

Adsorption of lead and cadmium ions in aqueous solutions onto modified lignin from alkali glycerol delignification

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Abstract

Adsorptions of toxic metal ions (Pb(II) and Cd(II)) onto modified lignin from beech and poplar woods by alkali glycerol delignification are presented in this paper. The material exhibits good adsorption capacity and the adsorption data follow the Langmuir model. The maximum adsorption capacities are 8.2–9.0 and 6.7–7.5 mg/g of the modified lignin for Pb(II) and Cd(II), respectively. The maximum adsorption percentage is 95.8 for Pb(II) for 4 h at 330 K and is 95.0 for Cd(II) for 10 h at 290 K. The adsorption of both the metal ions increased with increasing temperature indicating endothermic nature of the adsorption process. The maximum adsorption percentages of Pb(II) and Cd(II) ions decrease with time till 48 and 42 h and then again increase slightly with time. The adsorption of both heavy metal ions increases with pH. The adsorption of Pb(II) ions reached a maximum at a 5.0 value of pH.

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1. Introduction

The heavy metal content of industrial waste waters is an important source of environmental pollution. Pb, Cd, Cu, Hg, Cr, Ni, and Zn are the main trace elements that are of greatest concern on a waste treatment facility. The main sources of heavy metals are mining and metal industries. The removal of heavy metals from waste water because of their detrimental effects on living species is extremely important. Three most detrimental metals are cadmium, mercury, and lead. Cadmium has the most dangerous long-term effects on human health.

Modified lignin obtained from lignocellulosic materials is used for the removal of trivalent and hexavalent chromium, lead and zinc from aqueous solutions [1,2]. Lignin is known to adsorb many heavy metal ions [3].

The alkali lignin produced by the alkaline pulping of softwood consequently contains a low content of positions reactive towards electrophiles. In natural lignin the positions on the aryl rings *para*- and *ortho*- to the hydroxyl groups are usually occupied by alkoxy or alkyl substituents [4].

Lignin has an aromatic, three-dimensional polymer structure with apparent infinite molecular weight [5]. The cellulose is located predominantly in the secondary cell wall [6]. Lignin is covalently linked with xylans in the case of hardwoods and with galactoglucomannans in softwoods. Even though mechanically cleavable to a relatively low molecular weight, lignin is not soluble in water. Lignin has strong resistance to chemical reactions, a high surface area (180 m²/g) [7]. Molecular weight of the polymeric lignin changes from 2000 to 15 000 g/mol [8]. These properties of lignin reveal that it has a potential to be used as a possible adsorption material to remove heavy metals from waste waters.

Colloidal lignin extracted into pulping liquor by alkali digestion of plant tissue can be precipitated when pH of liquor is made acidic. By treating pulping liquor with selected polymeric flocculants, together with surfactant treatment in many applications, lignin solids agglomerate on reducing pH to 3–4. Typically, dense biomass aggregates form immediately on polymer reaction followed by acidifying, and precipitated biomass accumulations are easily collected from liquor or wash water.

In general, raw lignocellulosic bio-sorbents were modified by various methods to increase their sorption capacities because metal ion binding by lignocellulosic bio-sorbents is believed to take place through chemical functional groups

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such as carboxyl, amino, or phenolics. More recently, great effort has been contributed to develop new adsorbents and improve existing adsorbents. The removal of heavy metal ions using low-cost abundantly available adsorbents: agricultural wastes such as tea waste, coffee and nut shells [9], sawdust and bark [10–13], palm kernel husk [14], peanut skins [15], modified cellulosic materials [16], chemically modified cotton [17], corncobs [18], rice hulls [19], apple wastes [20], coffee grounds [21], bark [22,23], modified bark [24], wool fibers [25], tea leaves [26], and wool, olive cake, pine needles, almond shells, cactus leaves and charcoal [27] were used and investigated.

The present study undertakes the adsorption capacity of modified lignins from beech and poplar woods for the removal of Pb(II) and Cd(II) from aqueous solutions.

2. Experimental

The poplar and beech wood samples were obtained from the Eastern Black Sea region in Turkey. The structural and elemental analyses of the sample are given in Tables 1 and 2.

The ground wood sample (10.0 g), glycerol (75.0 g), and water (25.0 g) were loaded into autoclave in the presence of alkali (0.5–1.0 g). NaOH was used as alkali. The autoclave and its contents were placed on the heater and delignification was carried out at 500 K for 60 min. At the end of reaction, delignification fractions were separated from unreacted wood by filtration and washed with cold water in order to prevent foaming and then with hot water until a clear filtrate was obtained. Under rapid heat up conditions the water present in the mixture can undergo bulk evaporation causing severe foaming.

Aqueous solutions of Pb(II) and Cd(II) were prepared from analytical reagent grade lead and cadmium-sulfates (Merck) with a concentration of 50 mg/L.

Deionized water (200 ml) was added into alkali glycerol delignification solution (100.0 ml) in a 1 l flask. Aqueous HCl solution (3 N) was added into the flask contents till the precipitation was complete (pH about to 2.5). The resulting precipitate was centrifuged, washed repeatedly with equal volumes (5 × 50 ml) of deionized water to remove chloride ions, then dried at 378 K and stored in a vacuum dessicator. The product is purified by preparing a 10% (w/w) solution of lignin in dioxane and then adding it dropwise from a burette into vigorously stirred anhydrous ether, to precipitate lignin again [1]. The precipitate is filtered and washed im-

Table 2
Elemental analyses of wood samples (wt.% daf)

Fuel sample	C	H	N	O (by difference)
Beech wood	48.5	6.4	0.4	45.1
Poplar wood	49.7	6.2	0.4	43.7

mediately with diethyl ether and then benzene, and finally with low boiling petroleum ether, then dried over anhydrous magnesium sulfate under vacuum.

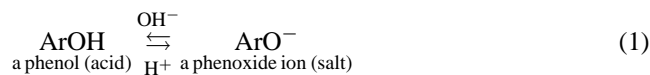
The pH was measured used a Hach-One pH-meter. The concentration of metal ion in the aqueous solution was analyzed by AAS before adsorption experiments. The experiments were carried out in the batch mode for the measurement of adsorption capacities. The bottles with 250 ml capacity were filled with the aqueous solutions and adsorbent. The bottles were shaken for a predetermined period at room temperature in a reciprocating shaker. The separation of the adsorbents and solution was carried out by centrifugation. The adsorption of metal ions by the adsorbents is subsequently calculated by mass balance. Pb(II) and Cd(II) concentrations of the solutions were determined using a GBC 3000 graphite furnace for AAS.

The wavelength and slit values, as nm, used for the determination of Pb(II) and Cd(II) were: 283.3 and 0.5, and 228.8 and 0.5, respectively.

3. Results and discussion

The mechanism for alkaline solvolysis has been suggested by Ivanov and Robert [28]. Their work suggests that an ethanol–water solution transforms soda into a superbase and doubles polysaccharide adsorption of hydroxyl ions. This high ion concentration then leads to rapid cleavage of the intermolecular lignin bonds (especially important in softwood such as poplar and beech) and speeds up delignification. Glycerol is a good delignification agent for wood samples [29]. The yield from non-alkali glycerol delignification of poplar wood was found as 78.2% at 500 K [30].

The organic materials in alkali glycerol delignification liquors consist mainly of dissolved lignin degradation products along with degradation products of hemicellulosic and cellulosic hexose and pentose sugars. The latter are present as saccharinic acids which are anhydrides of the various sugars. Aqueous hydroxides convert phenols into their salts; aqueous mineral acids convert the salts back into the free phenols. As we might expect, phenols and their salts have opposite solubility properties, the salt being soluble in water and insoluble in organic solvents [31].



The lignin degradation products and their sodium salts can be converted into very weak organic acids by treating mineral acids or carbon dioxide. Most phenols have acidity

Table 1
Structural analyses of wood samples (wt.% daf)^a

Fuel sample	Hemicelluloses	Cellulose	Lignin	Extractive matter ^b
Beech wood	33.3	42.1	21.9	2.7
Poplar wood	32.7	43.4	21.4	2.5

^a daf: dry and ash free.

^b Alcohol–benzene extractives.

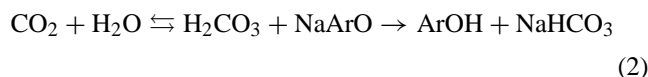
Table 3
Elemental compositions of lignins obtained from the wood samples (wt.%)

	Carbon	Hydrogen	Oxygen	Chemical formula
Lignin from beech wood	61.5	6.3	32.2	C _{5.12} H _{6.3} O _{2.01}
Lignin from poplar wood	63.7	6.2	30.1	C _{5.30} H _{6.2} O _{1.88}

Table 4
Elemental compositions of lignins obtained from alkali glycerol delignifications (AGD) (wt.%)

	Carbon	Hydrogen	Oxygen	Chemical formula
Lignin from AGD of beech wood	68.2	6.2	25.6	C _{5.68} H _{6.2} O _{1.60}
Lignin from AGD of poplar wood	69.4	6.2	24.4	C _{5.78} H _{6.2} O _{1.53}

constants in the neighborhood of 10^{-10} , and are thus considerably weaker than the carboxylic acids (acidity constant is about 10^{-5}). Most phenols are weaker than carbonic acid, and hence, unlike carboxylic acids, do not dissolve in aqueous bicarbonate solutions. Indeed, phenols are conveniently liberated from their salts by action of carbonic acid [32].

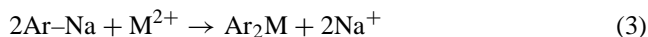


In the Eq. (2), H_2CO_3 is a stronger acid, ArOH is a weaker acid (insoluble in water) and NaArO is a salt (soluble in water). Acidic precipitates mainly consist of phenolics obtained from delignification solutions by aqueous HCl (3 N) precipitation were 38.1% for poplar wood and 35.6% for beech wood. The elemental compositions of lignins obtained from both wood samples are presented in Table 3. The elemental compositions of lignins obtained from alkali glycerol delignifications are given in Table 4.

Toxic metal ion adsorption isotherms of modified lignin are presented as a function of the equilibrium concentration of metal ions in the aqueous medium at 330 K in Fig. 1. The amount of metal ions adsorbed per unit mass of the modified lignin increased with the initial concentrations of metal ions, as expected. The initial concentrations were increased up to 8.0 mg/L for Pb(II) and 6.5 mg/L for Cd(II) in order to reach the plateau values which are available for interaction with metal ions on the lignin samples. The maximum adsorption capacities are 8.2–9.0 and 6.7–7.5 mg/g of the lignin for Pb(II) and Cd(II), respectively.

It is well known that the pH of the solution–lignin mixture is an important variable in the adsorption process. In an alkaline medium lignin molecules are in well dispersed micro-colloidal form. As the pH of the solution is brought down, the solubility of the lignin molecule decreases and a stage comes when due to charge neutralization, the lignin molecules start precipitating. There is variety of chemicals used for coagulation of lignin particles. Most of these coagulants can be placed in two groups—inorganic coagulants and organic polyelectrolytes.

Fig. 2 shows the effect of pH on the adsorption percentage of the modified lignin. As can be seen from Fig. 2, adsorption of both toxic metal ions increases with pH and almost reaches a plateau value around 4.5 for Pb(II) and Cd(II). High adsorption at higher pH values implies that metal ions interact with lignin by ion exchange. The following chemical equations explain this exchange:



where M represents metal, Ar is a functional group of the modified lignin and Ar-Na is the sodium salt of the functional group. Elution of the heavy metal using a mineral acid should occur by a reaction such as

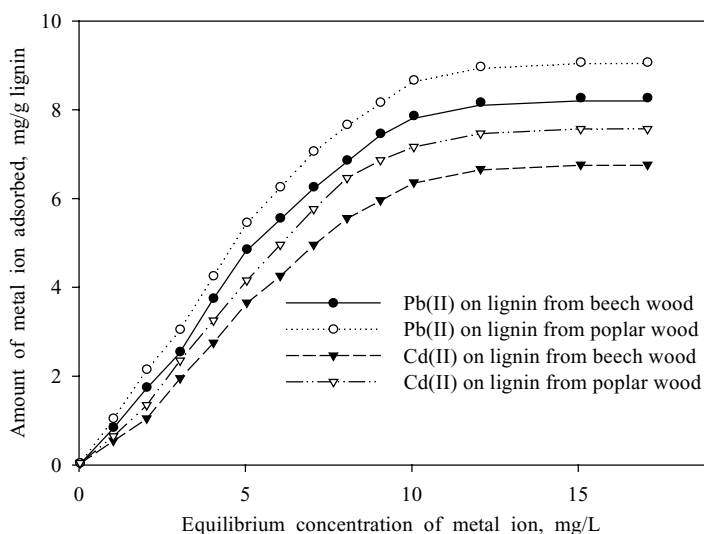
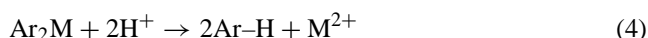


Fig. 1. Adsorption isotherms of metal ions at 330 K.

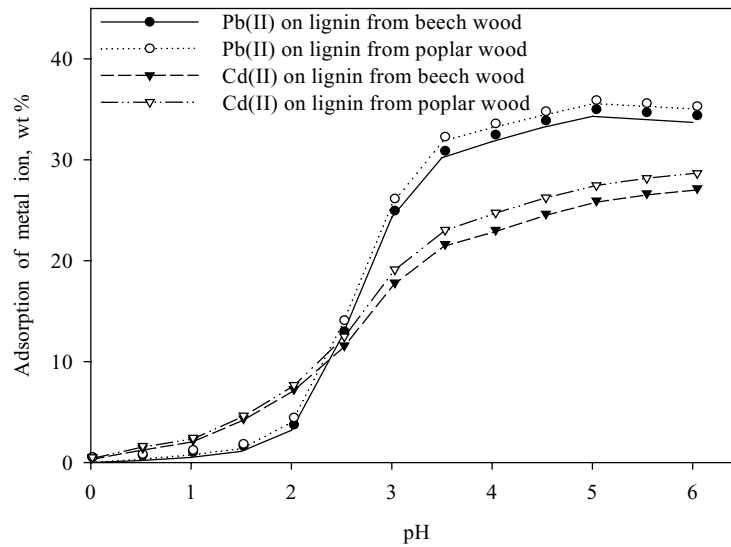
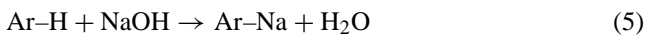


Fig. 2. Effect of pH on adsorption of metal ions by the modified lignin.

Regeneration of the Na^+ form of the Ar-H is possible by the addition of NaOH [33].



Isotherm adsorption models have been used in wastewater treatment to predict the ability of a certain adsorbent to remove a pollutant down to a specific discharge value. When a mass of adsorbent and a waste stream are in contact for a sufficiently long time, equilibrium between the amount of pollutant adsorbed and the amount remaining in solution will develop. For any system under equilibrium conditions, the amount of material adsorbed onto the media can be calculated using the mass balance of Eq. (6):

$$\frac{X}{M} = (C_0 - C_e) \frac{V}{M} \quad (6)$$

where X/M (typically expressed as mg pollutant/g media) is mass of pollutant per mass of media, C_0 is initial pollutant concentration in solution, C_e is concentration of the pollutant in solution after equilibrium has been reached, V is volume of the solution to which the media mass is exposed, and M is mass of the media.

The two commonly used isotherm adsorption models are the Langmuir and the Freundlich models [34,35]. The general Langmuir model defined by Eq. (7):

$$\frac{X}{M} = \frac{K_L C_e}{1 + a_L C_e} \quad (7)$$

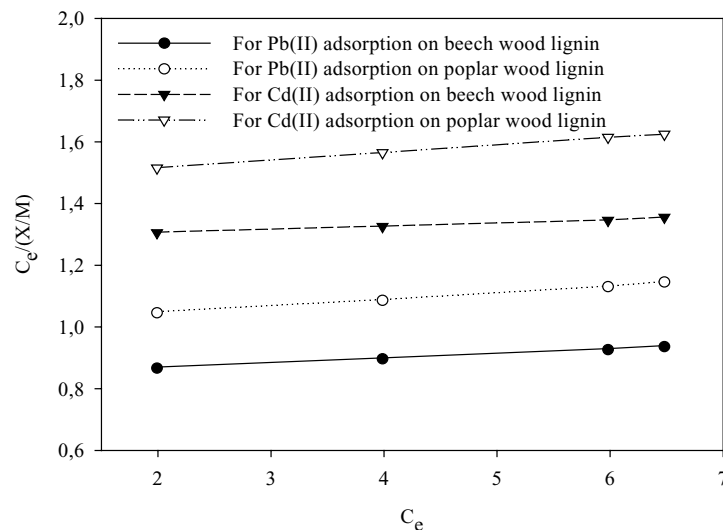


Fig. 3. Langmuir adsorption isotherms of metal ions on modified lignin samples.

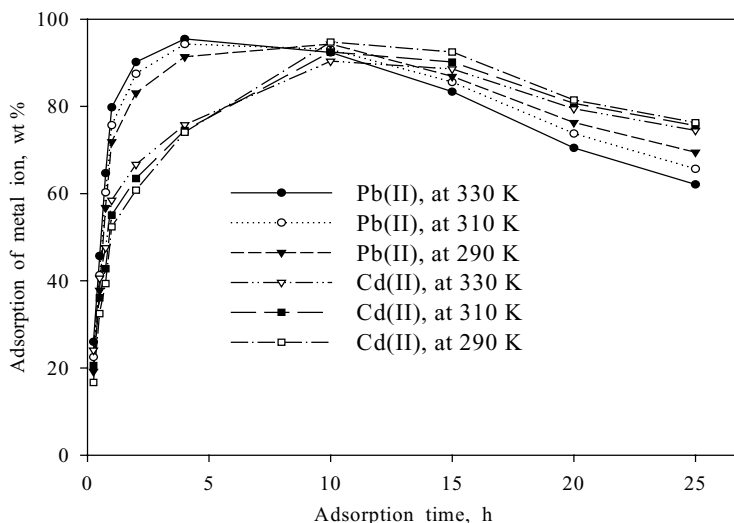


Fig. 4. Effects of time and temperature on percentage of adsorption of metal ions on modified poplar wood lignin.

where K_L and a_L are the isotherm constants. K_L and a_L values can be determined using linear regression. The Langmuir isotherm can be linearized to the following equation:

$$\frac{1}{X/M} = \frac{1}{K_L C_e} + \frac{a_L}{K_L} \quad (8)$$

The general Freundlich equation is:

$$\frac{X}{M} = K_F (C_e)^{1/n} \quad (9)$$

The Freundlich isotherm can also be linearized by the following:

$$\ln \left(\frac{X}{M} \right) = \ln K_F + \frac{1}{n} \ln C_e \quad (10)$$

where K_F and n are adsorption capacity and affinity, respectively.

Fig. 3 shows the plots of $C_e/(X/M)$ versus C_e for both metal ions adsorbed on modified lignin. The linear Langmuir equations for Pb(II) and Cd(II) on lignin in deionized water system were determined to be:

$$\frac{C_e}{X/M} = 0.0154C_e + 0.8389 \quad (11)$$

For Pb(II) adsorbed on poplar wood lignin:

$$\frac{C_e}{X/M} = 0.0220C_e + 1.004 \quad (12)$$

For Cd(II) adsorbed on beech wood lignin:

$$\frac{C_e}{X/M} = 0.0107C_e + 1.2878 \quad (13)$$

For Cd(II) adsorbed on poplar wood lignin:

$$\frac{C_e}{X/M} = 0.0246C_e + 1.4711 \quad (14)$$

For Eqs. (11)–(14), correlation coefficients (R^2) are 0.9990, 0.9972, 0.9920, and 0.9996, respectively.

Fig. 4 shows the effects of time and temperature on percentage of adsorption of metal ions on modified poplar wood lignin. It appears that for a relatively short time period, significant metal removal is obtained. The maximum adsorption percentage is 95.8 for Pb(II) for 4 h at 330 K and is 95.0 for Cd(II) for 10 h at 290 K. The maximum adsorption percentages of Pb(II) and Cd(II) ions decrease with time till 48 and 42 h and then again increase slightly with time. Desorption of metal ions after their initial adsorption (after about 10 h) is illustrated in Fig. 4. The main reason of desorption may be the repelling force between modified lignin surface and the metal ions. The repelling causes the metal ions to approach the lignin surface difficultly and restrains the desorption of the metal ions on the lignin in a great degree.

Cd(II) as well as Pb(II) removal is found to increase with temperature; however, the increase in Pb(II) adsorption with temperature is much greater than the corresponding increase for Cd(II) adsorption.

4. Conclusions

In this study, the inexpensive and effective metal ion adsorbents from wood sources of modified lignin to offer these adsorbents as replacements for existing commercial materials were investigated.

Cadmium is a toxic heavy metal that not only causes choking, abdominal pain, anemia, renal dysfunction, and diarrhea, but also has been listed as a carcinogen by the EPA [36]. Among current technologies used to reduce the amount of heavy metals in water, applications and studies of adsorption method with bio-sorbents have been expanded because of their low-cost [36,37].

The maximum adsorption capacities are 8.2–9.0 and 6.7–7.5 mg/g of the modified lignin for Pb(II) and Cd(II), respectively. The maximum adsorption percentage is 95.8

for Pb(II) for 4 h at 330 K and is 95.0 for Cd(II) for 10 h at 290 K. The maximum adsorption percentages of Pb(II) and Cd(II) ions decrease with time till 48 and 42 h and then again increase slightly with time. The adsorption of both heavy metal ions increases with pH. However, the solubility of modified lignin also increases with increasing pH. High adsorption at higher pH values implies that metal ions interact with lignin by ion exchange.

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