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# Adsorption properties of amine modified lignin-hydrogel composite for uranyl ions: Theoretical and experimental insights



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Keywords: Lignin Uranyl Adsorption Amine HSAB	A new modified material was synthesized and characterized as ethylene diamine modified (EA) Polyacrylamide (PAA)-Lignin (L). The adsorption features of EA modified PAA-L were studied for uranyl ions. The character- ization experiments were evaluated by FT-IR spectroscopic techniques, scanning electron microscopy (SEM), and PZC analysis. Adsorption of $UO_2^{2+}$ ions as a function of concentration, pH, temperature, and time of adsorption were studied. The adsorption phenomenon of $UO_2^{2+}$ ions onto PAA-L-EA from aqueous medium was successfully evaluated by various equilibrium models such as Langmuir, Freundlich, and Dubinin-Radushkevich (DR). The ( <i>Qe</i> ) maximum adsorption capacity values for Langmuir model was calculated as 0.792 kg mol <sup>-1</sup> by using experimental data. The constant values of thermodynamic parameters such as ( $\Delta G^{\circ}$ ), ( $\Delta H^{\circ}$ ) and ( $\Delta S^{\circ}$ ) were calculated and it has observed that the mechanism of adsorption was found compatible with endothermic and spontaneous owing to increasing disorderliness at solution/solid system. The adsorption between modified lignin and uranyl ion was explained in the light of Hard and Soft Acid-Base Principle.

# 1. Introduction

The uranium is a precious element with its unique properties as radiological and chemical in various industrial area. But, it is also dangerous for environment and life because it has possessed toxicity and radioactivity. The numerous studies showed that it can bond with chelating agents in blood and it can accumulate in organs and cause various health issues such as organ failure and cancer-diseases [1]. The daily intake permissible limits of uranium is near about 0.6  $\mu$ g kg<sup>-1</sup> of the total body weight [2].

Adsorption is commonly used technique for removal of uranyl ions by comparing various conventional methods such as ion exchange [3], nano filtration [4], precipitation [5], biological treatment [6] and extraction [7]. Adsorption approaches can be used as removal and enrichment method of uranium due to selectivity, simplicity, efficiency and practical use. For this purpose, several materials such as carbon [8], polymers [9], clays [10], composites [11], zeolites [12] and metal organic frameworks (MOFs) [13,14] have been using as adsorbent. Among these adsorbents, polymers are commonly preferred due to its containing a chelating group moieties which have high adsorption capacity, the fast adsorption kinetics, higher selectivity, and the environmental-friend.  $% \left( {{{\left[ {{{c_{1}}} \right]}_{i}}}_{i}} \right)$ 

Lignin (L) is a biopolymer present in the plants. It can exist in two forms as Kraft or sulfonated lignin [15]. Especially, the structure of sulfonated lignin has three-dimensional and is possess functional groups such as –OH, –COOH and –SO<sub>3</sub>H. In this way, it can strongly form complexes with metal ions as chelating agent. Since sulfonated lignin is a water-soluble polymer, it cannot be used as an adsorbent. However, when this structure is included in a water-insoluble material, for example, in the form of grafts or copolymers, then it is possible to use it as an adsorbent [16].

It has been proven by various studies that by immobilizing chelating ligands on a solid phase, these ligands will increase the adsorption capacity of adsorbents. The most used ligands for this purpose are amines, sulpha groups, carboxyl groups owing to high ability for target species. Especially, uranyl ions with hard acid character prefer ligands including azo groups as hard base. So, the modification of adsorbents with amine structures is one of the most used methods.

This study investigated that a new composite material containing amine modified lignin-polymer (PAA-L-EA) and the adsorption features

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of aminated structure for the adsorptive-removal of  $\mathrm{UO}_2^{2^+}$  ions from water. The synthesized material has been characterized by various analytical techniques such as FTIR, SEM and PZC. The added sulfonated lignin enabled the material to be used as an adsorbent and the adsorption capacity was increased with the effect of amine groups in the structure.

#### 2. Experimental work

# 2.1. Materials and instrumentations

The chemicals used during the experimental work were of analytical or (GR) grade. The acrylamide monomer, N, N, N', N'-tetramethylethane-1,2-diamine (CH<sub>3</sub>)<sub>2</sub>NCH<sub>2</sub>CH<sub>2</sub>N(CH<sub>3</sub>)<sub>2</sub> and 4-(2-pyridylazo) resorcinol (C<sub>11</sub>H<sub>9</sub>N<sub>3</sub>O<sub>2</sub>) were obtained from Sigma Aldrich.

Salphonated lignin, Lignosulfonic acid, sodium salt, REAX 85A; {(CH3O)NaO)Ar(CH2SO3Na)x(C3H6O)}y were supplied by Mead-Westvaco Corp. (USA). UO<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>.6H<sub>2</sub>O, was procured from Merck (Germany). The ultra-pure water was used to prepare the aqueous solutions (Labcanco water-purification system 18.2 M $\Omega$  cm). The FT-IR spectrophotometer (Bruker, Tensor II) was used to characterize the PAA-L-EA using KBr pellets.

The concentration of uranyl ions before and after the adsorption were determined through UV-VIS spectrophotometer (wavelenght190–1100  $\pm$  0.2 nm and bandwidth 2 nm). The pH of the solution has been optimized by pH meter with a glass-calomel electrode (Selecta, Spain). To enhance the phase separation, the centrifuge machine was used (Centurion Scientific). To keep the constant heat, a thermostat, water bath (Nuve NT 120, Turkey) was used. The experiments were made in twice.

# 2.2. Synthesized of PAA-L and amine modified PAA-L

50 mL of solution containing 2 g Lignin and 4 g acrylamide were mixed and stirred for 30 min. Polymerization was initiated by using 0.1 mL of N,N,N',N'-tetramethylethylenediamine (TEMED) at 25  $^\circ$ C. Eventually, PAA-L composite was the formed and new polymer was dried and stored.

Then, 2 g of PAA-L was dissolved was added on to this solution in order to convert PAA-L to PAA-L-EA. Then, the solution was mixed on a magnetic stirrer at 80 °C for 5 h. After this time, the obtained gel was filtered and washed ethanol and water. Finally, it was maintained in diluted HCl solution at pH 4 for 4 h. Then, it was washed with water and stored in glass bottle after dried.

# 2.3. Adsorption experiments

Adsorptive properties of amine modified PAA-L was studied for UO<sub>2</sub><sup>2+</sup>. Thus, 0.1 g of PAA-L-EA was added in 10 mL of UO<sub>2</sub><sup>2+</sup> (0.37–7.4)  $\times$  10<sup>-3</sup> mol L<sup>-1</sup> and equilibrated for 24 h at 298 K and the equilibrated solutions separated by centrifuging at 2.5 rpm for 6 min.

# 2.4. Determination of $UO_2^{2+}$ ions in aquatic medium

The concentration of  $UO_2^{2+}$  ions have been determined using PAR procedure [17,18]. According to this method,  $10^{-5}$  M PAR solution was prepared in pH 8.5 TRIS buffer. 50 µL of sample solution was mixed with 3 mL of PAR reagent. Absorbance of this solution was measured at 530 nm after 30 s blank solution was also prepared by using 50 µL of water instead of sample.

# 3. Results and discussion

## 3.1. Functional groups analysis

The FT-IR spectra of PAA-L and PAA-L-EA were performed as shown



Fig. 1. FT-IR spectra of PAA-L and PAA-L-EA

in Fig. 1. The detail analyses of PAA-L were given in our previous study [16]. The FT-IR spectrum of PAA-L-EA showed that the new peak at 1540 cm<sup>-1</sup> was evidence of amine modification as > NH- groups. Moreover, the increase of sharpness of peak at 1660 cm<sup>-1</sup>, the disappearance of peaks at 1350, 1310 cm<sup>-1</sup> and 1420 cm<sup>-1</sup> were evaluated as an evidence of amine modification.

# 3.2. SEM analysis

SEM images of PAA-L, PAA-L-EA, and  $UO_2^{2+}$  adsorbed PAA-L-EA were given in Fig. 2. As can be seen, the surface morphology of  $UO_2^{2+}$ adsorbed PAA-L-EA is obviously different from PAA-L and PAA-L-EA. The image of PAA-L-EA before adsorption displays a regular surface and smoother structure, while it exhibits a more heterogeneous, rougher, and more uneven structure after adsorption. Experimental observations showed that the surface morphology of new material changed before and after adsorption. It can be evaluated as an evidence of adsorption mechanism works as expected.

# 3.3. pH studies and determination of point zero charge

The one of the important parameter in adsorption experiments is the pH of solution. It affects the ionization equilibriums in the medium and surface charge and functional groups on adsorbent. Moreover, the structure of ligands in solution and precipitation of ions mainly depend on pH of solution.

The effect of pH on  $UO_2^{2+}$  (3.7 ×  $10^{-3}$  mol L<sup>-1</sup>) adsorption was presented in Fig. 3. It is clear that the adsorption of  $UO_2^{2+}$  ions increased with pH. These results can be explained with two approach. Firstly, a rivalry between  $UO_2^{2+}$  and H<sup>+</sup> ions for the same adsorption centres may cause a decrease of adsorption at low pH. Secondly, the electron supplier atoms could be at protonated form in the low pH. Therefore, electrostatic repulsion forces are effective between ions in the medium and surface. Moreover, the adsorption may increase in the presence of hydrolyzed uranyl species because the pH of the solution also affects the solubility of  $UO_2^{2+}$  as various polyatomic cationic forms [19]. The values above pH 7.0 has not studied due to hydroxide precipitates of the  $UO_2^{2+}$ ion.

The value of point of zero charge (PZC; isoelectric point) was determined by using a series solution having various pH solution (Fig. 4). The plateau of the pH<sub>i</sub>–pH<sub>f</sub> graph corresponds to the pH values where the buffer solution effect of the PAA-L-EA surface occurs [20]. The obtained plateau corresponds to pH<sub>pzc</sub> from 4.0 to 8 for PAA-L-EA. This indicates that the all values of pH<sub>i</sub>, in this range, the pH<sub>f</sub> is equals to pH<sub>pzc</sub>. The PAA-L-EA has positive surface charge at pH < 4, neutral



Fig. 2. SEM images of PAA-L (a), PAA-L-EA (b), and  $UO_2^{2+}$  adsorbed PAA-L-EA (c).



Fig. 3. pH dependence of the adsorption.



Fig. 4. PZC plot of PAA-L-EA.

between 4 and 8, and negative at pH>8. These results are evaluated together with pH results; it can be described in terms of  $pH_{pzc}$  of PAA-L-EA. The surface charge of adsorbent is more positive at pH<

 $pH_{pzc}.$  The force of electrostatic-repulsion in between  $UO_2^{2+}$  ions and surface of adsorbent becomes more effective at  $pH < pH_{pzc}.$ 

# 3.4. Influence of concentration of $UO_2^{2+}$ and adsorption isotherms

Generally, the evaluation of experimental results is carried out by using several theoretic models related adsorption such as Langmuir, Freundlich, and DR models. Each of these models describes different parameters for adsorption phenomenon such as surface properties of adsorbent and affinity for adsorbate, adsorption capacity, and amount energy to explain the nature of adsorption [21].

The total adsorbed amount of  $UO_2^{2+}$  ions (*Q*, mol.kg<sup>-1</sup>) can be calculated using following formulae given in equation (1);

$$Q = \left[\frac{(C_i - C_e)V}{w}\right]$$
(1)

In equation (1),  $C_i$  and  $C_e$  (mol L<sup>-1</sup>) shows the initial and equilibrium concentrations of UO<sub>2</sub><sup>2+</sup> ions respectively. The mass of adsorbent (Kg) is denoted by *w* while *V* is the volume of solution in (L).

The adsorption equilibrium models (Langmuir, Freundlich, DR) were applied onto experimental data using following equations (2)–(4);

$$Q_e = \frac{Q_L K_L C_e}{1 + K_L C_e}$$
<sup>(2)</sup>



Fig. 5. Experimentally obtained adsorption isotherms  $UO_2^{2+}$  and their compatibility to Langmuir, Freundlich and DR models.

# Table 1

Langmuir, Freundlich and DR parameters obtained for  $\mathrm{UO}_2^{2+}$  adsorption on to PAA-L-EA.

Langmuir	Parameters
Q <sub>L</sub>	0.792
K <sub>L</sub>	685.9
R <sup>2</sup>	0.960
Freundlich	
K <sub>F</sub>	9.726
n	0.499
R <sup>2</sup>	0.949
DR	
Q <sub>DR</sub>	2.113
-K <sub>DR</sub> x10 <sup>9</sup>	6.469
R <sup>2</sup>	0.987

$$Q_e = K_F C_e^n \tag{3}$$

$$Q_e = Q_{DR} e^{-K_{DR}e^2}$$
(4)

Where  $C_e$  (mol.L<sup>-1</sup>) and  $Q_e$  (mol.Kg<sup>-1</sup>) are equilibrium concentration of UO<sub>2</sub><sup>2+</sup> in solution and onto adsorbent respectively. Q<sub>L</sub>, Langmuir constant related to the maximum adsorption capacity (mol kg<sup>-1</sup>), K<sub>L</sub>, Langmuir adsorption equilibrium constant related to adsorption energy (L mol<sup>-1</sup>), K<sub>F</sub>, Freundlich constants indicating adsorption capacity, n, intensity of adsorption, K<sub>DR</sub>, shows the DR constant related to the adsorption energy (mol<sup>2</sup> K J<sup>-2</sup>), Q<sub>DR</sub>, DR adsorption capacity (mol kg<sup>-1</sup>),

 $\varepsilon$ , Polanyi potential calculated using the following formulae  $\varepsilon = RTln\left(1 + \frac{1}{C_{\varepsilon}}\right)$ , R: (8.314 J mol<sup>-1</sup> K<sup>-1</sup>) is an ideal gas constant, T, temperature (298K), E (J.mol<sup>-1</sup>) is energy can be calculated using following equation (5);

$$E_{DR} = \frac{1}{\sqrt{K_{DR}}} \tag{5}$$

The equilibrium models of  $UO_2^{2+}$  ions and their compatibility to the Langmuir, Freundlich and DR is given in Fig. 5. The adsorption parameters for uranyl ions were obtained by using three isotherm model with nonlinear method and results were presented in Table 1.

The maximum adsorption capacities  $(Q_L)$  and affinity coefficients  $(K_L)$  between adsorbent and adsorbate were found using Langmuir model.

 $Q_L$  value was calculated as 0.792 molKg<sup>-1</sup>. In our previous studies,  $Q_L$  was found as 0.19 molKg<sup>-1</sup> for PAA-L and 0.53 molKg<sup>-1</sup> for hydroxamic acid modified lignin composite, respectively [16]. These result shows that the amine modification is increased the amount of adsorbed uranyl ions.

Amine modified structures have high adsorption capacities because of they have unshared electron pair. Their hard bases properties make easy the complex formation with uranyl ions as hard cation. This could be explained that the existing functional groups in lignin structure which are carboxyl, hydroxyl and metoxyl, beside new groups were added as amines. K<sub>L</sub> value, demonstrate the adsorption affinity of  $UO_2^{2+}$  for PAA-L-EA and the adsorption was homogeneous and forms monolayer [22].



Fig. 6. SEM views and EDX map of adsorbent after  $UO_2^{2+}$  adsorption.



Fig. 7. The effect of temperature on the adsorption.

Table 2

Thermodynamic parameters for  $UO_2^{2+}$  onto PAA-L-EA.

$\Delta H^0/kJ mol^{-1}$	$\Delta S^0/J \; mol^{-1} \; K^{-1}$	$-\Delta G^0/kJ \ mol^{-1}$	$R^{2}$	E <sub>DR</sub> /kJmol <sup>-1</sup>
8.160	75.399	14.162	0.913	8.839

\*Coefficients of variations for the linearity of ln K vs. 1/T depictions used in obtaining  $\Delta H^0$  and  $\Delta S^0$  are significant at p<0.01.

Freundlich model demonstrates the heterogeneity of the adsorptive surface. The constant  $K_f$  is concerned with the degree of adsorption, and n shows the intensity of the adsorption [23]. The Freundlich parameter (n) was calculated as 0.499 for PAA-L-EA and this indicated that  $UO_2^{2+}$  could be removed effectively.

Different experiments were performed to analyse the ionic strength using various concentration ranges of  $\text{KNO}_3$ . The results showed that, the amount of adsorbed  $\text{UO}_2^{2+}$  at equilibrium has no any significant effect of  $\text{KNO}_3$  concentrations.

# 3.5. Energy dispersion X-ray (EDX) and SEM analysis

Structural analysis of  $UO_2^{2^+}$  adsorbed PAA-L-EA and were carried out by EDX and SEM instruments and results were shown in Fig. 6. It is clear that there are unique changes in the images at back scattered electron mode and the brightness is increased due to high atomic mass of uranium in some areas and this indicates the presence of uranium in the structure after adsorption (6b). Moreover, the red points shows the zones where  $UO_2^{2^+}$  ions were adsorbed (6d) that also confirms the adsorption of  $UO_2^{2^+}$  ions. The EDX diagram in Fig. 6c presents the elemental composition of surface and has the characteristic peak of uranium at (M $\alpha$  3.17).

# 3.6. Thermodynamic study and effect of temperature on adsorption of $\mathrm{UO}_2^{2^+}$ ions

The adsorption of  $UO_2^{2^+}$  ions were investigated under the influence of temperature (283, 298, and 313 K) were studied. To calculate the thermodynamic parameters, following equations were applied using equations (6)–(8):

$$K_d = \frac{Q}{C_e} \tag{6}$$

Where  $K_d$  is distribution coefficient. The ( $\Delta G^0$ ) is free energy and can be calculated by equation (7), while the ( $\Delta H^0$ ) and ( $\Delta S^0$ ) were calculated using equation-8.



**Fig. 8.** Compatibility of  $UO_2^{2+}$  adsorption kinetics to pseudo-first-order model, pseudo-second-order model, Elovich model and intraparticle diffusion model.

$$\Delta G^0 = -RT ln K_d \tag{7}$$

$$\ln K_d = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT}$$
(8)

The constant values of thermodynamic parameters were obtained the graph of 'lnKd vs. 1/T' (Fig. 7) using equations (6)–(8) and ( $E_{DR}$ ) was obtained from DR model (4) given in Table 2. From the values  $\Delta H^0$ ,  $\Delta S^0$  and  $\Delta G^0$  it is clear that the adsorption of  $UO_2^{2+}$  ion is endothermic and spontaneous ( $\Delta G^0$ <0) and increased entropy demonstrate that the good affinity of adsorption onto PAA-L-EA surface.

The value for  $\Delta$ H is positive meaning it utilize energy as the extent of adsorption is increased with temperature as endothermic. The positive value of  $\Delta$ S<sup>0</sup> shows a high affinity of the ion for the adsorbents and an increasing randomness at the adsorbate-adsorbent interface during the adsorption phenomenon [24]. Furthermore, (+ $\Delta$ S<sup>0</sup>) value show that the overall process are based on dissociative mechanism [25]. The equilibrium data is best fit the DR model with good  $R^2$  (0.987). Adsorption process is chemically controlled because the value of E<sub>DR</sub> is in the range from 8 to 16 kJ mol<sup>-1</sup> [26–28].

# 3.7. Kinetic studies

The one of important parameters in planning the adsorption process is the prediction of the change of adsorption by the time. The several mechanisms are used in order to explain adsorption mechanism such as mass transfer external boundary layer film, adsorption on the surface and diffusion of the molecules in pores. The kinetic of adsorption are described using pseudo 1st and 2nd order, intra particle diffusion, and Elovich models given below in equations (9)–(12) and the fitting of given equations are shown in Fig. 8 [29].

Pseudo 1<sup>st</sup> orderq<sub>t</sub> = q<sub>e</sub> 
$$\left[1 - e^{-k_1 t}\right]$$
 (9)

Pseudo 2<sup>nd</sup> orderq<sub>t</sub> = 
$$\frac{t}{\left[\frac{1}{k_2 q_e^2}\right] + \left[\frac{t}{q_e}\right]}$$
 (10)

Elovich – equation
$$q_t = \frac{1}{b} \ln (ab) + \frac{1}{b} \ln t$$
 (11)

Intraparticle diffusionmodel
$$q_t = k_i t^{0.5}$$
 (12)

In above equation  $q_t$ , is the adsorbed amounts at certain time t,  $q_e$  (mol.kg<sup>-1</sup>), shows the adsorbed amounts at equilibrium (mol kg<sup>-1</sup>),  $k_1$ ,  $k_2$  and  $k_i$  are the kinetic rate constants, a, is the initial adsorption rate (mol/kg min), b, related to the extent of surface coverage and the

Table 3

Kinetic parameters for  $UO_2^{2+}$  adsorption onto PAA-L-EA.

Pseudo-first order kinetic	Parameters		
$q_{exp}/mol \ kg^{-1}$	0.373		
$q_{cal}/mol kg^{-1}$	0.365		
$k/dk^{-1}$	0.042		
R <sup>2</sup>	0.542		
Pseudo-second order kinetic			
$q_{cal}/mol kg^{-1}$	0.356		
$k/mol^{-1}$ kg min <sup>-1</sup>	0.683		
H/mol kg <sup>-1</sup> min	0.087		
t <sub>1/2</sub> /dk	4.116		
$R^2$	0.714		
Elovich Model			
$a/mol kg^{-1} min^{-1}$	1.022		
b/kg mol <sup>-1</sup>	24.75		
R <sup>2</sup>	0.956		
Intrapartical diffusion			
$k_i$ /mol kg <sup>-1</sup> min <sup>0.5</sup>	$3.29\times 10^{-3}$		
$R^2$	0.894		

activation energy involved. The adsorption rate at initial stage (H) for 2nd order calculated from  $H=k_2q_e^2$ , and the time required for adsorption is the half of the concentrations ( $t_{1/2}$ ) was also obtained from  $t_{1/2}=q_e/H.$ 

The compatibility of experimental results to theoretical models were evaluated using correlation coefficients which are non-linear regression coefficient values for pseudo 1st,2nd, Elovich, and linear-regression coefficient for intra-particle diffusion mechanism. According to experimental outcomes, the used in these models are not compatible to the pseudo first order and pseudo second order models. The best  $R^2$  0.999 were obtained with Elovich and intra-particle diffusion models. The results demonstrated that the kinetics adsorption on to PAA-L-EA could be explained by Elovich model given in (Table 3). In the light of this model the adsorption is fast initially and becomes slower after certain time [30,31].

The intra-particle diffusion model shows that adsorption of uranyl ions on to amine modified polymer composite follows on a various mechanism because the q vs  $t^{1/2}$  plot is multi-linear [32]. This mechanism can be defined that the adsorption is fast on external adsorbent surface at initial period and then it is getting slower at after passage of time because the mass-transfer to internal parts, where intraparticle-diffusion was rate limiting. The results showed that the kinetic mechanism of adsorption on to PAA-L-EA can be explained by using Elovich and intra-particle diffusion models together.

# 3.8. Theoretical aspect of the interaction between modified lignin and uranyl ion

Chemical hardness is one of the important quantum chemical descriptors of theoretical and experimental chemistry. This parameter firstly reported by Pearson is known as the resistance against the polarization of electron clouds of atomic and molecular systems [33]. Maximum Hardness Principle [34] explain the relation with chemical hardness concept while Hard and Soft Acid-Base Principle (HSAB) [35] states that "hard acids prefer the binding to hard bases and soft acids prefer the binding to soft bases." Hard-hard and soft-soft interactions are electrostatic and covalent interactions, respectively. HSAB Principle is widely used in adsorption studies to predict the adsorption characteristics of chemical systems. Kaya and Kaya [36] proved that chemical hardness is a key reactivity parameter in solid state also like in gas phase introducing Kaya's composite descriptor. Now let us discuss the hard or soft nature of lignin and uranyl ion according to the hard and soft classification of Pearson. Uranium in uranyl ion has +6 of oxidation state for that reason the mentioned ion acts as a hard acid. This situation was reported in some important published paper [37]. Chemical systems including O and N donor atoms are among hard bases in general. Thanks

## Table 4

Comparison of UO <sub>2</sub> <sup>2+</sup>	adsorption	capacities	of	various	biopolymer	based	adsor-
bents extracted from	literature.						

Adsorbent	$Q_{\rm L}/$ molkg <sup>-1</sup>	References
Serine modified chitosan	0.33	[39]
Amidoximated biomass	0.47	[40]
Fungus-Fe <sub>3</sub> O <sub>4</sub>	0.37	[41]
Amidoximated modified alginate	0.57	[42]
Fe <sub>3</sub> O <sub>4</sub> —alginate-agarose	0.45	[43]
Polyethyleneimine modified biomass	1.61	[44]
Hydrolyzed amidoximated pine bark	1.05	[45]
Tetraethylenepentamine modified magnetic chitosan	0.67	[46]
hydroxyethylmethacrylate-grafted lignocellulosics	0.41	[47]
Organoclay modified lignin	0.42	[48]
Hydroxilamine-hydrochloride modified lignin composite	0.53	[16]
This study	0.79	

to the mentioned donor atoms in our designed polymer, this polymer acts as hard base. Some researchers noted that lignin has an important stabilization effect [38]. It is not difficult to predict that this situation is closely related to the hard nature of the lignin. Finally, we can tell that the power of the interaction between our designed polymer and uranyl ions is in good agreement with HSAB Principle.

# 4. Conclusions

A new adsorbent as amine modified PAA-L was synthesized and characterized successfully. The adsorption data was examined by using Langmuir, Freundlich, and DR isotherm models and the maximum adsorption capacity for Langmuir was found as 0.792 mol kg<sup>-1</sup> for Langmuir. The value of the mean adsorption energy ( $E_{DR}$ ) was calculated as 8.84 kJ mol<sup>-1</sup>. The values of  $\Delta$ H,  $\Delta$ S and  $\Delta$ G were founded as 8.16 kJmol<sup>-1</sup>, 75.40 JK<sup>-1</sup>mol<sup>-1</sup>, and -14.16 kJ mol<sup>-1</sup>; respectively. The positive value of  $\Delta$ H indicates that nature of adsorption is endothermic. The developed material can be used effectively for removal of uranyl ions in aqueous medium with high adsorption capacity.

The biopolymers and its modified structures based adsorbents are commonly used for removal of uranyl ions in aqueous solutions. After emphasizing the above mentioned adsorptive features, the adsorption capacity of the PAA-L-EA the ions of interest were compared with those extracted from literature (Table 4) showed that amine modified lignin composite should be considered amongst the favourite adsorbents besides its cost effectiveness. The powerful interaction between studied chemical systems can be explained in the light of HSAB Principle.

# Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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