAA240FS). The pH of the solution was measured using a pH meter (Extech 34135A Oyster Series pH/conductivity/TDS/ORP/salinity meter). The adsorption capacity of adsorbent q_e in (mg/g) was calculated according to the equation that follows:

$$q_e = \frac{(C_i - C_e)V}{m} \tag{1}$$

where C_i is the initial ion concentrations (mg/l), C_e is the equilibrium ion concentration (mg/l), V is the volume solution (L), and m is the mass of alluvial soil (g).

1- Ion solution
2- Adsorbent
3- Shaker
4- Atomic absorption spectrometry
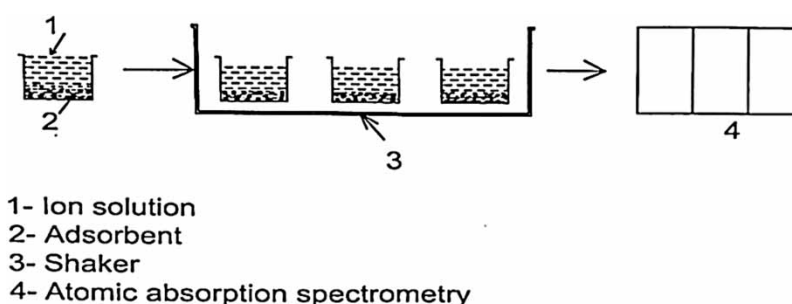
Figure 1 | Schematic of the adsorption system.

The following equation was used to calculate the removal efficiency of metal ions:

$$\text{Removal (\%)} = \frac{C_i - C_e}{C_i} \times 100 \tag{2}$$

The effect of adsorbent dosage on the adsorption performance was carried out by changing the dosage from 0.1 to 1 g in 100 ml of water solution. All mixtures were shaken at room temperature and pH equal to 7 ± 0.5.

The adsorption experiments were carried out at various pH values ranged from 2 to 9. The experiments were repeated twice and the average value was calculated where the experimental error had not exceeded 2%. PH of solution was adjusted using HCl and NaOH with concentration of 1 M.

RESULTS AND DISCUSSION

Characterization of alluvial

The Fourier transform infrared spectroscopy (FTIR) of AL was performed using a FTIR spectrometer (Thermo Scientific Nicolet IS10) as shown in Figure 2. IR spectra were performed within the range of
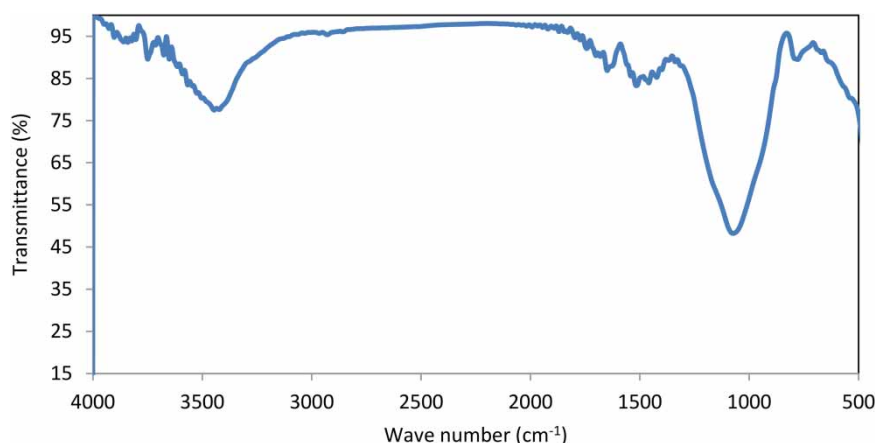
Figure 2 | FTIR spectra of alluvial soil.

4,000–500 cm^{-1}. Table 1 shows the main elemental compounds of AL. The precence of carboxyI groups, oxides and silica has been extensively confirmed, which is important for heavy metal binding (Volesky & Holan 1995). CarboxyI groups are also responsible for AL selectivity towards metals.

Table 1 | Alluvial soil composition

Peak Location	Elemental compounds	References
3,446 cm^{-1}	O-H	Ahmed & Ahad (2016)
1,649 cm^{-1}	H-O-H associated with Al(OH)$_3$	Ahmed & Ahad (2016)
1,515 cm^{-1}	C=O	Hanafiah *et al.* (2009)
2,929 cm^{-1}	C-H	Hanafiah *et al.* (2009)
1,074 and 779 cm^{-1}	Si-O-Al	Vempati *et al.* (1996)
461 cm^{-1}	O-Si-O	Vempati *et al.* (1996)

Scanning electron microscopy SEM represents an additional important tool concerning the examination of the surface morphology and the porous nature of an adsorbent. Figure 3 shows that the adsorbent has a porous nature and irregular surface structure. The average pore diameter was in
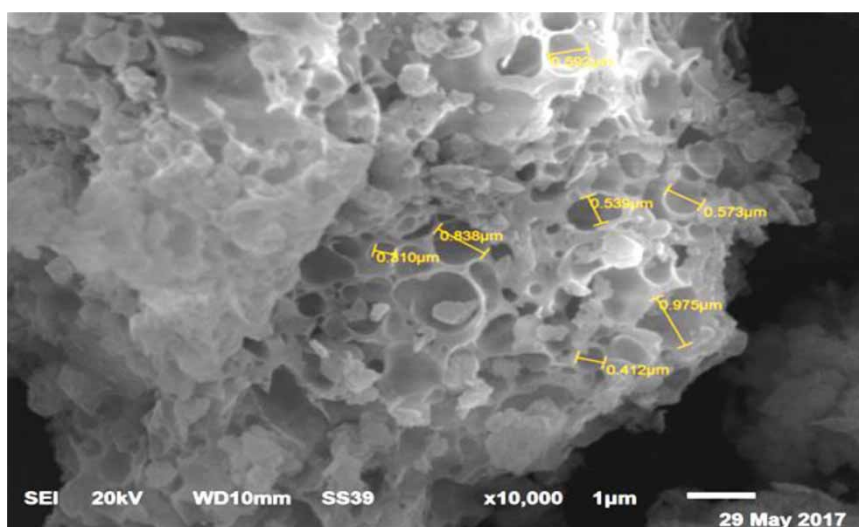

Figure 3 | SEM micrographs of surface (AL).

the range between 0.975 μm to 0.310 μm. The surface of AL beads is irregular with many spaces, channels and holes, which are helpful for mass transfer of metal ion into AL soil.

Effect of pH on the adsorption performance

The initail pH value of solution is an important controlling parameter that influences the adsorption process because it may effect both the properties of the adsorbent and the composition of the solution. The pH can affect both the adsorbent's surface, as well as the adsorbent's degree of ionization. Figure 4 shows the effect of pH on the adsorption of heavy metals ions on to AL.
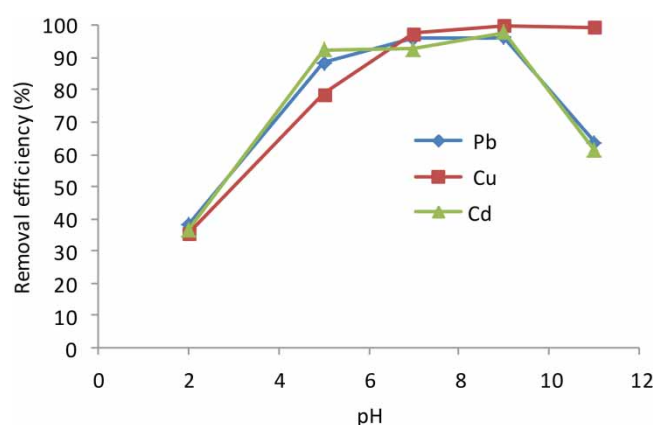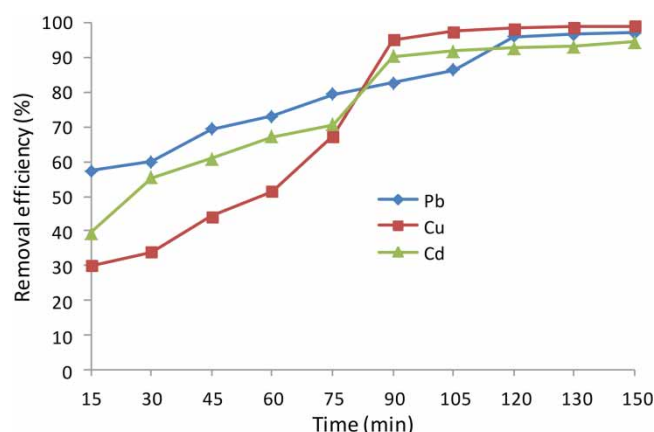

Figure 4 | Effect of pH on cations adsorption on to (AL) (initial ions concentration 30 mg/L, dose 0.5 g/100 ml, agitation speed 100 rpm, contact period 120 minutes at room temperature).

It is clear that the ions removal efficiency was the lowest at pH 2. At low pH more H^+ competed with cations for available adsorption sites, which made it harder for the cations to bind to activated sites and negatively impacted the removal efficiency of ions. Also, a large number of adsorbent active sites may become positively charged at very low pH. The highest removal efficiency was achieved at pH 9. The increase in cations removal efficiency at higher pH may also be attributed to the reduction of H^+ ions, which compete with metal cations at lower pH (Ofomaja et al. 2010).

FTIR spectral analyses showed the presence of carboxylate (–COO–) and hydroxyl –OH functional groups on the AL surface, which may essential for the adsorption of specific metal ions (Zhang et al. 2016). At low pH, the –OH functional group is protonated and restricts the approach of cations toward the adsorbent surface, which results in lower removal efficiency of metals. While at higher pH, the –OH functional group is deprotonated, which increases the negative charge density on the adsorbent surface and results in higher metals up take.

Effect of contact time on the removal efficiency

The sorption of Pb(II), Cu(II) and Cd(II) ions onto AL depends mainly on the reaction time. Physical properties of the adsorbent, especially the amount of available sorption sites, are the main factors that affects the time required to achieve the thermodynamic equilibrium. Cations sorption onto AL has the characteristic time evolution of saturation phenomena that is shown in Figure 5. In the beginning, the experiments were carried out for 3 hours, and no change in the removal efficiency was noticed after 120 min. AL achieved removal efficiency of 96.00%, 98.23% and 92.73% for Pb^{+2}, Cu^{+2} and Cd^{+2}, respectively at an equilibrium time of 120 min.

Figure 5 | Effect of contact time on cations adsorption (initial ions concentration 30 mg/L, adsorbent dose 0.5 g/100 ml, agitation speed 100 rpm, pH = 7 at room temperature).

The removal efficiency was high at the beginning and then gradually decreased with time until it reached equilibrium after an operation time of 120 min. This may be due to the availability of large specific areas of adsorbents and more active sites for metal sorption during the beginning of the experiment. The higher adsorption rate is a function of the concentration gradient between the liquid layer of the adsorbate and the surrounding active sites of adsorbent available for adsorption of cations. After the equilibrium time the adsorption rate becomes slower, which is probably due to diffusion of cations into the pores of the adsorbent. When these sites are exhausted, the uptake rate is controlled by the rate at which the adsorbate is transported from the exterior to the interior sites of the adsorbent particles (Verma *et al.* 2008).

Due to the difference in the ionic size of metals and the nature and distribution of active groups on the adsorbent, the removal efficiency of cations varies from one metal to the other, as well as the mode of interaction between the cations and the adsorbents. Ion selectivity on the used adsorbent followed the order of $Pb^{+2} > Cu^{+2} > Cd^{+2}$. Ions with the higher charge and the smaller hydrate radius have a higher affinity, as do ions with greater polarization, which facilitates electrostatic ion exchange (Papageorgiou *et al.* 2006).

Effect of adsorbent dose

In this study, the adsorbent dosage of AL was raised from 0.1 to 1 g /100 ml, using an ions concentration of 30 mg/l at pH 7 ± 0.5. The obtained results are presented in Figure 6. The removal efficiency increased with increasing the adsorbent dosage from 0.1 to 0.5 and no further significant increase was achieved after words. The highest removal efficacy of Pb^{+2}, Cu^{+2} and Cd^{+2} achieved was 96%, 98% and 96%, respectively. This adsorption trend is commonly due to the increase of exchangeable sites available for the ions' sorption. The maximum adsorption of Pb^{+2} was achieved using an adsorbent dosage of 0.5 g, while for Cu^{+2} and Cd^{+2} this was achieved using an adsorbent dosage of 1 g. This may be due to the non-availability of active sites on the adsorbent and establishment of equilibrium between the cations on the adsorbent and in the solution. The equilibrium adsorption capacity of adsorbents is shown in Figure 7. It was clear that as the adsorption dosage increased the adsorption capacity decreased. This may be due to the decrease in total adsorption surface area and increase in diffusion path length resulting from overlapping or aggregation of adsorption sites (Akar *et al.* 2009). Thus, the amount of cations adsorbed onto the adsorbent get reduced with increasing adsorbent mass, which decreased the sorption capacity of the adsorbent.
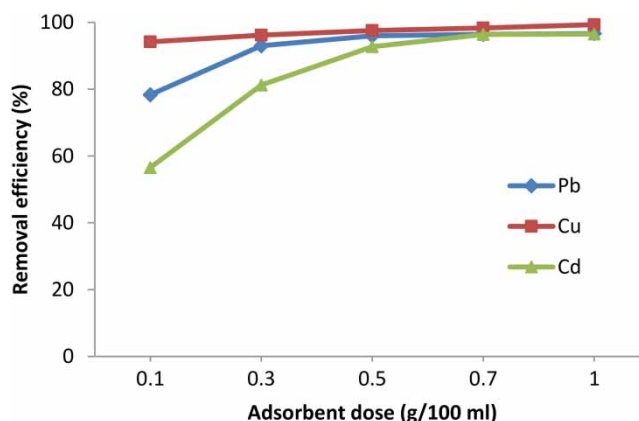
Figure 6 | Effect of adsorbent dose on cations removal efficiency (initial concentration 30 mg/L, agitation speed 100 rpm, pH = 7.0, contact time 120 min at room temperature).
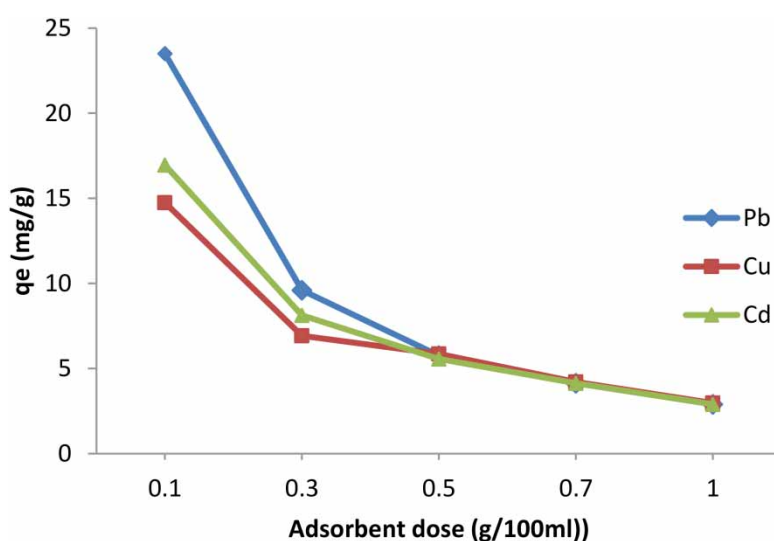
Figure 7 | Adsorption capacity of alluvial soil (initial concentration 30 mg/L, agitation speed 100 rpm, pH = 7.0, contact time 120 min at room temperature).

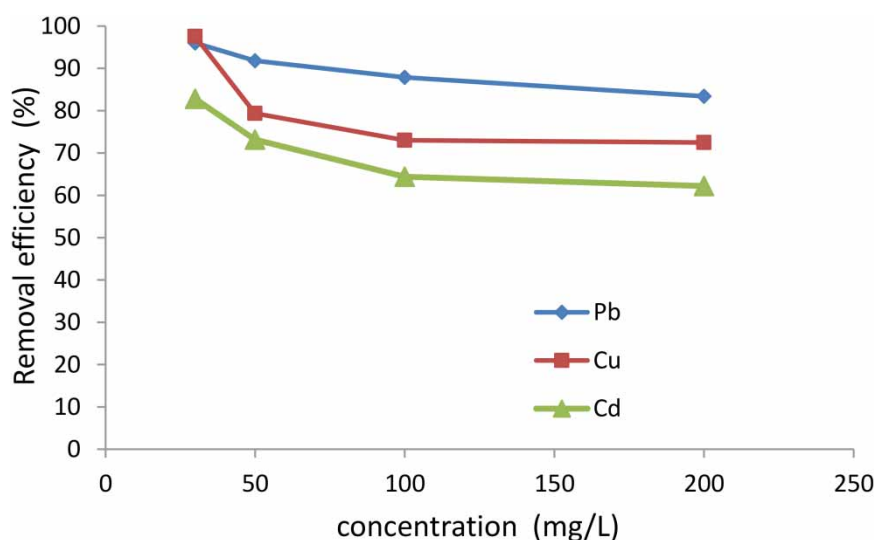### Effect of initial ion concentration

The rate of adsorption is a function of initial concentration of the adsorbate. The effect of different initial cations concentrations on the removal efficiency of AL at a dose of 0.5 g/100 mL is presented in Figure 8. For all metal ions the removal efficiency decreased with increasing the initial ions concentration.

By increasing the ions' initial concentration from 30 to 200 mg/l, the removal efficiency of Pb^{+2} decreased from 96.00% to 87.40%, from 97.6% to 72.50% for Cu^{+2} and from 82.80% to 62.20% for Cd^{+2}.

Increasing the cations' concentration increased the number of ions competing for the accessible adsorption sites, since the number active sites on the AL is constant. Pb^{+2} and Cu^{+2} can be classified as intermediate acids while Cd^{+2} is regarded as a 'soft' acid (Papageorgiou *et al.* 2006). According to the hard-soft-acid-base (HSAB) theory, 'hard' acids would prefer to bind with 'hard' bases rather than with 'soft' bases. AL with the 'hard' carboxyl base would achieve higher sorption capacity towards Pb^{+2} and Cu^{+2} compared to Cd^{+2}.

Sorption isotherms

Isotherm models can be used in order to determine the equilibrium modeling of sorption systems. Freundlich and Langmuir models are the most widely used models to observe the sorption process.

Figure 8 | Effect of initial ions concentration on the removal efficiency of cations (adsorbent dose 0.5 g/100 ml, agitation speed 100 rpm, pH = 7.0, contact time 120 min at room temperature).

The **Langmuir isotherm model** suggests that every adsorbate molecule occupies a single site and the surface is homogenous. The linear form of the langmiur isotherm equation can be written as follows:

$$1/q_{eq} = 1/(q_{max}K_LC_e) + 1/q_{max} \tag{3}$$

where C_e is the adsorbate concentration at equilibrium (mg/L), q_{eq} is the mass of ions adsorbed into adsorbent (mg/g), q_{max} is the maximum adsorption capacity (mg/g), and K_L is Langmuir constant (L/mg).

The **Freundlich isotherm model** illustrates absorption-complexation reactions taking place in the adsorption process. The Freundlich adsorption isotherm is the relation between the amount of metals adsorbed per unit mass of adsorbent (q_e) and the concentration of similar metals at equilibrium (C_e). The linear form of the Freundlich isotherm is as follows:

$$\text{Log } q_{eq} = \log K_F + 1/n \log C_e \tag{4}$$

where K_F represents the Freundlich constant (mg/g) and n is adsorption intensity of the adsorbent.

Langmuir and Freundlich adsorption constants and the correlation coefficients are shown in Table 2.

Table 2 | Adsorption isotherm constants for adsorption of Pb^{+2}, Cu^{+2} and Cd^{+2} onto AL

Isotherm	Model equation	Parameter	pb	cu	cd
Langmuir	$q = \dfrac{q_m K_L C}{1 + K_L C}$	q_m	854.5	228.8	148.9
		K_L	0.0002	0.0007	0.0009
		R^2	0.99	0.99	0.99
Freundlich	$q = K_F C^{\frac{1}{n}}$	K_F	0.182	0.270	0.268
		N	0.987	1.142	1.177
		R^2	0.99	0.99	0.99

Figure 9 shows Langmuir and Freundlich isotherm models for the experimental results for various conditions. The results show that the sorption of ions onto the used adsorbent is well correlated with both Freundlich and Langmuir equations within the studied concentration range.
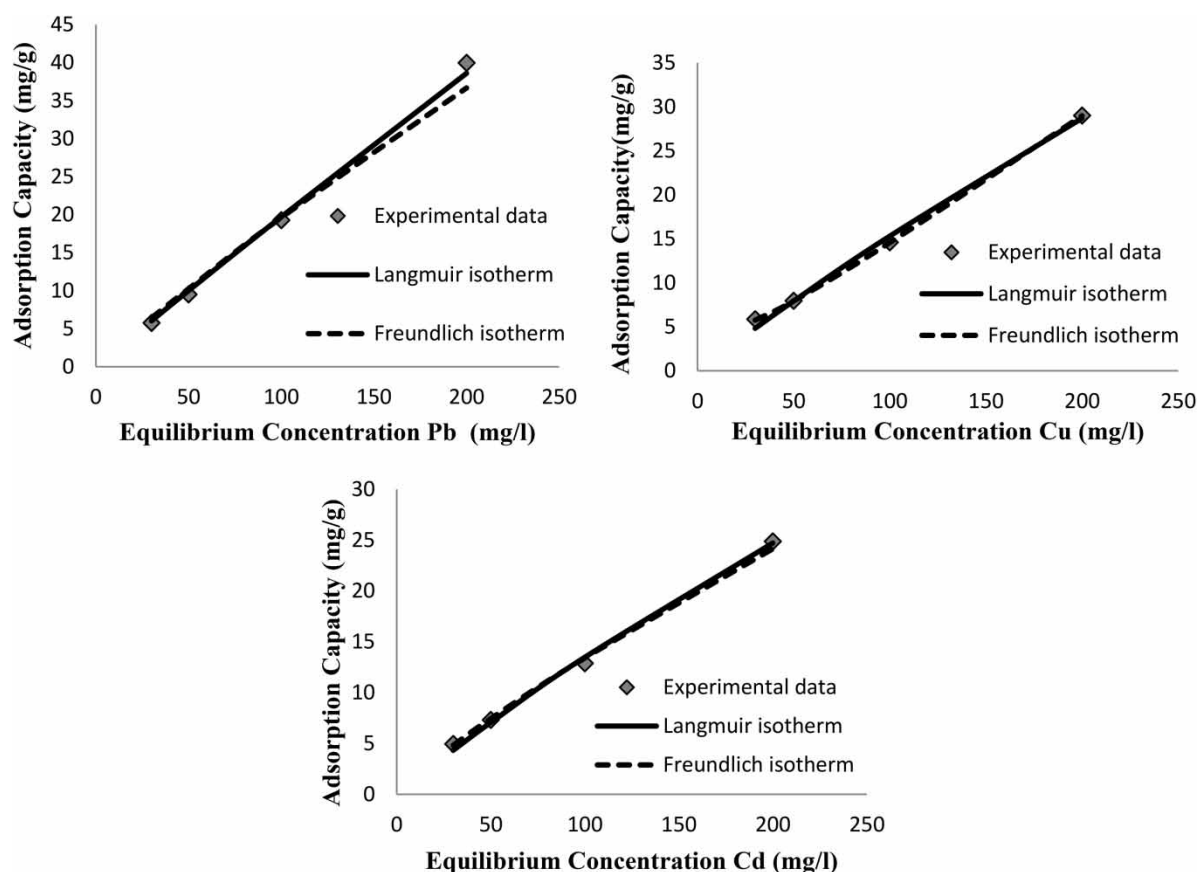
Figure 9 | Freundlich and Langmuir isotherm models for adsorption of cations onto AL (adsorbent dose 0.5 g/100 ml, agitation speed 100 rpm, pH = 7.0, concentration 30 mg/l, contact time 120 min at room temperature).

In the current study, the Freundlich isotherm model can be suitably explained by the surface precipitation model, which describes both the precipitation reaction and the adsorption occurring on the heterogeneous surface (Robertson & Leckie 1997).This model describes the multilayer adsorption mechanism, and that the adsorbed amount increases with the concentration.

The Langmuir isotherm model illustrates monolayer adsorption with homogeneous distribution of active sites on the AL. The Langmuir equation assumes that the surface is homogenous, which results in a lower concentration. This is ascribed to the surface complexion model, which has limited utility since it explains the adsorption behavior only at lower ions concentrations (Bradl 2004).

Kinetics of adsorption

The rate of adsorption and possible adsorption mechanism of metals onto AL was carried out using pseudo-first order and pseudo-second order equations. Kinetic modeling is a suitable rate expression characteristic of possible reaction mechanisms.

The pseudo first order rate equation is represented as:

$$\text{Log } (q_e - q_t) = \log q_e - \frac{k1t}{2.303} \tag{5}$$

where q_t is the amount of metal ions removed at time t (mg/g), q_e is the adsorption capacity at equilibrium (mg/g), k_1 is the pseudo-first order rate constant (min^{-1}) and t is the contact time (min). Values of q_e and k_1 at different concentrations determined from the model are presented in Table 3.

Table 3 | Kinetic parameters for adsorption of Pb^{+2}, Cu^{+2} and Cd^{+2} on to AL

| Kinetics	Parameter	Value		
		Pb	Cu	Cd
First-order	q_e	5.42	9.83	5.75
	K_1	0.039	0.008	0.025
	R^2	0.64	0.98	0.89
Second-order	q_e	6.71	11.48	7.19
	K_2	0.006	0.0007	0.0036
	R^2	0.95	0.90	0.97

The pseudo-second order model is represented as:

$$\frac{t}{q_t} = \frac{1}{k_2 \; q_2 e} + \frac{t}{q_e} \tag{6}$$

where K_2 is the pseudo-second order rate constant of adsorption (g/mg/min). The respective constant values are given in Table 3.

It was observed that the second–order kinetic model showed linearity with high correlation coefficient at all the studied concentrations in comparison to the first-order kinetic model. On the other hand, the calculated results of qe by means of the first-order kinetic model as shown in Figure 10 agreed perfectly with the experimental results. This indicated that chemisorption controls the rate
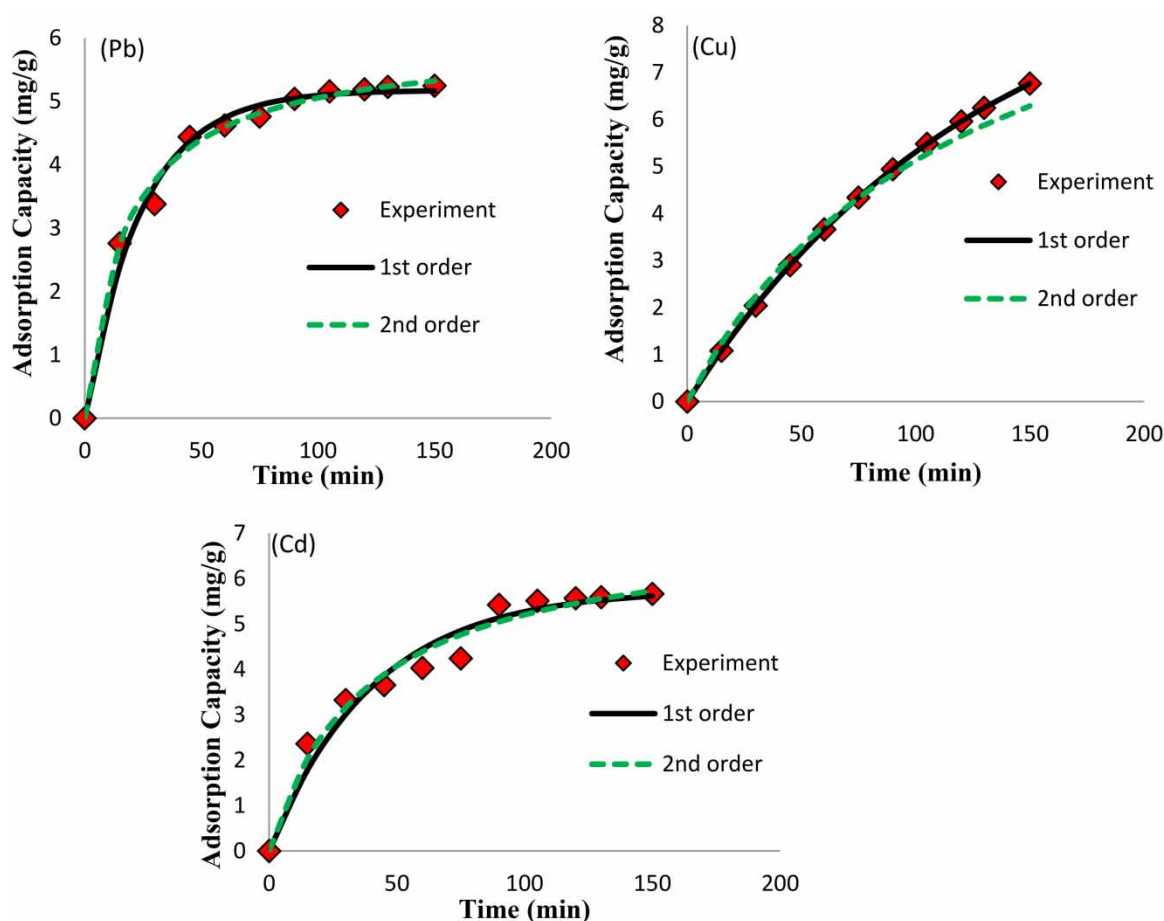
Figure 10 | First and second–order kinetics for the adsorption of cations onto AL (adsorbent dose 0.5 g/100 ml, agitation speed 100 rpm, pH = 7.0, concentration 30 mg/l, contact time 120 min at room temperature).

of reaction. In chemisorptions the adsorbate molecules usually occupy certain adsorption sites on the adsorbent surface by formation of a chemical bond and searches for sites that will maximize their coordination number with the surface (Kumar & Kirthika 2009). The second order equation revealed that the initial adsorption rate increased with the increase of initial cations concentration. The lower the metal ion concentration, the lower the chance of collisions between them.

Competition among metals ions

The ion selectivity of AL was investigated using a solution composed of Pb^{+2}, Cu^{+2} and Cd^{+2} with concentrations of 30 mg/l, adsorbent dose 0.5 g/100 L, agitation speed 100 rpm, contact time 120 min, pH = 7 at room temperature for all metal ions as shown in Figure 11. It follows the order of $Pb^{+2} > Cu^{+2} > Cd^{+2}$. The HSAB concept agrees with the obtained results. Pb^{+2} and Cu^{+2} can be classified as intermediate acids while Cd^{+2} is regarded as a 'soft' acid (Papageorgiou et al. 2006). The HSAB theory shows that the 'hard' acids would bind with 'hard' bases while 'soft' acids bind with 'soft' bases. AL, with the 'hard' carboxyl base, would exhibit higher affinity towards Pb^{+2} and Cu^{+2}.
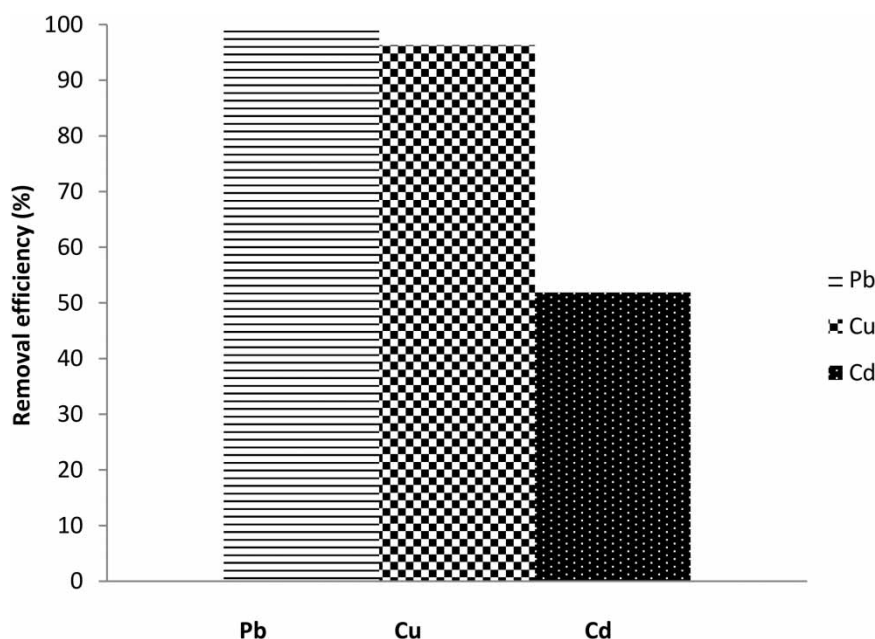
Figure 11 | Selectivity of alluvial soil for various ions (adsorbent dose 0.5 g/100 ml, agitation speed 100 rpm, pH = 7.0, concentration 30 mg/l, contact time 120 min at room temperature).

Ions adsorbed onto AL depend mainly on three factors: metal ion charge density, hydrated radius and electronegativity. The values of the above mentioned factors are 0.0272, 0.802 and 2.33 for Pb^{+2}, respectively, 0.0290, 0.838 and 1.9 for Cu^{+2}, respectively and for Cd^{+2} 0.0270, 0.852 and 1.68, respectively. Ions with the smaller hydrate radius have higher affinity. Also ions with greater polarization facilitate electrostatic ion exchange. The electrostatic bonding strength is a measure of the strength of covalent bonding relative to ionic bonding. The electrostatic bonding strength values are equal 798, 498 and 422 for Pb^{+2}, Cu^{+2} and Cd^{+2}, respectively. It can be observed that since the value of the ion charge density is similar for all metals, the strength of covalent bonding follows the sequence $Pb^{+2} > Cu^{+2} > Cd^{+2}$.

CONCLUSION

In this study, the adsorption of heavy metal ions (Pb^{+2}, Cu^{+2} and Cd^{+2}) onto AL was investigated. FTIR and SEM were used for the characterization of AL. The operating parameters, such as solution pH, adsorbent dose, ions concentration and contact time have a great effect on the adsorption process. It was found that the optimum ions removal can be achieved in alkaline solutions. Ions removal efficiency is directly related to contact time and adsorbant dose and inversely related to the initial ions concentration. The amount of ions removal was increased as the contact time and adsorbent dose were increased. The adsorption isotherm was well fitted using the Langmuir and Freundlich equations. The adsorption kinetics follows pseudo second-order kinetic model with a good correlation. Ion selectivity on AL followed the order of $Pb^{+2} > Cu^{+2} > Cd^{+2}$. The results confirm that AL can remove heavy metals from wastewater efficiently, which is a cheap and environmentally friendly adsorbent.

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