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# Study on adsorption mechanism of Pb(II) and Cu(II) in aqueous solution using PS-EDTA resin

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ABSTRACT

Batch sorption experiments were conducted using a PS-EDTA resin as a sorbent to adsorb Cu(II) and Pb(II) ions from single component system. The results showed that both the Cu(II) and Pb(II) ions sorption capacity and efficiency reach a high level at an initial pH value of 6, the adsorption capacity of Cu(II) and Pb(II) ions were 42.1 mg/g and 32.1 mg/g at initial concentration of 100 mg/L, and the maximum efficiency were 99.8% and 99.6% at 5 mg/L, respectively. The equilibrium data for the adsorption of Cu(II) and Pb(II) on PS-EDTA resin were tested with three adsorption isotherm models which were found to be suitable for the two ions' adsorptions. In addition, the kinetic adsorption fitted well to the pseudo-second-order model and the corresponding rate constants were obtained. Furthermore a higher desorption efficiency of Cu(II) and Pb(II) from the PS-EDTA resin using acid treatment was available. The column capacity for Cu(II) and Pb(II) adsorption for the bed height of 0.15 m, hydraulic loading rate of 2.5 $m^3/(hm^2)$ and the feed concentration of 50 mg/L and 100 mg/L for 50% breakthrough concentration were found to be 49.8 mg/g, 87.4 mg/g and 48.7 mg/g, 91.2 mg/g, respectively.

## 1. Introduction

Water contamination by toxic organic chemicals and heavy metals from the micro-polluted wastewater discharges has become a worldwide environmental concern. Thus, heavy metal pollution is considered as a major problem of increasing magnitude. Heavy metals are persistent, and therefore, very difficult to eliminate naturally from the environment, even at a presence of trace amounts. Nearly all heavy metals are highly toxic, non-biodegradable, non-thermo degradable and readily accumulate to toxic levels [1–3]. Heavy metal removal from wastewater has progressed significantly and can now be applied for the protection of the environment and human health. Lead ion has the toxicities, such as Encephalopathy, seizures and mental retardation, reduces hemoglobin production [4,5]. Copper ion has the toxicities, such as Liver damage, Wilson's disease, insomnia [6,7]. Therefore, it is necessary to eliminate Pb(II) and Cu(II) from the source water, in order to prevent the deleterious impact of Pb(II) and Cu(II) on ecosystem and public health. Precipitation methods are particularly reliable but require high installation cost (large settling tanks for the precipitation) and usually a further treatment is also needed, in order to meet the law requirements.

Adsorption, which is a more sophisticated technique, has the advantage of allowing the recovery of metallic ions, though is sometimes more expensive than the other techniques. Studies on the treatment of effluents containing heavy metals have revealed the adsorption to be a highly effective technique for the removal of heavy metals from wastewater. Additionally, adsorption is a more economic process, simple to design and easy to operate. So, in late 1980s and 1990s, EDTA (ethylene diamine tetraacetic acid) was suggested as a nice small molecular chelating agent for exhibiting extremely high metal-chelating capacity because it contains abundant functions being able to chelate with metal ions [8–11]. In this study, the PS-EDTA resin as a low-cost effective sorbents with high mechanical strength to adsorb trace Cu(II) or Pb(II) in micro-polluted water source was investigated. The goal of the present work is to investigate the adsorption potential of PS-EDTA for removal of Cu(II) and Pb(II) ions in the individual aqueous solutions. Firstly, PS-EDTA resin was synthesized and then the pH, contact time and initial concentration effect on the adsorption capacity of PS-EDTA were studied. The Langmuir, Freundlich and Tempkin isotherm models were used to describe equilibrium data. The adsorption mechanisms of metal removal by the adsorbents are also presented

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## 2. Experimental

### 2.1. Characterization of adsorbent [12]

The adsorbent was synthesized and provided by our laboratory. The PS-EDTA resin, a novel chelating resin containing many amino and carboxyl functional groups, was prepared from chloromethylated polystyrene bead by reacting with ethylenediamine and chloroacetate in aqueous phase in sequence. It also has uniform and rich aperture with large surface area (42.5 $m^2/g$). Having a number of functional groups, large surface area, good cost effectiveness, synthesis all in aqueous and moderate reaction conditions, the PS-EDTA performs a wide application prospect in the removal and even recovery of heavy-metal ions from their aqueous solutions or wastewater.

### 2.2. Preparation of Cu(II) and Pb(II) solutions and measurement

In this section, $Cu(NO_3)_2{\cdot}3H_2O$ and $Pb(NO_3)_2$ were used, Sodium dehydrogenate phosphate, phosphoric acid, ammonium acetate, acetic acid, ammonium chloride and ammonia were used to prepare different basic and acidic buffer solution. All the chemicals used with purity more than 99.99%. Distilled water is used in all experiments. Lead and copper atomic spectroscopy standard solution of 1000 mg ± 0.3% were used for measurements. Calibration curves between 10 mg/L and 100 mg/L were prepared and detection limit were found as 0.1 mg/L. Quality assurance of analytical measurements was performed in this study. In the present study, a GBC Avanta A 5450 atomic absorption spectrophotometer (AAS) determination is used for the analysis of these two heavy metals in the solution. This method has been reportedly used in many studies for analysis of Cu(II) and Pb(II) [13–15].

### 2.3. Batch equilibration method

The batch experiments were carried out in 250 mL conical flask with stopper. A specific amount of dry resin was added in 100 mL of aqueous Cu(II) and Pb(II) solution, and then stirred for a predetermined period (found out from the kinetic studies) in water bath-cum-mechanical shaker. Afterwards, the PS-EDTA resin was filtered off and the concentrations of the two metal ions in the filtrate were determined. Adsorption isotherm study was carried out with different initial ions' concentrations (5–200 mg/L). The adsorption capacity of the PS-EDTA resin and the percentage removal of Cu(II) and Pb(II) were calculated using the following Eqs. (1) and (2), respectively.

$$Q_t = \frac{(C_0 - C_e)V/1000}{W} \tag{1}$$

$$\%\ \text{removal of ions} = \frac{C_i - C_0}{C_i} \times 100 \tag{2}$$

where $Q_t$ is the adsorption capacity in mg/g at time $t$, $C_i$, $C_o$ and $C_e$ is the initial, outlet and equilibrium concentration of Cu(II) and Pb(II) in mg/L, respectively, $V$ is the volume of Cu(II) and Pb(II) solution in mL and $W$ is the total amount of resins in g.

The experiments were carried out as the effect of contact time with time ranges of 5 min–6 h. The process of Cu(II) and Pb(II) removal from an aqueous phase by any adsorbent can be explained by using kinetic models and examining the rate-controlling mechanism of the adsorption process such as chemical reaction, diffusion control and mass transfer. All the batch experiments were performed in triplicate and the average data were used in data analysis.

### 2.4. Column equipment

Fixed bed column experiments were conducted using borosilicate glass columns of 1 cm internal diameter and 55 cm length. The column was packed with PS-EDTA between two supporting layers of absorbent cotton to prevent the floating of adsorbent from outlet. The bed length used in the experiments was 15 cm. In a typical experiment the metals of concentration (5–200 mg/L) was pumped at a fixed flow rate to the filled with known bed height of adsorbent. The pH of the solutions was maintained constant at 6.0. The temperature of stream feeding solution and of the column was controlled at 293 ± 1 K through a thermostatic bath.

## 3. Results and discussion

### 3.1. Metal adsorptions

#### 3.1.1. Effect of contact time

In order to optimize contact time for the adsorption, PS-EDTA resin was prepared. The time intervals used were from 5 min to 6 h. Amounts of 0.1 g of PS-EDTA were placed under constant stirring (100 rpm). The adsorption experiments were done with 50 mg/L of concentration, in pH 6 and $T = 293 \pm 1$ K. No pH corrections were done along the experiments. The concentration of adsorbed ions on the surfaces was analyzed by AAS. Fig. 1 shows the amount of Cu(II) and Pb(II) ions adsorbed as a function of contact time. It can be seen that the amounts of Cu(II) ions adsorbed onto the resins are more than the amounts of Pb(II). Also with increasing the contact time to 120 min, the percentage of adsorption increased. Giving time more than 120 min, the amount of adsorbed ions remained unchanged. So, this duration was chosen as the optimum contact time for all further experiments. This short time period required to attain equilibrium suggests an excellent affinity of the adsorbent for both the two metals from aqueous solution. The same equilibrium times have been reported in several earlier works which related with the adsorption of Cu(II) and Pb(II) ions on various adsorbents [16–18].

#### 3.1.2. Effect of pH solution on adsorption

The pH of solution is one of the most important variables affecting metal ions adsorption. This is partly because hydrogen ions themselves are strongly competing with metal ions. Fig. 2 shows the effect of pH on the adsorption of Cu(II) and Pb(II) ions onto PS-EDTA surfaces. In this section, concentration of each ion was respectively chosen to be 50 mg/L and $T = 293 \pm 1$ K. The effect of pH

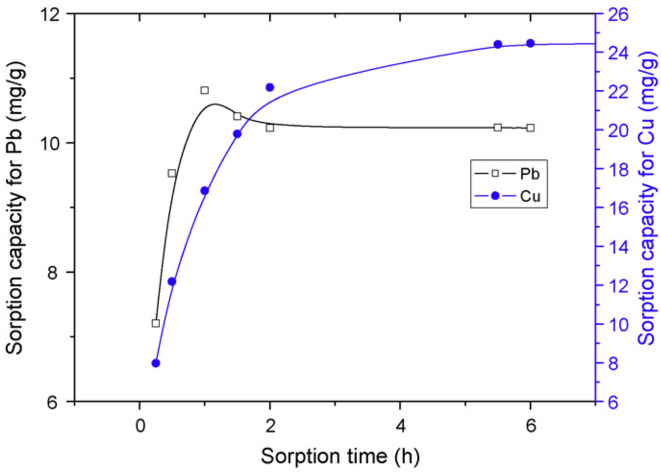

**Fig. 1.** Effect of contact time on the adsorption Cu(II) and Pb(II) ions onto PS-EDTA surfaces (metal ions concentration, 50 mg/L; pH 6; $T = 293 \pm 1$ K).

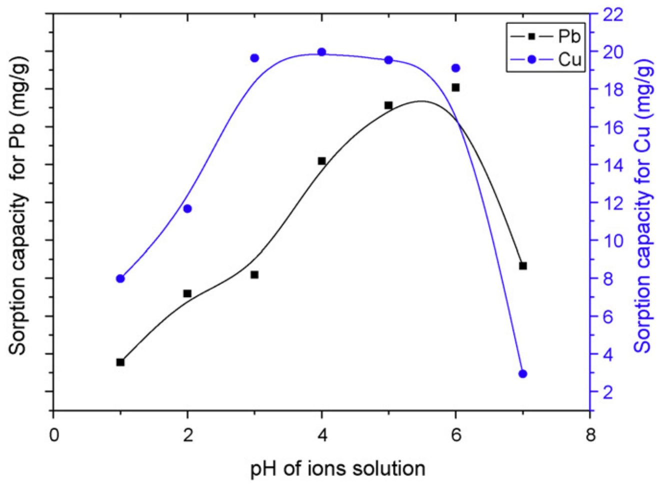

**Fig. 2.** Effect of pH solution on Cu(II) and Pb(II) ions adsorption onto PS-EDTA surfaces (metal ions concentration, 50 mg/L; $T = 293 \pm 1$ K and both Cu(II) and Pb(II) contact time = 120 min).

on Cu(II) and Pb(II) removal was investigated in the pH ranges of 1–7 for 2 h. The extractability of the cations from the solution phase is pH dependent because of its effect on the solubility of the metal ions, concentration of the counter ions on the functional groups of the adsorbent and the degree of ionization of the adsorbate during reaction [19]. At a low pH very low removal efficiencies of the adsorbents for all metal ions were found, similar to that of the other amino hybrid inorganic–organic materials [20,21].

Both the two heavy metals have the same tendency, but still exists some differentia. At the beginning, there was nearly no adsorption of both the two metals at pH 1.The Cu(II) ion arrive maximum amount earlier than Pb(II) at about pH 3.With increasing the pH, results in Pb(II) being better and more adsorbed, A considerable increase in the adsorption was occurred at pH 6–7 and the maximum amount of Pb(II) ion adsorption was observed at these pH values, And there nearly no change of Cu(II) adsorption which at its maximum amount. At higher pH values, metal precipitation took place and the adsorbent was deteriorated with the accumulation of metal ions in the solutions. Acidification was needed to prevent the formation of polynuclear hydroxo-bridged species and the precipitation of basic salts [22]. In general, adsorption of the two metal ions was affected significantly by pH values. The results indicated that the solution pH remarkably impacted on the adsorption of both Cu(II) and Pb(II) onto the chelating resin. It should be stressed that, the maximum metal uptake at pH 6 allows this low-cost chelating resin be used for the two metals removal from natural waters without requiring pH adjustments. From the corresponding data, an increase in pH corresponds to an increase in adsorption, reaching the maximum adsorption rate at pH 6. Therefore, pH 6 was selected as the optimum pH for further studies. Similar results were reported by several earlier workers for metal ions adsorption on different adsorbents [23,24].

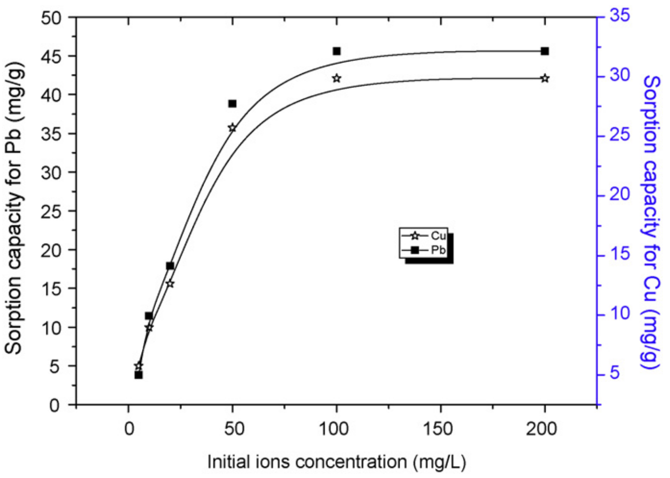

**Fig. 3.** Effect of initial Cu(II) and Pb(II) ions concentration on the sorption capacity onto PS-EDTA surfaces (pH 6; $T = 293 \pm 1$ K and contact time = 120 min).

### 3.1.3. Effect of initial Cu(II) and Pb(II) ions concentration on the adsorption

The adsorption of both Cu(II) and Pb(II) ions was carried out at the same initial concentration at pH values of 6, at 293 K with 120 min of contact time. As shown in Figs. 3 and 4, when the initial concentrations of ions Cu(II) and Pb(II) increased from 5 mg/L to 200 mg/L, respectively. The results may be explained by the fact that, at the defined pH, the surface of adsorbent would be also surrounded by hydronium ions which enhance ions interactions with binding sites of the adsorbent by greater attractive forces. At low concentration (5–100 mg/L), as the concentration increased, the adsorption capacity increased. But, there was no change of the adsorption of both the two ions when the concentrations continue to be increased (100–200 mg/L). As can be seen from Fig. 3, the adsorption capacity on the resin in 100 mg/L both the two heavy metals solution reached the maximum (42.1 mg/g for Cu(II) and 32.1 mg/g for Pb(II), respectively). Different to the tendency of the capacity, the percentages of the adsorption of both Cu(II) and Pb(II) were reduced as shown in Fig. 4. Note that, the maximum adsorption percentage for both the two ions onto PS-EDTA surface was achieved. The maximum adsorption efficiencies of Cu(II) and Pb(II) were 99.8% and 99.6% when the dose of each ion was 1 g/L and initial concentration 5 mg/L, respectively. This indicates that this chelating resin was fit for being used to treat micro-polluted water with Cu(II) and Pb(II) ions respectively of low concentrations (≤100 mg/L).

### 3.2. Equilibrium point adsorption

Equilibrium data can be analyzed using commonly known adsorption isotherms, which provide the basis for the design of adsorption systems. The most widely used isotherm equation for modeling of the adsorption data is the Langmuir equation, which is valid for monolayer adsorption onto a surface with a finite number

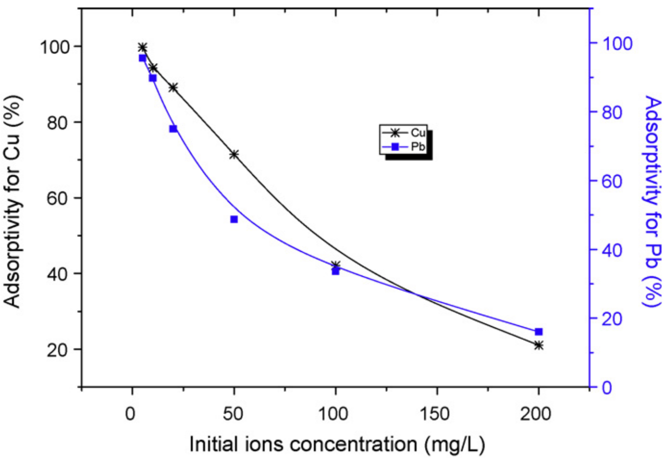

**Fig. 4.** Effect of initial Cu(II) and Pb(II) ions concentration on the adsorption efficiency onto PS-EDTA surfaces (pH 6; $T = 293 \pm 1$ K and contact time = 120 min).

of identical sites and is given by Eq. (3)

$$q_e = \frac{K_L q_m C_e}{1 + K_L C_e} \tag{3}$$

where $K_L$ is the adsorption equilibrium constant including the affinity of binding sites (L mg$^{-1}$), $q_m$ is the maximum adsorption capacity (mg g$^{-1}$), $C_e$ is the equilibrium metal ion concentration in the solution (mg L$^{-1}$), and $q_e$ is the amount of adsorbed ion at equilibrium point (mg g$^{-1}$). It represents a practical limiting adsorption capacity when the surface is fully covered with ions. The $q_m$ and $K_L$ can be determined from the linear plot of Eq. (4). This equation can be written as follows [25,26]:

$$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{q_m K_L}\frac{1}{C_e} \tag{4}$$

Tempkin isotherm equation assumes that the heat of adsorption of all the molecules in the layer decreases linearly with the coverage of molecules due to the adsorbate–adsorbate repulsions and the adsorption of adsorbate is uniformly distributed [31] and that the fall in the heat of adsorption is linear rather than logarithmic. The Tempkin equation is given by Eq. (5) [27]:

$$Q_e = B_T \ \ln A_T + B_T \ln C_e \tag{5}$$

where $B_T = (RT)/b_T$, $T$ is the absolute temperature in K and $R$ is the universal gas constant (8.314 J mol$^{-1}$ K$^{-1}$). The constant $b_T$ is related to the heat of adsorption, $A_T$ is the equilibrium binding constant (L min$^{-1}$) corresponding to the maximum binding energy. The slope and the intercept from a plot of $Q_e$ versus $\ln C_e$ determine the isotherm constants $A_T$ and $b_T$.

The Freundlich model is an empirical equation based on adsorption onto a heterogeneous surface. The Freundlich model in linear form is [28]:

$$\ln \ q_e = \ln K_f + \frac{1}{n} \ln C_e \tag{6}$$

where $K_f$ and $n$ are the Freundlich constants, related with adsorption capacity and intensity, respectively. Linear plots of $1/q_e$ versus $1/C_e$ and $\ln q_e$ versus $\ln C_e$ were drawn and summarized. Eqs. (4)–(6) are plotted by the fitting equations of Langmuir, Freundlich and Tempkin isotherms are depicted in Fig. 5. In this section, adsorption of Cu(II) and Pb(II) onto PS-EDTA surface at 293 ± 1 K was used.

The sorption of Cu(II) and Pb(II) was also investigated as a function of concentration at the same temperature in the range of 5–200 mg/L using 0.1 g of adsorbent, 100 mL of adsorbate solution, and 120 min shaking time at a shaking speed of 100 rpm. The results indicate that the uptake of metal ions is above 95% at low adsorbate concentrations (5–20 mg/L) and 38–54% at high concentrations (80–100 mg/L). The equilibrium data for the adsorption of Cu(II) and Pb(II) on PS-EDTA resin was tested with various adsorption isotherm models (Langmuir, Freundlich and Tempkin isotherm) all of the three models were found to be suitable for both Cu(II) and Pb(II) adsorptions.

Electrostatic forces and exchange of ions also cause sorption of adsorbate onto the adsorbent. If it is assumed that the uptake of the two ions by the adsorbent (here PS-EDTA) is the result of physical attraction or chemical co-ordination between the two ions and chemical moiety on the adsorbent, then the maximum number of such sites must be finite. When the adsorbent and adsorbate come in contact with each other, a dynamic equilibrium is established between the adsorbate concentrations in both the phases. This state is dynamic in nature, as the amount of adsorbate migrating onto the adsorbent would be counterbalanced by the amount of adsorbate migrating back into solution. The relation between the amount adsorbed by an adsorbent and the equilibrium concentration of the adsorbate at a constant temperature can be expressed by the three isotherms.

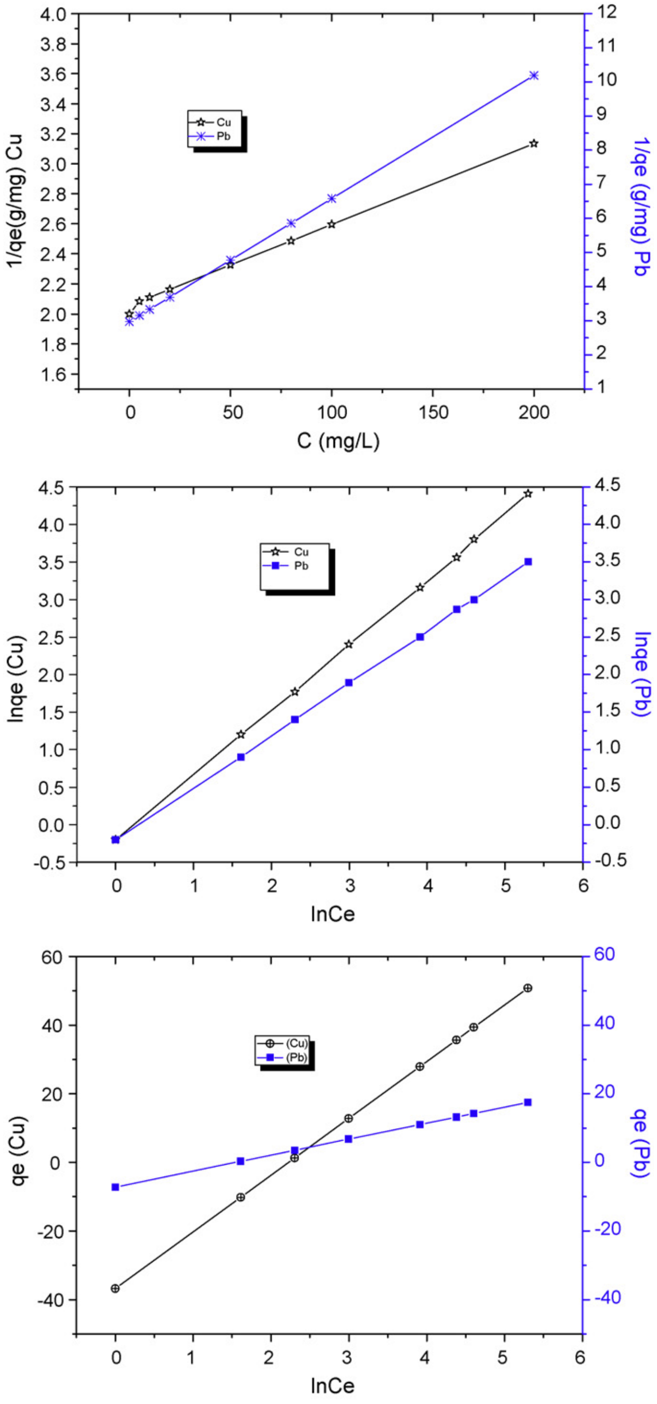

**Fig. 5.** Comparison among the Langmuir, Freundlich and Tempkin isotherms.

The Langmuir isotherm model applied to the estimation of maximum adsorption capacity corresponding to complete monolayer coverage on the resin surface. The correlation coefficient was found to be 0.986 and 0.985 for Cu(II) and Pb(II) ions onto PS-EDTA surface, respectively. The main reason for this trend is the electrostatic interaction between adsorbent molecules (polymeric surfaces) and adsorbate (heavy metal ions). When electrostatic interaction between PS-EDTA with negative surface charge and ions with positive charge exists, the Langmuir isotherms do not result as well as when other interactions exist between adsorbent and adsorbate [29]. Also the hydrophobic interaction exists between PS-EDTA surface and heavy metal ions [30]. According to the aver-

**Table 1**
Parameters of the three adsorption isotherm for Cu(II) and Pb(II) ions onto surfaces.

| Ion | Langmuir | | | | Freundlich | | | Temkin | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | $Q_m$ (mg/g) | $b$ (L/mg) | $R_L$ | $R^2$ | $K_f$ (mg/g) | $n$ | $R^2$ | RT/$b_T$ | $A_T$ | $R^2$ |
| Cu(II) | 42.1 | 0.012 | 0.32–0.99 | 0.986 | 0.263 | 1.130 | 0.978 | 8.157 | 1.117 | 0.970 |
| Pb(II) | 32.1 | 0.017 | 0.34–0.99 | 0.985 | 0.083 | 1.094 | 0.980 | 9.314 | 1.304 | 0.969 |

age percentage deviations given in Table 1, the Freundlich equation gives a good fit, too. This fact can be justified both physical and chemical adsorption of the resin were exist at the same time, since the resin used in this study contains many amino and carboxyl functional groups, which are responsible for their effective adsorption capacity. And at high concentrations, multilayer adsorption was existing. The major contributing factors for adsorption capacity are 42.1 mg/g and 32.1 mg/g for Cu(II) and Pb(II) ions onto PS-EDTA, respectively, and the $Q_m$ was higher than some $Q_m$ values of other sorbents reported by literatures [16,31–33]. The Temkin adsorption isotherm model was to evaluate the adsorption potentials of the adsorbent for adsorbates. Temkin constants $b_T$ and $A_T$ were calculated at 293 K. These isotherm parameters are given in Table 1. The obtained $A_T$ values indicated a good potential for Cu(II) and Pb(II). The regression coefficients of determining $R^2$ from the linearization of the three two-parameter isotherm models are listed in Table 1. The $R^2$ values suggest that all three of the isotherm models provide good correlations for the sorption of the two ions [34]. The good correlation confirms the formation of a monolayer of Pb(II) and Cu(II) on the surface of the resin. The main reason for this trend is the electrostatic interaction between adsorbent molecules (polymeric surfaces) and adsorbate (heavy metal ions).

### 3.3. Kinetics of Pb(II) and Cu(II) adsorption

#### 3.3.1. Adsorption kinetics

*3.3.1.1. Pseudo-first-order kinetic.* Lagergren showed that the rate of adsorption of solute on the adsorbent is based on the adsorption capacity and followed a pseudo-first-order equation [35,36] which is often used for estimating $k_{\mathrm{ad}}$ considered as mass transfer coefficient in the design calculations. The linear form of the pseudo-first-order equation is described by Eq. (7):

$$\frac{dQ_t}{d_t} = k_{ad}(Q_e - Q_t) \tag{7}$$

where $Q_e$ and $Q_t$ are the amounts of Cu(II) and Pb(II) adsorbed (mg g$^{-1}$) at equilibrium time and at any instant of time, $t$, respectively, and $k_{ad}$ (L min$^{-1}$) is the rate constant of the pseudo-first-order sorption.

*3.3.1.2. Pseudo-second-order kinetic.* Ho developed a pseudo-second-order kinetic expression for the sorption system of divalent metal ions using sphagnum moss peat [37]. This model has since been widely applied to a number of metal/sorbent sorption systems. The adsorption of Cu(II) and Pb(II) onto the chelating resin at a short time scale may involve a chemical sorption which implies the strong electrostatic interaction between the negatively charged surface and Cu(II) and Pb(II). The linear form of the diffusion equation is described in the following form:

$$\frac{t}{Q_t} = \frac{1}{K_2 Q_e^2} \tag{8}$$

where $Q_e$ is the amount of Cu(II) and Pb(II) adsorbed at equilibrium (mg g$^{-1}$), $Q_t$ is the amount of Cu(II) and Pb(II) adsorbed at time $t$ (mg g$^{-1}$) and $k$ is the rate constant of the pseudo-second-order sorption (g mg$^{-1}$ min$^{-1}$). The initial sorption rate $h$ (g mg$^{-1}$ min$^{-1}$) was obtained according to Eq. (9), as $t/Q_t$ approaches zero.

$$h = kQ_e^2 \tag{9}$$

*3.3.1.3. Elovich kinetic.* Elovich equation is a rate equation based on the adsorption capacity commonly expressed as Eq. (10) [38]:

$$\frac{dQ_t}{dt} = \alpha \ \exp(-\beta Q_t) \tag{10}$$

where $\alpha$ (mg g$^{-1}$ min$^{-1}$) is the initial adsorption rate and $\beta$ (g mg$^{-1}$) is the desorption constant related to the extent of the surface coverage and activation energy for chemisorptions. Eq. (8) is simplified by assuming $\alpha\beta \gg t$ and by applying the boundary conditions $Q_t = 0$ at $t = 0$ and $Q_t = Q_t$ at $t = t$, as given by Eq. (11):

$$Q_t = \frac{1}{\beta} \ \ln(\alpha\beta) + \frac{1}{\beta} \ \ln t \tag{11}$$

The slope and intercept of the plot of $Q_t$ versus $\ln t$ result in the estimation of the kinetic constants, $\alpha$ and $\beta$. Elovich equation described adsorption on highly heterogeneous adsorbents and confirms the chemisorptions even though do not predict any definite mechanism [39].

#### 3.3.2. Kinetics of Cu(II) and Pb(II) adsorption

The rate of metal sorption is an important factor and prerequisite for determining the reactor design and process optimization for a successful practical application. The rate kinetics of Cu(II) and Pb(II) adsorption on PS-EDTA resin at initial metal ion concentration 10 mg/L, 50 mg/L and 100 mg/L, respectively. Both of them were analyzed using pseudo-first-order, pseudo-second-order and Elovich kinetic models (Fig. 6). Degrees of error between experimental and model predicted values were analyzed by employing chi-square test [40] (Eq. (12))

$$\chi^2 = \sum \frac{(Q_t - Q_m)^2}{Q_m} \tag{12}$$

where $Q_t$ and $Q_m$ (mg g$^{-1}$) are total Pb(II) and Cu(II) adsorption capacity at time $t$ using experimental data and predicted model data respectively. Pseudo-first-order model showed correlation coefficient ($R^2$) of 0.90–0.99 (Table 2) where as that of second order kinetic order is 0.99. It can be seen (Table 2) that $\chi^2$ value for second order is much lesser than pseudo-first-order kinetic model suggesting Cu(II) and Pb(II) adsorptions on PS-EDTA resin followed pseudo-second-order kinetic model. The insufficiency of the pseudo-first-order model to fit the kinetics data could possibly be due to the limitations of boundary layer controlling the sorption process. Moreover, functional groups existing on the surface of PS-EDTA resins such as hydroxyl, carboxyl and amine groups also contributed to the chemisorptions of Cu(II) and Pb(II) on PS-EDTA resin in solutions. The experimental data was observed to fit well to the pseudo-second-order equation [41–43]. The correlation coefficient ($R^2$) for the liner plots of $t/Q_t$ against $t$ for the pseudo-second-order equation was observed to be close to 1 for Cu(II) and Pb(II). These observations suggest that metal sorption by PS-EDTA resin followed the pseudo-second-order reaction, which suggests that the process controlling the

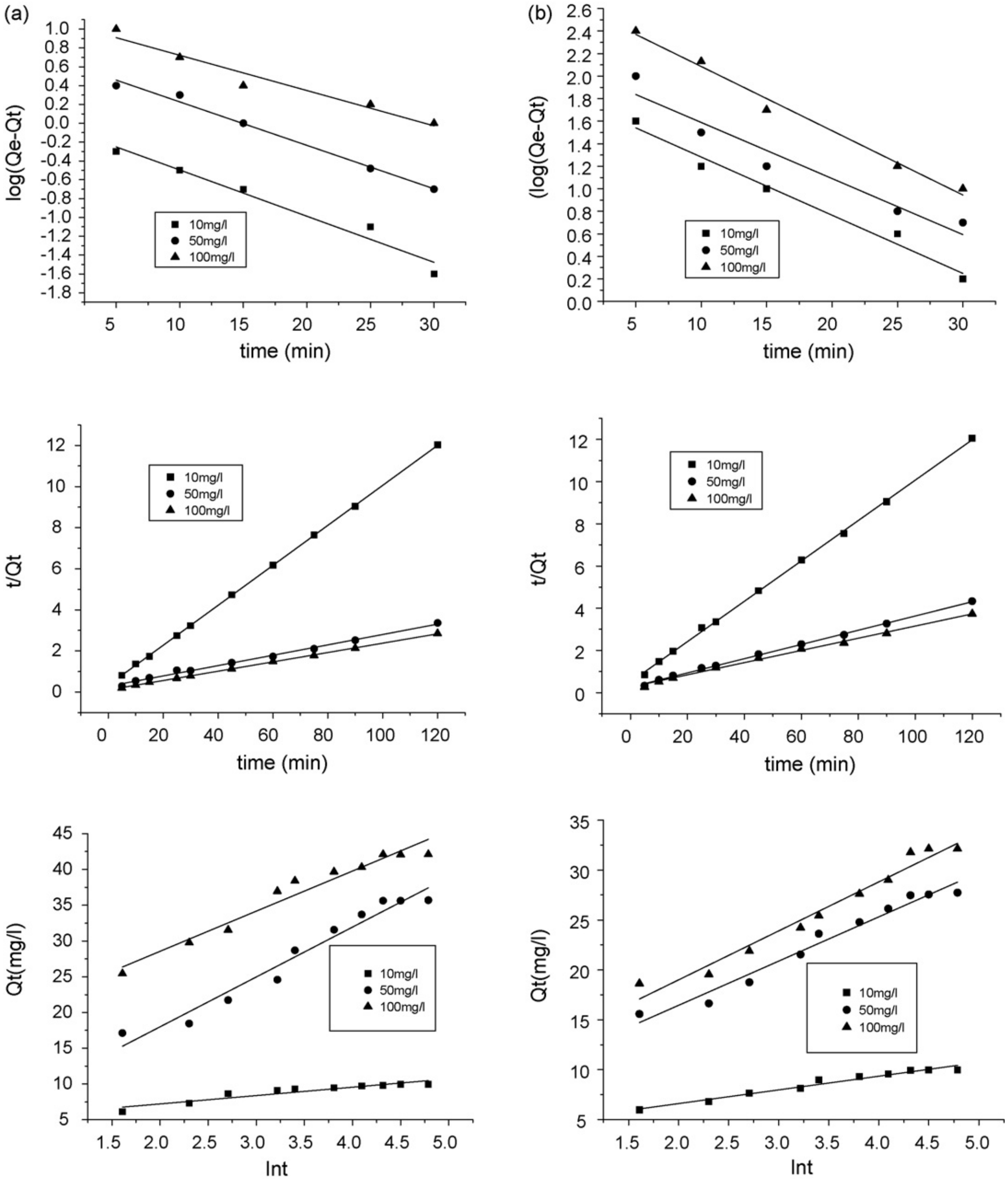

**Fig. 6.** (a) Sorption kinetics (pseudo-first order, pseudo-second order and Elovich models) of Cu(II) onto PS-EDTA resin under pH 6.0 at 293 K. (b) Sorption kinetics (pseudo-first order, pseudo-second order and Elovich models) of Pb(II) onto PS-EDTA resin under pH 6.0 at 293 K.

rate may be a chemical sorption. The correlation coefficients of above 0.97 at pH values of 6 for all different initial Cu(II) and Pb(II) also confirm the applicability of Elovich equation suggesting the predominant chemical nature of Cu(II) and Pb(II) adsorption on PS-EDTA resin which was also deduced from adsorption isotherm as above.

### 3.3.3. *Desorption experiments*

To make the adsorption process more economical and to obtain practical information about the recovery of heavy metal ions using PS-EDTA, desorption from spent adsorbent material was studied. Desorption experiments were performed maintaining the process condition similar to the batch experiments. The various desorbing

**Table 2**
Comparison of first and second order kinetic model and for Cu(II) and Pb(II) ions adsorption.

| Initial ions (mg/L) | | First order kinetic model | | | Second order kinetic model | | | Elovich model | | | $h$ (mg/g min$^{-1}$) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | $k_1$ (min$^{-1}$) | $R^2$ | $\chi^2$ | $k_2$ (g/mg min) | $R^2$ | $\chi^2$ | $R^2$ | $\alpha$ | $\beta$ | |
| Cu | 10 | 0.04188 | 0.9653 | 0.2819 | 0.3152 | 0.9972 | 0.1110 | 0.9913 | 9.2216 | 0.5721 | 31.33116 |
| | 50 | 0.01363 | 0.9927 | 0.3825 | 0.1596 | 0.9988 | 0.0303 | 0.9753 | 2.9564 | 1.0079 | 203.5226 |
| | 100 | 0.03584 | 0.9067 | 1.0396 | 0.02131 | 0.9993 | 0.0254 | 0.9868 | 1.2568 | 1.3742 | 37.77006 |
| Pb | 10 | 21.2174 | 0.9594 | −0.6755 | 0.6845 | 0.9961 | 0.1125 | 0.9935 | 8.3721 | 0.6435 | 67.76721 |
| | 50 | 0.9865 | 0.9437 | 0.8546 | 0.3786 | 0.9943 | 0.0542 | 0.9826 | 3.1764 | 1.1378 | 291.3356 |
| | 100 | 0.7089 | 0.9338 | 0.1675 | 0.1499 | 0.9903 | 0.0229 | 0.9762 | 1.1129 | 1.4056 | 154.7473 |

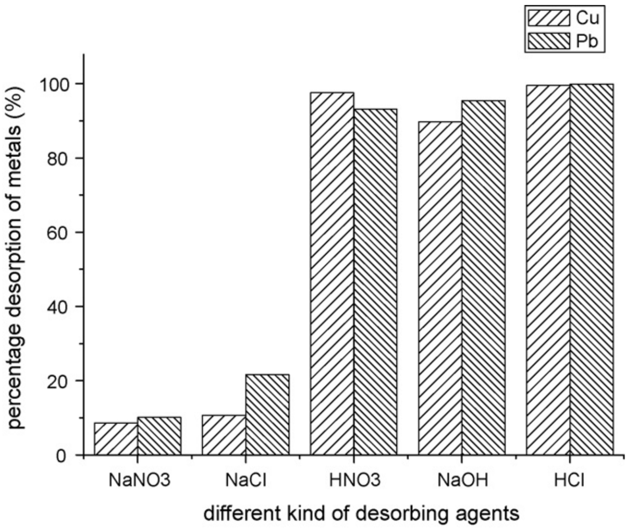

**Fig. 7.** Desorption of Zn(II) from metal-loaded PS-EDTA resin by different kind of desorbing agents (10 mL).

**Table 3**
Performance of fresh and recycled PS-EDTA resin.

| Absorbent | Conc. of metal solution (mg/L) | | | | Removal percent (%) | |
|---|---|---|---|---|---|---|
| | Cu | | Pb | | Cu | Pb |
| | Initial | Final | Initial | Final | | |
| Fresh | 10 | 0.078 | 10 | 0.083 | 99.22 | 99.17 |
| First recycle | 10 | 0.089 | 10 | 0.094 | 99.11 | 99.06 |
| Second recycle | 10 | 0.097 | 10 | 0.099 | 99.03 | 99.01 |
| Third recycle | 10 | 0.101 | 10 | 0.113 | 98.64 | 98.77 |
| Fourth recycle | 10 | 0.114 | 10 | 0.121 | 98.47 | 98.53 |
| Fifth recycle | 10 | 0.135 | 10 | 0.130 | 98.03 | 97.99 |

agents, 0.1 M NaOH, HCl, $HNO_3$, NaCl, $NaNO_3$ were used. Desorption of heavy metal ions in 2 h was observed. The optimum desorption was happened in 0.1 M HCl [44,45]. Results of batch desorption experiment studies are depicted in Fig. 7. The metal ions loaded on the adsorbent creates disposal problem as it is hazardous in nature. This problem may be overcome to some extent by using elution methods. The elution of the heavy metals allows recovery of the metal ions in the concentrated solution and the regenerated adsorbents. The concentrated metal solution may be suitable for recovery of the metal. The regenerated adsorbent may be recycled for reuse and ultimately the adsorbents must be incinerated. Table 3 shows the performance of the regenerated adsorbent. Adsorption/desorption cycle of PS-EDTA resin decreased slightly as the number of cycle increases. More than 90% of both the two metal ions removal was possible using five cycles.

### 3.4. Column adsorptions of Cu(II) and Pb(II) on PS-EDTA resin

### 3.4.1. Column adsorption capacity

To evaluate the practical application of PS-EDTA to the continuous removal the two metallic ions from solution, we conducted a column adsorption test. Table 4 presents the column adsorption capacity for both the two metals onto the adsorbent for varying operating variables that is feed concentration at the bed height 15 cm. The column capacity for Cu(II) and Pb(II) adsorption for the bed height of 0.15 m, hydraulic loading rate of 2.5 $m^3/(hm^2)$ and the feed concentration of 50 mg/L and 100 mg/L for 50% breakthrough concentration were found to be 49.8 mg/g, 87.4 mg/g and 48.7 mg/g, 91.2 mg/g, respectively. From comparison of adsorption capacity from Langmuir isotherm and column experiments, We can see that the Cu(II) and Pb(II) adsorption capacity on PS-EDTA in column mode are higher than stir adsorption respectively.

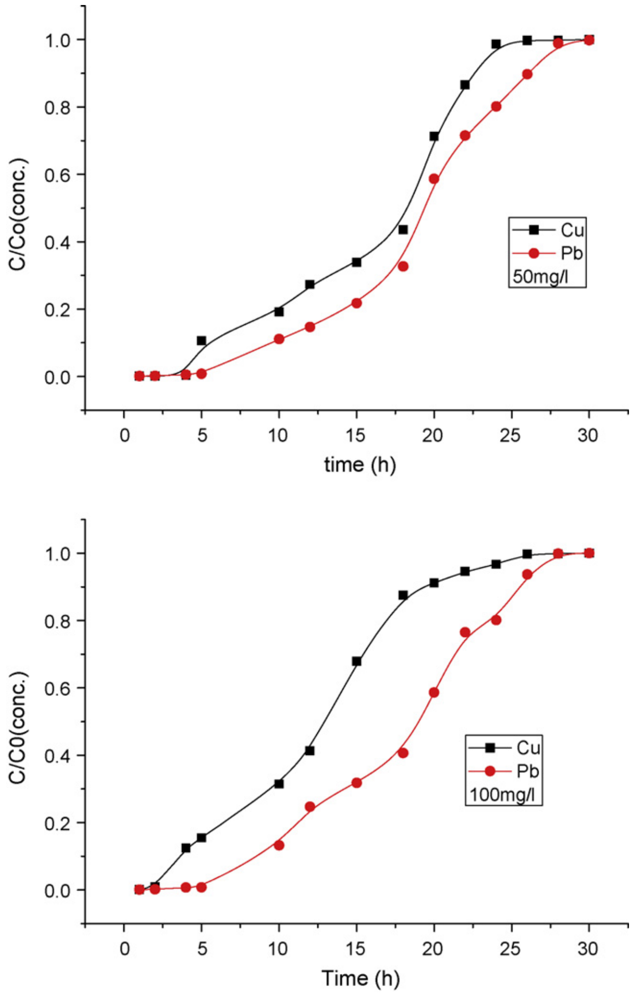

**Fig. 8.** The breakthrough curves of Cu(II) and Pb(II) onto PS-EDTA resin s of different concentrations (initial Cu(II) and Pb(II) conc. = 50 mg/L and 100 mg/L, h = 0.15 m, flow rate = 2.5 $m^3/hm^2$).

### 3.4.2. Effect of the influent concentrations on the breakthrough curves

To evaluate the practical application of PS-EDTA to the continuous removal Pb(II) and Cu(II) from solution, we conducted a column adsorption test. In this work, two initial concentrations were respectively used to evaluate the performance in the contin-

**Table 4**
Column adsorption capacity, $Q_{0.5}$ at different concentrations at 50% breakthrough concentrations.

| Initial ions (mg/L) | | Breakthrough time 50% (h) | Hydraulic loading rate ($m^3/hm^2$) | Bed height (m) | Adsorption column capacity (mg/g) |
|---|---|---|---|---|---|
| Cu | 50 | 24 | 2.5 | 0.15 | 49.8 |
| | 100 | 20 | 2.5 | 0.15 | 87.4 |
| Pb | 50 | 28 | 2.5 | 0.15 | 48.7 |
| | 100 | 26 | 2.5 | 0.15 | 91.2 |

uous system (50 and 100 mg/L) at the same flow rate 0.5 mL $\text{min}^{-1}$. Fig. 8 shows the effect of the influent concentrations of Pb(II) and Cu(II) on the shape of breakthrough curves at the same flow rate (0.5 mL $\text{min}^{-1}$). Results shown in Fig. 8 indicate that breakthrough time decreases as metal concentration increases, with the curve showing an S-type mode. The column adsorption capacity of Pb(II) and Cu(II) by PS-EDTA resin is 87.4 and 91.2 mg/g when influent concentrations are 100 mg $\text{L}^{-1}$, respectively. The $q_{ed}$ at 100 mg $\text{L}^{-1}$ is higher than that at 50 mg $\text{L}^{-1}$; this can be attributed to the concentration gradient which will enhance the adsorption process [46–48].

## 4. Conclusions

Adsorption of Cu(II) and Pb(II) ions from aqueous solutions onto PS-EDTA at different conditions such as contact time, pH and metal ions concentration, were studied to investigate optimum values of the mentioned parameters for removal of the metal ions. It is shown that the changes in the variables affect the adsorption process and changes the obtained values of the amounts of ions adsorbed. It was found that pH 6, contact time 120 min and the concentration 100 mg/L was the optimum conditions to have the maximum adsorption amount, it is illustrated that PS-EDTA surface adsorbs copper much better than Lead (42.1 mg/g for Cu(II) and 32.1 mg/g for Pb(II), respectively) and seems to be a better adsorbent for removal of both ions off the aqueous single solutions. The adsorption percentage has its maximum value when 0.2 g PS-EDTA was used as copolymer (99.8% for Cu(II) and 99.6% for Pb(II), initial concentration each of ions is 5 mg/L). The Langmuir, Freundlich and Tempkin isotherms for Cu(II) and Pb(II) ions onto the polymeric surfaces were studied. It is illustrated that all of the three isotherms fit the experimental data well. Moreover, the PS-EDTA resin can be fully regenerated using brine solution and subsequent use of the regenerated resin end up in practically no change in sorption effectiveness. The high recovery of the prepared sorbent material from the regeneration process makes this comparatively low-cost resin excellent effective for Pb(II) and Cu(II) removal from solutions of concentration lower than 100 mg/L with a possibility of repeated use. On the basis of the experimental results of column adsorption, the increase of influent concentration decreased the breakthrough time, and an acceptable level of both the two metal removals were achieved using the PS-EDTA column. Having a powerful adsorb ability of the two heavy metal ions, high regeneration rate and several advantages in synthesis, good cost effectiveness, synthesis all in aqueous and moderate reaction conditions, the PS-EDTA perform a wide application prospect in the removal and even recovery of heavy-metal ions from their aqueous solutions or wastewater.

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