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Removal of Pb^{2+} and Cu^{2+} from their aqueous solutions by functionalized polyamide 6.6 yarns with N-allyliminodiacetic acid

M. El Bouchti[1,3], A.M. Grancaric[2], L. Botteri[2], H. Hannache[3], O. Cherkaoui[1,]*

[1]Higher School of Textile and Clothing Industries, Laboratory REMTEX, Km 8, Route d'El Jadida;BP 7731, Oulfa, Casablanca, Morocco.
[2]University of Zagreb, Faculty of Textile Technology, Prilaz baruna Filipovića 28a, HR-10 000 Zagreb, Croatia.
[3]University Hassan II, F. S. Ben M'Sik, Laboratory LIMAT, Boulevard Cdt Driss Harti, BP 7955, Ben M'Sik, Casablanca, Morocco.

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** Corresponding author. E-mail: cherkaoui@esith.ac.ma*

Abstract

The removal of copper (Cu^{2+}), and lead (Pb^{2+}) ions from aqueous solutions with the functionalized Polyamide 6.6 Yarns with N-Allyliminodiacetic Acid to 20% (PA6.6-ALD-20%) chelating ion exchange fiber is described at different conditions. The removal of the above mentioned heavy metal ions from aqueous solutions was studied by batch method. The effects of initial metal concentration, contact time and pH on the removal of Cu^{2+} and Pb^{2+} ions were investigated. The percentage adsorption of Cu^{2+} and Pb^{2+} ions increased with an increase in contact time. The binding process was strongly affected by pH and the optimum pH for Cu^{2+} and Pb^{2+} ions were 5.0 and 6.0, respectively. The kinetic data was evaluated with the pseudo-first order and pseudo-second order models. Kinetic data correlated well with the pseudo-second-order kinetic model, indicating that the chemical adsorption was the rate-limiting step. The adsorption parameters were determined based on Langmuir and Freundlich isotherm models. The maximum adsorption capacity of the adsorbent for Cu^{2+} and Pb^{2+} ions was calculated from the Langmuir isotherm and found to be 6.17 and 8.06 mg/g, respectively. Actually the percentage of removing Cu^{2+} and Pb^{2+} ions reached maximum to 55% and 78%, respectively.

Keywords: Adsorption, Chelating ion exchange fiber, N-allyliminodiacetic acid, Isotherms, Kinetics

1. Introduction

Industrial wastewaters contain harmful heavy metal ions that should be removed by wastewater treatment in view of the prevention of environmental pollution [1,2]. There are various methods for the removal of heavy metals in the literature. Some of them are chemical precipitation, ion exchange, adsorption, biosorption and electrocoagulation [3]. Nevertheless many of these approaches are marginally cost effective or difficult to implement in developing countries [4,5]. Ion exchange is a well-established technique, particularly in water purification, the concentration and removal of metal ions at very low concentrations in chemical process industries [6]. The main advantages of ion exchange over other techniques are the recovery of the metals value, high selectivity, less sludge volume produced and the ability to meet strict discharge specifications. In addition, the simplicity of ion exchange operation makes it attractive to the chemical purification field. In this regard, ion-exchange resins hold great potential for the removal of metals from water and industrial wastewater [7-8].

The application of ion exchangers with iminodiacetic acid groups (IDA) in water purification from the heavy metal ions have been also described in numerous publications [9-11]. The main problem in applications of granular chelate sorbents is poor kinetics of sorption processes. It has been shown in a number of publications that filtering layers of fibrous ion exchangers with the same or similar functional groups have significantly higher sorption rate and a better performance in dynamic processes [12,13]. Applications of chelating fiber containing IDA has more success to its large specific surface area [14], containing an important amount of metal chelate-forming functional group, where metal ions are adsorbed or desorbed on its surface, and therefore has an improved adsorption and desorption capability. This is because IDA group have three binding points per anchor group via three interlinked ligands - the two acid groups and the free electron pair of the imino nitrogen, which react with the divalent metals to form stable covalent bonds coordination [15-17].

In the present work, we have employed the batch equilibration technique and inductively coupled plasma (ICP-AES) to evaluate the sorption properties of the chelating ion exchange fiber (PA6.6-ALD-20%) toward the divalent metal ions Pb^{2+} and Cu^{2+} in aqueous solutions by a batch. The effect of the different experimental factors such as pH, contact time and metal ion amount on the sorption capacity of the PA6.6-ALD-20% will be discussed. Langmuir and Freundlich isotherm models were used for describing the relationship between the amount of metal ions and PA6.6-ALD-20% and the equilibrium kinetic was also evaluated. Finally desorption studies have been also carried out in different solutions to test the reusability of chelating ion exchange fiber.

2. Materials and Methods

2.1. Adsorbent

PA6.6-ALD-20% was synthesized by grafting the allyliminodiacetic acid, on the polyamide 6.6 yarns to 20% by radical polymerization with presence of benzoyl peroxide (Aldrich) as initiator [18]. The grafted PA6.6 fiber was washed with a 0.1 M HCl solution to remove impurities, subsequently rinsed with distilled water and dried at 60°C for 12 hours. The pH measurements were performed with a pH meter (model Orion4). An inductively coupled plasma (ICP-AES) was used to analyze the ion concentration in the solution. All the chemicals used were of ACS grade and obtained from Sigma-Aldrich, France. Stock solutions of Pb^{2+} and Cu^{2+} of 1000 mg/l concentration were prepared by dissolving, 1.598 g of $Pb(NO_3)_2$, 3.931g of $CuSO_4.5H_2O$, respectively in 1000 ml of bi distilled water.

2.2. Equilibrium studies

The batch experiments were carried out in glass bottle at room temperature (20±2 °C) using a fixed mass 0.2g of dry of PA6.6-ALD-20% in 50 ml standard solution of 20 mg/l concentration of metal ion in ordinary mixing conditions using a magnetic stirrer (398 rpm). pH adjustments were carried out by using 0.1N HCl and 0.1N NaOH.

The samples were taken after regular time interval and filtered through whatman's filter paper. The filtrate was then eluted with hydrochloride acid at optimum concentration and volume. The concentrations of metal ions were determined using ICP-AES. These data were used for comparative removal studies and kinetic establishment. Control experiments in absence of PA6.6-ALD-20% have been carried out in order to correct any adsorption of metal on container surface. These experiments indicated that no adsorption by the container walls was detectable. The concentration of metal on the PA6.6-ALD-20% was calculated as the difference between the original concentration in the solution without PA6.6-ALD-20% and the concentration in solution after contact.

Desorption studies of metal containing PA6.6-ALD-20% have also been carried out to test the reusability of PA6.6-ALD-20% in 0.1N HCl, 0.1N NaOH and distilled water.

3. Results and discussion

Chelating ion exchange fiber (PA6.6-ALD-20%) was studied in removal of Pb^{2+} and Cu^{2+} from aqueous solutions under different experiment conditions such as contact time, pH, metal ion dosage. The experimental results and the relevant observations are discussed in the following sections.

3.1. Effect of pH

Hydrogen ion concentration is an important parameter affecting the ion exchange process. Experiments were performed in the pH range 2-7.0 to prevent hydrolysis of metal ions at higher pH. Effect of pH on removal efficiency is shown in Figure 1.

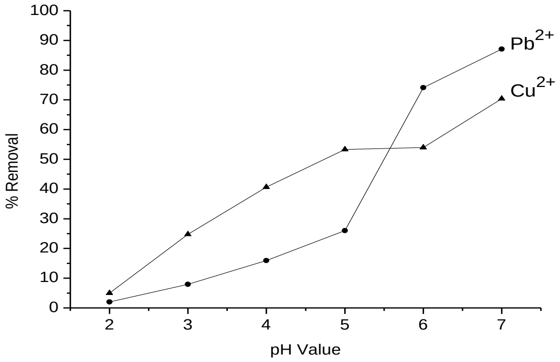


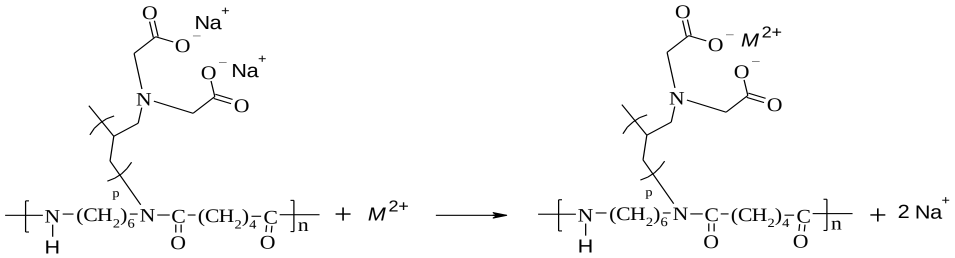
Figure 1: Effect of pH on removal of lead, and copper by PA6.6-ALD-20% (initial metal conc. 20 mg/l, PA6.6-ALD-20% amount 0.2 g/50 ml and stirring time 2 h).

The removal of metals was increased with increasing pH values. When pH was below 3-4, the strong electrical repulsion prevented the metal ions from contacting the surfaces of the fibers, resulting in little adsorption of metal ions to the fibers. With the increase of solution pH values, the electrical repulsion force became weaker

and the metal ions may be transported to the surface of the fibers and become attached on the surface due to the action of other factors such as the van der Waals force, the formation of chemical or non-chemical bonds, and particularly the formation of metal complexes through chelating or ion exchanges [15,16].
The highest uptake was observed at pH equal to 5 for Cu^{2+} and pH equal to 6 for Pb^{2+}. The removal of lead is greater than copper at pH 6 (removal efficiency of lead is 74.08%, and copper is 53.96%). In order to avoid the removal of lead and cooper by precipitation and keep the adsobante property of chelating fiber, we have chosen to work at pH 6.0 for lead and pH 5.0 for cooper. The similar result has been noted by Liu et al. using synthesized IDA (iminodiacetic acid)-chelating resin (NJC-702) to uptake of Cu^{2+} and Pb^{2+} [19].

3.2. Effect of contact time on removal of Pb^{2+}, Cu^{2+}

Figure 2 shows the effect of contact time on the removal efficiency. The metal ions displace the sodium ions inside the chelating exchange ions fiber (PA6.6-ALD-20%) when it was equilibrated with the metal-ion solution as shown in the Scheme 1.The results show that the percentage of metal ion adsorbed increased with increasing time till reaching the equilibrium and it reached the plateau value at 60 minutes.



Scheme 1: Ion exchange between metal ions and sodium ions.

The curves of metal uptake versus time are single, smooth and continuously leading to saturation, suggesting the possible monolayer coverage of metal ions on the surface of the chelating fiber. The adsorption rate of Pb^{2+} was faster than that of Cu^{2+} and the equilibrium adsorption capacity of Pb^{2+} was higher than that of Cu^{2+} in this study. The maximum removal was 78% and 55% for Pb^{2+} and Cu^{2+}, respectively. Similar results reported by Misra et al. using iminodiacetic acid functionalized cation exchange resin for adsorptive removal of Pb^{2+} from its aqueous solution [20].

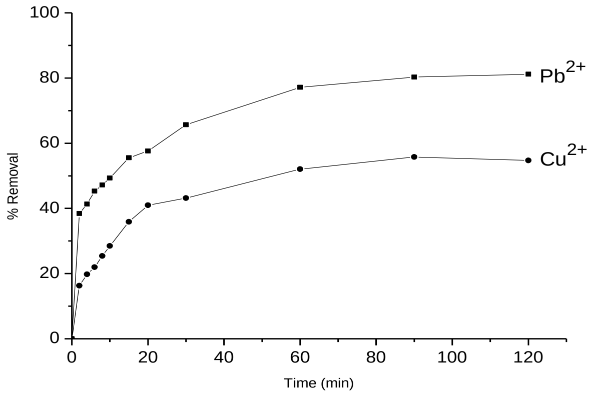


Figure 2: Effect of contact time on removal of lead, and copper by PA6.6-ALD-20% (initial metal conc. 20 mg/l, pH 6, PA6.6-ALD-20% amount 0.2 g/50 ml).

3.3. Effect of Initial Metal Concentrations

Figure 3 shows the effect of varying metal concentrations 20-150 mg/l on the adsorption under the optimized conditions. It was found that the metal amounts retained were almost stable in the concentration ranges of copper and lead. At high concentrations the removal efficiency decreased because of the slow motion of metal ions. The maximum removal efficiency on PA6.6-ALD-20% was obtained as 57.18 % and 73.8% for lead and copper respectively for 20 mg/l initial metals concentration.

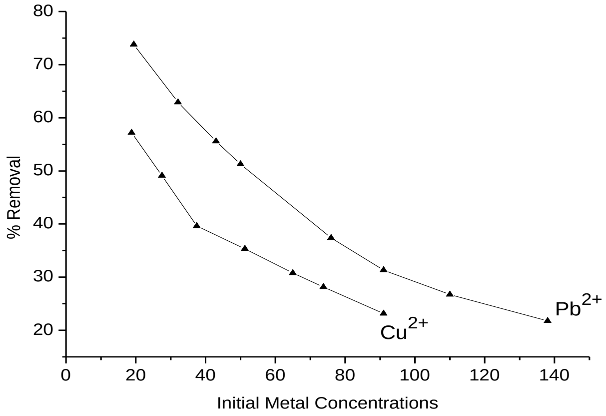


Figure 3: Effect of Initial Metal Concentrations on removal of lead, and copper by PA6.6-ALD -20% (pH 6 for lead and pH 5 for copper, PA6.6-ALD-20% amount 0.2 g/50 ml).

3.4. Adsorption isotherms

Adsorption isotherms are very powerful tools for the analysis of adsorption process. Adsorption isotherms establish the relationship between the equilibrium pressure or concentration and the amount of adsorbate adsorbed by the unit mass of adsorbent at a constant temperature. The Langmuir and Freundlich isotherm models are widely used to investigate the adsorption process.

3.4.1. Langmuir Isotherm Model

Langmuir sorption isotherm models the monolayer coverage of sorption surfaces and assumes that sorption occurs on a structurally homogenous adsorbent and all the sorption sites are energetically identical. The saturated monolayer curve can be represented by the expression [21]:

$$Q_e = \frac{X}{m} = \frac{Q_0 K_L C_e}{1+K_L C_e} \qquad \text{(non-linear)} \qquad (1)$$

Alinear form of this aquation is :

$$\frac{C_e}{Q_e} = \frac{1}{bQ_0} + \frac{C_e}{Q_0} \qquad \text{(linear)} \qquad (2)$$

where X is the initial concentration of solute minus the final concentration of solute in solution at equilibrium (mg/l), m is the concentration of adsorbent (mg/l), C_e is the equilibrium concentration of metal in solution (mg/l), Q_e is the amount of metal ion (Pb^{2+} or Cu^{2+}) sorbed onto PA6.6-ALD-20% (mg/g), K_L, Q_0 is Langmuir constants representing the equilibrium.

Constant for the adsorbate-adsorbent equilibrium and the monolayer capacity K_L and Q_0 were determined from the slope, intercept of the Langmuir plot (Figure 4).

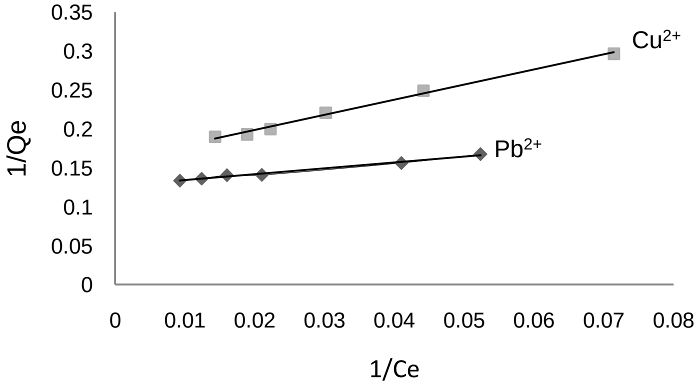


Figure 4: Langmuir adsorption isotherm for removal of copper and lead by PA6.6-ALD-20%.

The essential features of the Langmuir isotherm may be expressed in terms of equilibrium parameter R_L, which is a dimensionless constant referred to as separation factor or equilibrium parameter [22].

$$R_L = \frac{1}{1+(1+K_L C_0)} \qquad (3)$$

Where:

C_0 = initial concentration

K_L = the constant related to the energy of adsorption (Langmuir Constant). R_L value indicates the adsorption nature to be either unfavourable if R_L>1), linear if R_L =1, favourable if 0< R_L<1 and irreversible if R_L=0. From the data calculated in table 1, the RL is greater than 0 but less than 1 indicating that Langmuir isotherm is favourable. From this research work, The maximum adsorption capacity of the adsorbent for Pb^{2+} and Cu^{2+} ions was calculated from the Langmuir isotherm and found to be 8.06 and 6.17 mg/g, respectively, K_L (Langmuir isotherm constant) is 0.15 and 0.08 L/mg for $Pb^{2+}$and Cu^{2+}, respectively, R_L (the separation factor) is 0.08 and 0.06 for $Pb^{2+}$and Cu^{2+}, respectively, indicating that the equilibrium sorption was favourable.

3.4.2. Freundlich Isotherm Model

Freundlich equation is derived to model the multilayer sorption and for the sorption on heterogeneous surfaces. The Freundlich isotherm theory says that the ratio of the amount of solute adsorbed onto a given mass of sorbent to the concentration of the solute in the solution is not constant at different concentrations [23].

The Freundlich equation is:

$$Q_e = K_f C_e^{\frac{1}{n}} \qquad \text{(non- linear)} \qquad (5)$$

$$LnQ_e = LnK_f + \frac{1}{n} LnC_e \qquad \text{(linear)} \qquad (6)$$

where Q_e is the amount of solute adsorbed (Pb^{2+} or Cu^{2+}) per unit weight of adsorbent (PA6.6-ALD-20%)(mg/g), C_e is the equilibrium concentration of solute in the bulk solution (mg/l), K_f is a constant indicative of the relative adsorption capacity of the adsorbent (mg/g), 1/n is a constant indicative of the intensity of the adsorption. Both K_f and n are constants, being indicative of the extent of adsorption and the degree of nonlinearity between solution and concentration, respectively.

The constants k_f and n of the Freundlich model are, respectively, obtained from the intercept and the slope of the linear plot of log Q_e versus log C_e (Figure 5) according to Eq. (6). The constant K_f can be defined as an adsorption coefficient which represents the quantity of adsorbed metal ion for a unit equilibrium concentration. Higher values of K_f (3.57 for Pb^{2+} and 1.03 for Cu^{2+}) indicate higher affinity of PA6.6-ALD-20% for Pb^{2+} than Cu^{2+}.

The slope 1/n is a measure of the adsorption intensity or surface heterogeneity [24].

For 1/n=1, the partition between the two phases is independent of the concentration. The situation 1/n<1 is the most common and corresponds to a normal L-type Langmuir isotherm, while 1/n> 1 is indicative of a cooperative adsorption which involves strong interactions between the molecules of adsorbate. From the data in table 2, that value of 1/n = 0.17 and 0.41 while n=5.88 and 2.44 for Pb^{2+} and Cu^{2+}, respectively, indicating that the sorption unto PA6.6-ALD-20% is favourable.

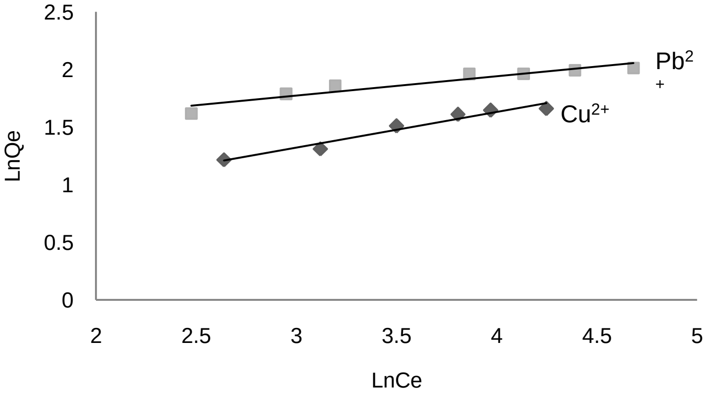


Figure 5: Freundlich adsorption isotherm for removal of copper and lead by PA6.6-ALD-20%.

3.4.3. Dubinin–Radushkevich (D-R) isotherm model

The D-R isotherm model is more general than the Langmuir isotherm. It was applied to determine if the adsorption occurred by physical or chemical processes. The linearized form of the D-R isotherm [25] is as follows:

$Ln_{Q_e} = Ln_{q_m} - \beta\varepsilon^2$ (linear) (7)

Where β is a constant related to the mean free energy of sorption ($mol^2\ J^{-2}$), q_m is the theoretical saturation capacity, ε is the Polanyi potential which is equal to $RT\ln(1+1/C_e)$, R is the gas constant ($8.314\ J\ mol^{-1}\ K^{-1}$) and T (K) is the absolute temperature. The D–R isotherm is applied to the data obtained from the empirical studies. A plot of $\ln(q_e)$ against ε^2 is given in figure 6.

The constant β gives an idea about the mean free energy of sorption. The mean adsorption energy, *E* (kJ/mol) is as follows:

$$E = \frac{1}{\sqrt{2\beta}} \qquad (8)$$

This adsorption potential is independent of the temperature, but it varies depending on the nature of adsorbent and adsorbate. The magnitude of E is used for estimating the type of adsorption mechanism. If the *E* value is between 8 and 16 kJ/mol, the adsorption process follows by chemical adsorption and if $E < 8$ kJ/mol, the adsorption process is of a physical nature [26].

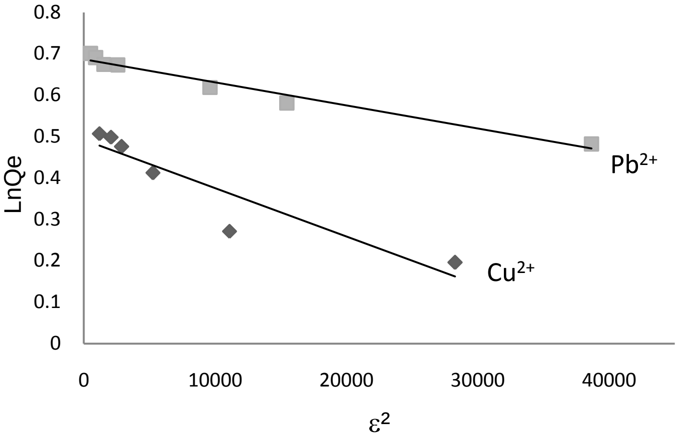


Figure 6: D-R adsorption isotherm for removal of copper and lead by PA6.6-ALD-20%.

The calculated value of E gives information about sorption mechanism as chemical ion-exchange or physical sorption. The mean free energy of Pb^{2+} and Cu^{2+} sorption at the temperature of 293.15 K is 0.289 $kJ.mol^{-1}$ and 0.316 $kJ.mol^{-1}$ for Pb^{2+} and Cu^{2+} respectively. This result is attributed to a physical ion exchange mechanism for the both metal ions process.

All constants determined from Langmuir Freundlich and Dubinin-Radushkevich isotherms are given in Table 1.

Table 1: Isotherm parameters calculated for copper and lead removal by PA6.6-ALD-20%.

Metals	Langmuir				Freundlich			Dubinin-Radushkevich		
	q_m (mg/g)	R_L	b_1	R^2	K_f	1/n	R^2	q_m (mg/g)	E (kJ/mol)	R^2
Pb^{2+}	8.06	0.08	0.15	0.991	3.57	0.17	0.908	1.988	0.289	0.971
Cu^{2+}	6.17	0.06	0.08	0.994	1.03	0.41	0.960	1.64	0.316	0.860

The Langmuir, Freundlich and D-R adsorption constants evaluated from isotherms and their correlation coefficients are presented in Table 1. It is clear that the Langmuir isotherm model provide an excellent fit to the equilibrium adsorption data, giving correlation coefficients of 0.991 for Pb^{2+} and 0.994 for Cu^{2+}, respectively.

In that way, the value of q_m derived from Langmuir model is higher than that derived from D–R model.

The maximum adsorption capacity estimated by means of the Langmuir model of PA6.6-ALD-20% remains substantially similar than the maximum adsorption capacities reported for some other fibrous adsorbents with the iminodiacetic acid groups in the available literature and collected in Table 2.

Table 2: Comparative of the adsorption capacities of metal ions by two chelating fibres

Adsorbent	Metals	Optimum pH	Adsorption capacity (mg/g)	Ref.
MWCNTs-IDA	Pb^{2+}	8	8.98	[27]
	Cu^{2+}	8	6.64	
MPAN	Pb^{2+}	5	9.5	[28]
	Cu^{2+}	5	7	
PA6.6-ALD-20%.	Pb^{2+}	6	8.06	In this work
	Cu^{2+}	5	6.17	

But in our case, the maximum adsorption capacity of metal ions can be increased by increasing the degree of grafting of PA6.6-ALD.

3.5. Kinetics of adsorption

Adsorption kinetics provides valuable information about the mechanism of adsorption [29]. Rate of adsorption uptake, which is required for selecting optimum operating condition for the full-scale batch process, can be described with adsorption kinetics [30].

Kinetic studies for lead and copper were performed by using metal concentration 20 mg/l, pH was adjusted to 6 for lead and 5 for copper and PA6.6-ALD-20% mass was 0.2g/50 ml. Samples were taken with different time intervals ranging between 5 and 120 minutes.

3.5.1. Pseudo-first order reaction kinetic

Simple linear equation for Pseudo-first order reaction kinetic is [31].

$$\ln(q_e - q_t) = lnq_e - k_1 t \qquad (9)$$

where k_1 is the rate constant of the first-order adsorption, q_t is the amount of heavy metal adsorbed at time t (mg/g) and q_e is the amount of heavy metal adsorbed at saturation (mg/g). Plot of ln (q_e- q_t) versus t allows calculation of the rate constant k_1 and q_e (Figure 6).

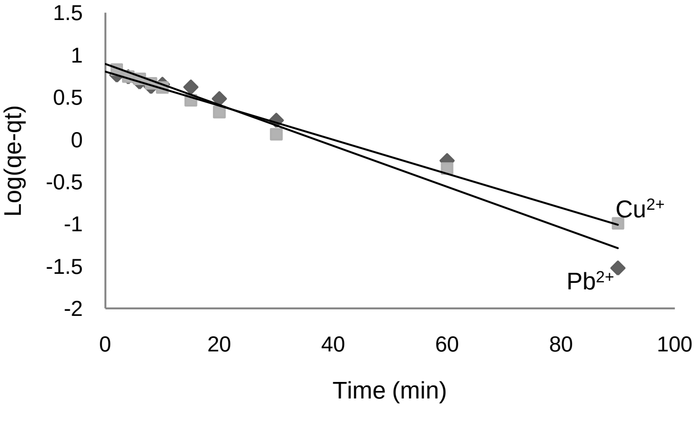


Figure 6: Pseudo-first-order reaction kinetics for the adsorption of copper and lead.

3.5.2. Pseudo-second order reaction kinetic

Pseudo-second order reaction kinetic can be expressed as [32]:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \qquad (10)$$

where k_2 is the pseudo-second order rate constant (g/mg h), q_e is the amount adsorbed at equilibrium and q_t is the amount of metal adsorbed at time t.

Calculated rate constants (k_1 and k_2), adsorbed amounts of heavy metals per unit chelating Fiber mass (q_e) and linear regression correlation coefficients (r^2) for pseudo-first and pseudo-second-order reaction kinetics are summarized in Table 2. In pseudo-second-order reaction kinetic, calculated values of q_e are closer to experimental values for copper and lead. These results thus obtained are in agreement with other studies that

have found that the kinetics of adsorption of lead and copper process follows a pseudo-second order. The similar results were reported by wang et al. for adsorption of Cu^{2+} and Pb^{2+} on MWCNTs-IDA [27].
Furthermore as seen from Table 2, correlation coefficients are higher for pseudo-second order kinetic studies. Similar to pseudo-first order reaction kinetic, q_e and k_2 can be determined from the slope and intercepts of plot t/q_t versus t (Figure 7).

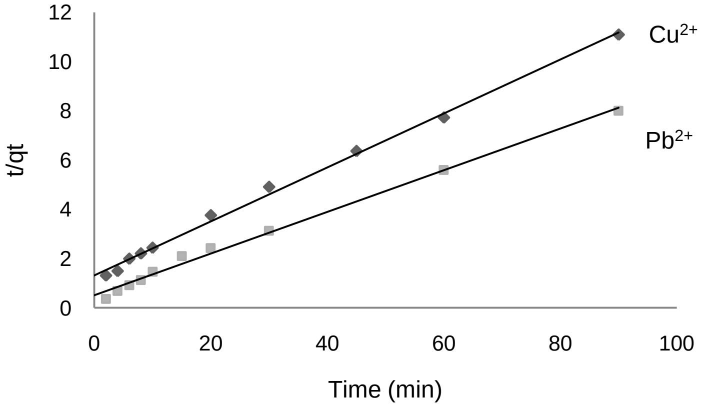


Figure 7: Pseudo-second order reaction kinetics for the adsorption of copper and lead.

Table 2: Comparison of adsorption rate constants, experimental and calculated q_e values for the pseudo-first and–second-order reaction kinetics of removal of copper and lead by PA6.6-ALD-20%.

Metals	qe (exp) ($mg.g^{-1}$)	Pseudo -first Order Kinetics			Pseudo-second-order kinetics		
		K_1 (min^{-1})	q_e (cal) [mg,g^{-1}]	r^2	K_2 ($g.mg^{-1}.min^{-1}$)	q_e (cal) [mg,g^{-1}]	r^2
Pb^{2+}	7.5	0.039	1.69	0.993	0.033	7.69	0.997
Cu^{2+}	5.7	0.051	1.81	0.981	0.028	5.98	0.997

3.6. Regeneration studies

Desorption and regeneration studies have also been carried out in different solutions, to test the reusability of PA6.6-ALD-20%. It has been observed that up to 55%, 65% for $Cu^{2°}$ and Pb^{2+}, respectively can be recovered in solution of 0.1N HCl. No recovery has been observed in distilled water indicating the absence of physical bonding. As the reaction is reversible, the PA6.6-ALD-20% can be reused many times.

Conclusion

Applications of chelating fiber containing IDA have been identified as potentially and efficient materials for use in the treatment of water contaminated with selected heavy metals. In this paper optimal removal conditions were determined with batch experiments. Ion exchange processes was pH-dependent and optimal removal efficiencies for copper at pH 5 and lead at pH 6. Adsorption of the two metal ions reached equilibrium within 60 minutes and 0.2g/50 ml of chelating ion exchange fiber PA6.6-ALD-20% and it can be reused for different cycles after desorption and regeneration treatment.
Experimental results were evaluated with Langmuir, Freundlich and Dubinin-Radushkevich. The results show Langmuir isotherm fit the ion exchange equilibrium data better than the Freundlich and Dubinin-Radushkevich. The maximum adsorption capacity of the adsorbent for Cu^{2+} and Pb^{2+} ions was calculated from the Langmuir isotherm and found to be 6.17 and 8.06 mg/g, respectively. The result of Dubinin-Radushkevich mechanisms is attributed to a physical ion-exchange. Pseudo-second-order reaction kinetic has provided a realistic description of removal of Pb^{2+} and Cu^{2+} with closer experimental and calculated values of q_e. Also correlation coefficients are higher in pseudo-second-order kinetics.
Experimental and theoretical results of this study demonstrate that the chelating ion exchange fiber (PA6.6-ALD-20%) is suitable for adsorption of lead and copper from aqueous solutions and can be reused many times. This data makes the operation of PA6.6-ALD-20%, economically interesting.

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