

# Adsorptive properties of sulfolignin–polyacrylamide graft copolymer for lead and uranium: Effect of hydroxylamine–hydrochloride treatment

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## ABSTRACT

Sulfolignin–polyacrylamide graft copolymer (PAAm–SL) was synthesized and its adsorptive features were compared with those of PAAm and PAAm–SL modified to their hydroxamic acid and amidoxime forms for  $Pb^{2+}$  and  $UO_2^{2+}$  ions. The increase in adsorption with increasing pH inferred that the main adsorption mechanism could be complex formation between electron donor terminals of lignin and the metal ions via proton exchanger. The modification of PAAm–SL significantly increased the adsorption capacity for  $UO_2^{2+}$ . The adsorption kinetics of both ions was well compatible to second-order model. The enthalpy and entropy changes were positive, and the negative Gibbs free energy change was the proof for the spontaneity of adsorption. Sulfolignin as a water soluble lignin derivative was reusable after its grafting on PAAm having inert feature for metal ion adsorption.

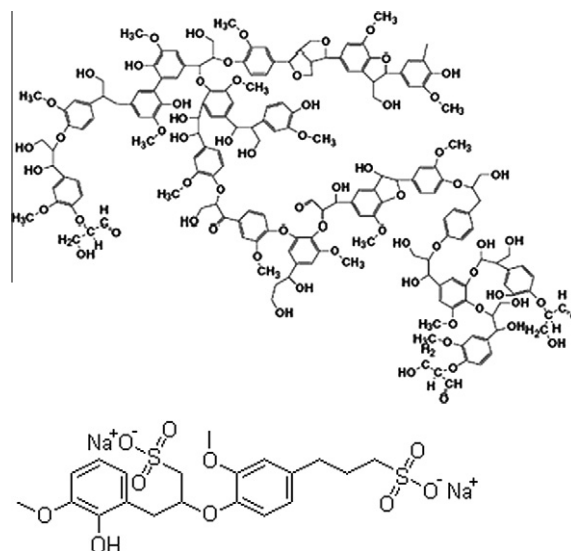
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## 1. Introduction

Adsorption is introduced as a favorable process for removal/recovery of metal ions from aquatic environment because of its effectiveness, versatility, simplicity, applicability at very low concentrations, suitability for using batch and continuous processes, ease for operation, little sludge generation, and possibility of regeneration and reuse beside its cost-effectiveness [1,2].

Principally, a good adsorbent should have a high adsorption capacity and fast adsorption kinetics beside which it should be cost effective. Minerals such as clay and zeolites [3] and hydroxyapatite [4], and biodegradable/renewable bio-polymers such as chitin/chitosan and lignin [5,6] are amongst favorable naturally occurring low cost adsorbents. As the interest of this investigation, lignin for instance is present in large quantities in the cell walls of terrestrial plants. It is the main binding agent for fibrous plant components comprising from 16% to 33% of plant biomass. As a three-dimensional amorphous polymer consisting of methoxylated phenylpropane structures, it is biosynthesized from the polymerization of three types of phenylpropane (monolignols); coniferyl, sinapyl, and *p*-coumaryl alcohol [7]. Approximately 50 million tons of lignin is generated annually by the paper industries all over the world, but less than its 10% are utilized. There are three types of industrial lignin; liginosulfonate derived from the sulfite pulping

of wood, kraft lignin also called alkali lignin obtained from black liquor by precipitation with acid, and organosolv pulping lignin extracted from hardwood chips cooked in an aqueous ethanol or methanol liquor [8].



Representative chemical structure of lignin and liginosulfonic acid, sodium salt.

*Abbreviations:* PAAm, polyacrylamide; KL, kraft lignin; SL, sulfolignin; PHA, polyhydroxamic acid; SLA, amidoximized sulfolignin.

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Lignin derivatives have been used as adsorbent since their inherent metal binding ability via surface functional groups. Lignin has been utilized as an adsorbent for e.g.,  $\text{Pb}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Zn}^{2+}$ , and  $\text{Ni}^{2+}$  [9–13], for  $\text{Cr}^{3+}$  and  $\text{Cr}^{6+}$  [14,15], and for also cationic dyes [16].

Grafting of lignin (especially sulfolignin which is not usable in adsorption practices due to its solubility in aquatic environment) onto a polymer network could enable its practical usage in the adsorption procedures. Beside this, adsorptive features of such composition could be enhanced by additional surface modifications. For such an approach, a hydrogel (a cross-linked polymer) especially polyacrylamide as a backbone polymer provides additional advantages since it is not soluble in water but swells and allows transferring of solvent together with its solved contents into the structure. However, the possibility of this phenomenon has been proved by Meister et al., 1984 [17] where the insoluble kraft lignin was grafted onto polyacrylamide to test its usability in drilling mud. Recently, the IPN hydrogels were synthesized by using peat and kraft lignin as the interpenetrated phase into an acrylamide–starch matrix to investigate its adsorptive features for  $\text{Ni}^{2+}$  and  $\text{Cu}^{2+}$  ions [18]. As a biotechnological method, chemoenzymatical grafting of acrylamide onto organosolv lignin has been proposed for conversion of lignin into the marketable plastics [19]. In consequence, none of the aforementioned studies has considered the grafting of water soluble lignin derivatives onto a polymer for adsorption purpose. By such grafting procedures, the direct use of black liquor for preparation of the polymer–lignin adsorbents could be possible.

The principle concern of this investigation was to introduce the preparation of sulfolignin–polyacrylamide graft copolymer (PAAm–SL) from lignosulfonic acid to facilitate lignin and its sulfonate terminals for adsorptive purpose and to investigate its adsorptive features for  $\text{Pb}^{2+}$  and  $\text{UO}_2^{2+}$ . The features of PAAm–SL further functionalized by conversion of its amide/carbonyl groups to hydroxamic acid/amidoxime terminals (PHA–SLA) by hydroxylamine hydrochloride treatment were also considered. The adsorption properties of PAAm–SL and PHA–SLA were compared with those of kraft lignin (KL) and PHA prepared by the conversion of PAAm. The choice of  $\text{Pb}^{2+}$  and  $\text{UO}_2^{2+}$  was due to the environmental concerns associated with their hazardness associated with toxicity and radioactivity beside which the recovery of  $\text{UO}_2^{2+}$  from nuclear waste may be of economical interests.

## 2. Experimental

### 2.1. Reagents

Kraft [Lignin, kraft; INDULIN AT;  $\{(\text{CH}_3\text{O})(\text{OH})\text{Ar}(\text{C}_3\text{H}_4\text{O})\}_x$ ] and sulfonated lignin [Lignosulfonic acid, sodium salt; REAX 85A;  $\{(\text{CH}_3\text{O})\text{NaOAr}(\text{CH}_2\text{SO}_3\text{Na})_x(\text{C}_3\text{H}_6\text{O})\}_y$ ] were kindly supplied by MeadWestvaco Corp. (USA). *N,N'*-methylene-bisacrylamide (MBAm), *N,N,N',N'*-tetramethylethylenediamine (TEMED) and 4-(2-pyridylazo) resorcinol (PAR) were purchased from Sigma. Acrylamide (AAm) monomer, ammonium peroxydisulfate (APS),  $\text{Pb}(\text{NO}_3)_2$ ,  $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and all other chemicals were obtained from Merck. All chemicals were of analytical reagent grade. Distilled water was used throughout the investigation. No pre-treatment was applied to any of the reagents.

All experiments were always performed in duplicates for which  $\pm 5\%$  was the limit of experimental error.

### 2.2. Preparation of PAAm and PAAm–SL

Two gram of AAm monomer and 0.2 g of MBAm were dissolved in 20 mL distilled water and mixed with 1 g of sulfolignin (SL) in

10 mL of water. APS (100 mg) and TEMED (200  $\mu\text{L}$ ) were used for initiation of the polymerization. Pure PAAm was also prepared by the same prescription. The formed PAAm–SL and PAAm were sequentially washed with distilled water having  $\approx 1 \mu\text{S cm}^{-2}$  conductivity ( $\text{pH} = 6.5$ ) to remove SL not grafted to the gel and other impurities until the effluent attained  $\approx 10 \mu\text{S cm}^{-2}$  conductivity ( $\text{pH} \approx 8$ ), dried at ambient temperature, ground and sieved to a particle size 50–100 mesh, and stored. To avoid inter sample variations, the required amount of each composition was synthesized at once to conduct overall investigation As previously reported for  $\text{Cu}^{2+}$  and  $\text{Fe}^{3+}$  [20], the inertness of PAAm for the studied ions was also proved by preliminary adsorption investigations.

### 2.3. Hydroxamic acid and amidoxime modification

A hydroxylamine procedure was applied to PAAm and PAAm–SL for the conversion of the amide terminals of PAAm to hydroxamic acid, and carbonyl groups of SL to amidoxime (PHA and PHA–SLA). 100 mL of hydroxylamine–hydrochloride (3.3 M) was added on 10 g of PAAm or PAAm–SL in 300 mL water and agitated at room temperature in a round bottom flask assembled to a rotary mixer for 30 min. After addition of 25 mL of 3.9 M NaOH, the reaction was continued for 24 h during which ammonia was liberated [20,21]. The resulting polymer was washed with water, acidified with 3 M HCl and then rinsed with several washes until chloride free solution was obtained. The final production was dried at ambient temperature, ground and sieved to particle size 50–100 mesh and stored.

### 2.4. Characterization

FT-IR spectra were recorded with pellets obtained by pressing a mixture of 2 mg of sample and 100 mg of KBr under reduced pressure using a FT-IR spectrophotometer (Unicam, Mattson 1000) by 20 completed scans at a resolution of  $4 \text{ cm}^{-1}$ . Marmara Research Centre (TÜBİTAK, Gebze, Turkey) facilities were employed for SEM and BET-porosity analysis. The internal faces of the samples were observed under SEM; the samples were gold-coated and the morphology of the samples were taken in detail using a JEOL/JSM-6335F model SEM with an accelerating voltage of 10 or 20 kV and different levels of magnification. Measurements of nitrogen adsorption/desorption isotherms were performed at 77 K with by Quantachrome (Quantachrome Instruments) apparatus. The samples were degassed about 48 h at 323 K prior to the experiments. The specific surface area was calculated by BET equation using the adsorption data in the relative pressure of 0.03–0.3. Adsorption pore diameters and pore volumes were calculated with reference to the BJH method.

The change in swelling features of the compositions was also investigated. 0.1 g of each dried material was let to swell in water and weighed to find the swelling ratio with reference to its dry mass. Point of zero charge (PZC) and univalent sodium exchange capacities (NaEC) of KL and PAAm–SL was determined. For determination of PZC values, 0.1 g of material was interacted with 10 mL of  $\text{KNO}_3$  solutions having initial pHs in the range of 3–11 for 24 h. 0.1 M of HCl or NaOH were used for the pH adjustments. The PZC values were derived from the fitted linear functions to plots of  $\Delta\text{pH}$  ( $\Delta\text{pH} = \text{pH}_e - \text{pH}_i$ ) vs.  $\text{pH}_i$  for  $\Delta\text{pH} = 0$ , where  $\text{pH}_e$  and  $\text{pH}_i$  were pHs of the solutions at equilibrium and initial [22]. Ammonium acetate method [23] was applied for the determination of NaECs.

### 2.5. The adsorptive features for $\text{Pb}^{2+}$ and $\text{UO}_2^{2+}$

For the adsorption dependence on initial pH, a set of  $\text{Pb}^{2+}$  or  $\text{UO}_2^{2+}$  solutions ( $1000 \text{ mg L}^{-1}$ ) with adjusted pH ( $\text{pH} = 1\text{--}5$ ) by

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