

ADSORPTION OF HEAVY METALS ON CHARCOAL FROM LIGNIN

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Lignin precipitated from black liquor was carbonized at a temperature of 600 °C and the resulting charcoal was used as adsorbent for the removal of heavy metals from aqueous solutions (Pb²⁺, Cd²⁺, Hg²⁺ and Ni²⁺). The particle diameters and the morphology of the prepared coal were investigated. The adsorption properties of charcoal from lignin were explored under batch conditions and the results were compared to a commercial homologue used in water treatment. The kinetic study of the investigated adsorbent (lignin-based coal, CL), as well as that of the commercial (CC) substrate, was also performed. Then, the regeneration of the charcoal was achieved using diluted ethylene diamine tetra-acetic acid (EDTA) and nitric acid (HNO₃) as desorbing solution. Finally, the thermodynamic parameters, free energy of adsorption ΔG° , entropy ΔS° and enthalpy ΔH° for the adsorption process were determined and the mechanism of the adsorption was studied by zeta potential measurement. It was concluded that the charcoal from lignin may be used as a high capacity and reusable sorbent material in heavy-metal removing processes.

Keywords: lignin, charcoal, heavy metals, adsorption

INTRODUCTION

Increasing amounts of heavy metals are currently rejected by industrial and agricultural activities. The presence of such substances leads to the accumulation of metal ions in various animal and vegetal organisms and their transfer to humans through the food chain. They are not biodegradable, potentially toxic and tend to accumulate in living organisms. Consequently, various diseases have appeared, thus constituting a serious public health problem. The treatment of heavy metals is of particular concern because of their recalcitrance and persistence in the environment.

Today, the squeezing of heavy metals is a priority in terms of environmental issues. In fact, they have become one of the most serious environmental problems.¹ In this context, the accumulation of heavy metals in water, air and soils is a serious environmental problem that affects almost all countries. It is, therefore, necessary either to totally eliminate the heavy metal ions present in various industrial effluents, or at least to reduce their concentrations below tolerated thresholds established by common standards.

Lignin, a natural polymer derived from plant biomass, is a largely generated industrial waste. It is present in high quantities in the cell walls of the plants; typically comprising 16 to 33% of the plant biomass.² Lignin has a three-dimensional complex aromatic structure, containing a number of functional groups, such as methoxyl, hydroxyl, carboxyl and aldehyde groups.^{3,4} It was recently found that lignin has a potential for adsorbing heavy metals from wastewater. In fact, it was used for the removal of heavy metal ions from aqueous effluents.^{2,5-9} Moreover, lignin has recently found applications in the field of adhesives, cosmetics and as a precursor for producing activated carbon, a well-known and extremely useful adsorbent.¹⁰⁻¹³

The composition and structure of lignin units varies depending on the source of the biomass from which the lignin is extracted. Globally, each year about 50 million tons of lignin are generated by the paper industry,¹⁴ but less than 10% of them are used in applications other than combustion in order to achieve an energy recovery. The reuse of lignin can bring additional revenue for the industry.¹⁵

In kraft pulping, lignin is separated from cellulose fibers. Cellulose is used for papermaking, and the lignin is dissolved in the pulping phase (known as the "black liquor"), and then is sent to a recovery system.

The objective of the present work is to investigate the potential use of charcoal from lignin (CL) as an adsorbent of heavy metal ions in water solutions. The tested lignin was extracted from black liquor before being carbonized. The evolution of the adsorption kinetics and isotherms was investigated according to the metal concentration and the metal type. A possible mechanism for the metal adsorption is proposed and discussed. For comparison purposes, commercial charcoal (CC) was also used and the data were compared to those obtained for the coal produced from lignin, i.e., CL. This material is cheap, biodegradable, renewable and environmentally friendly.¹⁶

EXPERIMENTAL

Materials

Commercial charcoal was purchased from Aldrich Company. Black liquor, containing the lignin under investigation, was obtained from the National Pulp and Paper Company in Kasserine (Tunisia). It was a kraft lignin from *Stipa tenassissima* annual plant. The precipitation process was carried out as follows: 100 g of concentrated black liquor was diluted in 500 mL of distilled water and filtered on a Nylon screen with aperture of 70 μm . This operation induced the precipitation of some fibers and solid objects, which were removed. Then, diluted sulfuric acid was dropwisely added and the obtained black liquor centrifuged at 4000 rpm, for 15 min. The precipitated lignin was isolated by filtration, extensively washed and centrifuged several times using distilled water. The purification process was stopped when no acid traces were detected, as indicated by the pH of the filtrate. The obtained lignin was dried for 24 h at room temperature, and then in an oven at 40 °C till a constant weight was reached.

Pyrolysis consists of the thermal decomposition of organic materials under vacuum or under inert atmosphere at temperatures between 400 and 1000 °C. The studied material becomes richer in carbon, indicating that heteroatoms (oxygen and hydrogen) are eliminated under the effect of heat. The remaining carbon atoms are organized in the form of layered aromatic planar structure. Then, these sheets are arranged in an irregular manner, leaving interstices.

Lignin precipitated from black liquor has been carbonized in an electric tube furnace, equipped with a gas system, temperature control, as well as heating rate and residence time programmers. This operation was carried out at a heating rate equal to 10 °C/min up to a

temperature of 600 °C and under continuous nitrogen flow rate between 200 and 300 cm³/min, in order to prevent the combustion of lignin.

The carbonization rate and the "Burn-off" index are determined according to the following equations:

$$\text{Yield (\%)} = (\text{final weight}/\text{initial weight}) * 100 \quad (1)$$

$$\text{Burn off (\%)} = [(\text{initial weight} - \text{final weight}) / \text{initial weight}] * 100 \quad (2)$$

Generally, in the industry, heavy metals have a density greater than 5 g/cm³, high atomic number, typically higher than that of sodium ($Z = 11$), and present a hazard for the environment and/or man. The heavy metals usually associated with the concepts of pollution and toxicity are: arsenic (As), cadmium (Cd), chromium (Cr), copper (Cu), mercury (Hg), manganese (Mn), nickel (Ni), lead (Pb), tin (Sn), and zinc (Zn).

In this work, Pb, Cd, Hg and Ni were used, in the form of lead nitrate (Pb (NO₃)₂), cadmium acetate dihydrate (CH₃CO₂)₂Cd.2H₂O, nickel nitrate hexahydrate (Ni(NO₃)₂.6H₂O) and mercuric chloride (HgCl₂). They were commercial products with the highest purity available. All the other reagents were commercial products and were used as received.

Characterization

Laser diffraction is a common technique for measuring airborne particle size. Its principle is based on the fact that particles passing through a light beam (here a monochromatic laser beam) diffract light at a different angle, depending on their size. Small particles diffract at high angles, while larger particles diffract at small angles. Knowing the wavelength of the incident beam and measuring the angles of diffraction, the particle size may be determined based either on Fraunhofer's theory, or on that of Mie.

Fraunhofer's approximation applies only for particles whose size is much larger than the incident wavelength. Otherwise, if the particle size is less than or comparable to the wavelength, Mie's theory applies.¹⁷

The laser sizer used was a Cilas device 1190. It can measure particle diameters varying from 0.04 to 2500 microns. The suspensions to be analyzed were injected into the tank, under continuous stirring for better dispersion. The amount of injected particles is controlled by the obscuration bar. During the dispersion phase, the particles are subjected to a treatment with ultrasound to break down the aggregates. The morphology of the samples was examined by scanning electron microscopy, using an ULTRA55 Zeiss, with an acceleration voltage of 12.5 kV.

Adsorption

Different concentrations of the metal solutions ranging from 1 to 800 ppm were prepared. After adjusting the pH to 5 by dilute solutions of

hydrochloric acid (HCl) and sodium hydroxide (NaOH), 100 mg of charcoal were added to each tube.

The sealed vials were thermostated at the desired temperature on a BIOSAN rotary shaker (Rocker-Shaker MR-12) at a constant speed of 90 rpm. Once equilibrium was reached, the samples were filtered through membrane filters of 0.45 μm . Then, the concentration of residual metal remaining in the aqueous solution was analyzed by atomic absorption using a Perkin-Elmer 560 spectrophotometer (Perkin Elmer Cetus Instruments, Norwalk, CT). The solutions were diluted prior to analysis.

The quantity of the adsorbed cation, q_e (mg/g), was calculated following Eq. 3:

$$q_e = (C_0 - C_e)V / m \quad (3)$$

where: C_0 is the concentration of the initial solution in (mg/L); C_e is the concentration of the final solution in (mg/L); V is the volume of the solution containing metallic cations in (ml); m is the weight of charcoal used as adsorbent in (g).

Adsorption experiments were also carried out continuously under isothermal conditions and using a column filled with granular carbon. The column used was a glass jacketed column of 10 mm in diameter and 10 cm length, packed with about 2.7 g of charcoal. Isothermal conditions in the column were obtained by passing water at ambient temperature. The metal solution was introduced through the column in the countercurrent mode (from bottom to top) using a highly precise peristaltic pump. The effluent samples were taken at regular intervals (15 tubes per minute at the beginning and then every 5 minutes) and the concentrations were titrated by the atomic absorption technique.

Kinetic study

The kinetic study of the investigated CL adsorbent, as well as that of commercial substrate CC, was performed. A metal solution of 10 ppm was prepared and divided into several vials; each one of them contained 10 ml of the solution. Then, 10 mg of coal

were added to each vial and then left under stirring. Finally, the samples were taken within regular intervals of 5 min during 3 hours of experiments.

Regeneration of charcoal

The regeneration of the charcoal was carried out using ethylene diamine tetra-acetic acid (EDTA) and nitric acid (HNO_3) as desorbents. The coals were soaked in 100 mL of 10^{-2} M EDTA solution or HNO_3 to pH 5, and maintained under stirring for 3 h. The regeneration cycles were repeated several times.

Thermodynamic parameters (ΔH° , ΔG° and ΔS°)

The thermodynamic evaluation of the adsorption process was carried out with the preparation of metal solutions with a fixed concentration and pH. The temperature varied from 35 to 55 $^\circ\text{C}$ in a thermostated bath for 24 hours.

RESULTS AND DISCUSSION

Charcoal characterization

The analyses of the two charcoal types (Table 1) show that the content of carbon atoms in the lignin-based material is relatively low compared with that associated to the commercially available adsorbent, which could indicate that the pyrolysis process did not remove all the heteroatoms. This is confirmed by the higher amount of residual hydrogen, oxygen and nitrogen. The lignin-based charcoal is much more contaminated by sulfur atoms.

A morphological study was conducted to observe the structure of the charcoal particles. In fact, both commercial and experimental samples were assessed by scanning electron microscopy (SEM). The SEM observations show clearly that the morphology of the two materials is quite similar (see Fig. 1).

Table 1
Yield, ash content and elemental analysis (in % w/w) of both investigated materials

Coal	Yield	Ash content	Elemental analyses(%)				
			C	O	H	N	S
Lignin-based	37.63	14.75	70.05	13.01	2.61	1.93	1.12
Commercial	-	-	81.64	11.74	1.59	0.48	0.2

The particle size and particle size distribution were also determined and the results are given as curves representing the cumulative volume particle size for each class, as shown in Fig. 2. The particle diameters at 10%, 50% and 90% by volume percentage for CL are 9.5, 51.4 and 119.8

microns, respectively, whereas for the commercial coal, these values are lower, i.e., 5.5, 33.9 and 90.6 microns, respectively. This result indicates that the apparent specific surface area of the lignin-based charcoal is lower than that of the commercial one.

Kinetic study

The change in the adsorbed amount of metal ions with time was studied in order to determine the equilibration time for the maximum adsorption capacity and to assess the adsorption kinetics. These data allow establishing the efficiency of the sorbent in continuous flow systems. Indeed, the faster is the adsorption kinetics, the lower is the required contact time and the quicker is the trapping of the metal pollutant under dynamic filtration. For this study, a number

of kinetic models have been used and Pb^{2+} and Cd^{2+} were selected as the metal ions.

From Fig. 3a, it can be seen that the adsorption process was not quick enough and approached approximately 77% of the capacity of maximum adsorption in 60 min for both studied metals. After this period, the adsorption rate decreased and the saturation of the surface was reached after 2 hours. For the commercial charcoal (shown in Fig. 3b), the adsorption process was faster, with about 60% of the adsorption capacity reached in 20 min. The saturation was attained after 80 min.

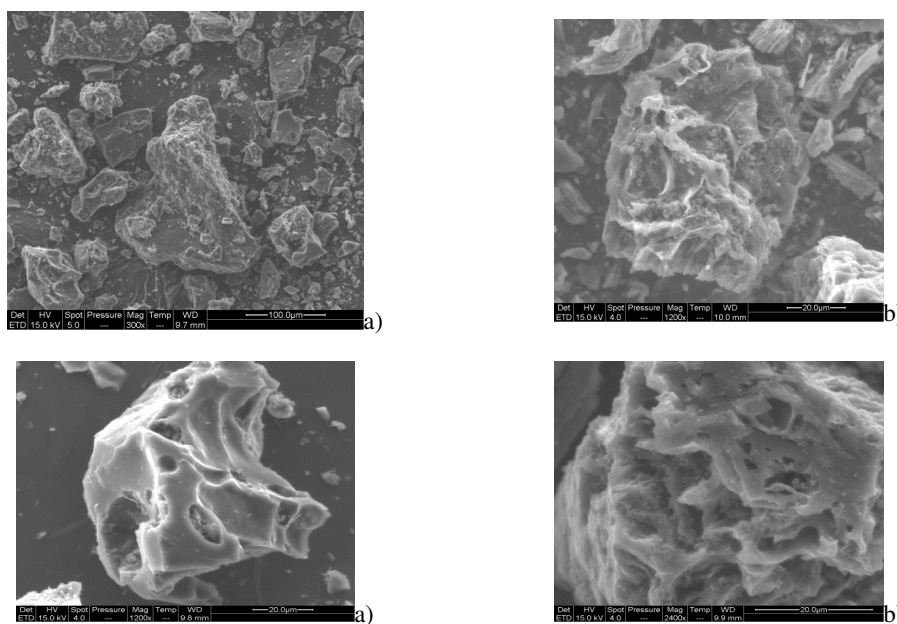


Figure 1: SEM images of lignin charcoal (a) and of commercial charcoal (b) – two different magnifications

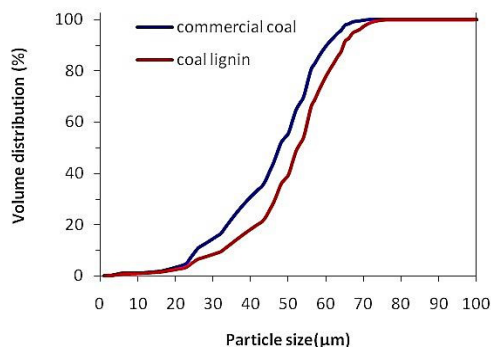


Figure 2: Particle size distribution of coal lignin and commercial coal measured by laser diffraction

From the graphical representation of the variation of $\ln(q_e - q_t)$ as a function of time, K1 and q_e can be determined, as shown in Fig. 4. Such a presentation shows clearly that the adsorption kinetics obeys the first order model.

Thus, applying the first order equation to the CL for both metals, one can observe that the correlation coefficient (R2) is relatively good. Table 2 summarizes the values of these kinetic

parameters for both lignin-based and commercial

charcoals.

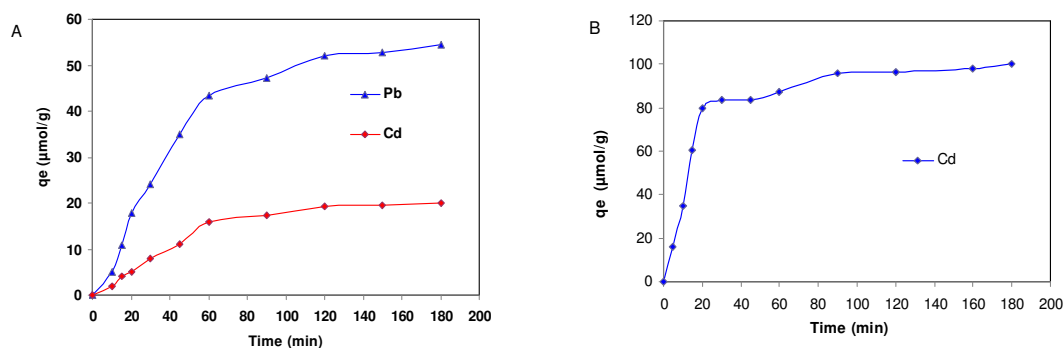


Figure 3: Kinetics of adsorption of Pb^{2+} and Cd^{2+} on (A) lignin-based charcoal and Cd^{2+} on (B) commercial coal at pH 5

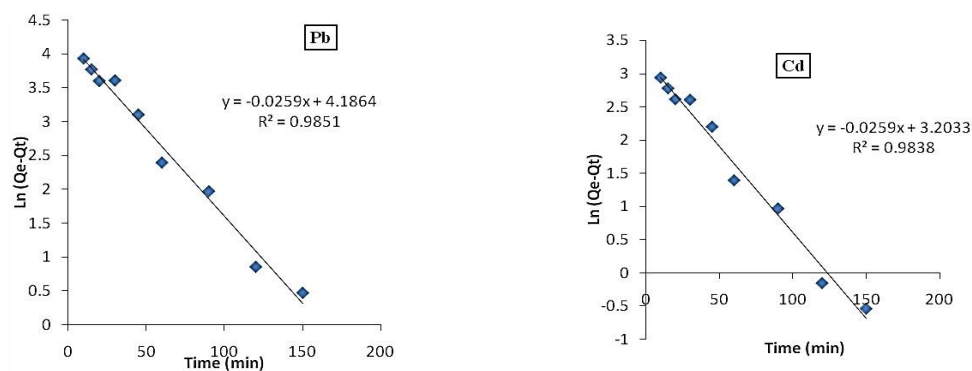


Figure 4: First order kinetics plot for the adsorption of Pb^{2+} and Cd^{2+} on lignin-based charcoal

Table 2
Values of maximum Pb^{2+} and Cd^{2+} adsorption and kinetic parameters

Coal	Metal	First order		Second order	
		Adsorption parameters	Value	Adsorption parameters	Value
Lignin-based	Pb^{2+}	R^2	0.99	R^2	0.18
		K_1 (min^{-1})	0.0259	K_2	$2.24 \cdot 10^{-5}$
	q_e ($\mu mol \cdot g^{-1}$)	65.78	q_e ($\mu mol \cdot g^{-1}$)	169.5	
	R^2	0.98	R^2	0.40	
Commercial	Cd^{2+}	K_1 (min^{-1})	0.0259	K_2	$1.6 \cdot 10^{-3}$
		q_e ($\mu mol \cdot g^{-1}$)	24.61	q_e ($\mu mol \cdot g^{-1}$)	50
	R^2	0.80	R^2	0.96	
	K_1 (min^{-1})	0.04	K_2	0.0106	
		q_e ($\mu mol \cdot g^{-1}$)	45.53	q_e ($\mu mol \cdot g^{-1}$)	1.22

Table 3
Langmuir constants associated to Hg^{2+} and Pb^{2+} for the two charcoals tested here

Absorbent	Metal	Parameters	Values
Lignin-based (CL)	Hg^{2+}	R^2	0.99
		K_L ($L \cdot mol^{-1}$)	59149
		Q_s	$2.35 \cdot 10^{-4}$
		R^2	0.94
Commercial (CC)	Pb^{2+}	K_L ($L \cdot mol^{-1}$)	16543
		Q_e	$3.15 \cdot 10^{-4}$

Table 4
Freundlich constants associated to the four metals, for the two charcoals tested here

Absorbent	Metal	Parameters	Values
CL	Cd ²⁺	R ²	0.97
		K _F	4020
		N	2.96
	Pb ²⁺	R ²	0.94
		K _F	207443
		N	0.95
	Ni ²⁺	R ²	0.83
		K _F	121059
		N	0.91
	Commercial coal	Cd ²⁺	R ²
K _F			6781
n			2.53
Hg ²⁺		R ²	0.96
		K _F	10957
		n	1.90
		R ²	0.91
Ni ²⁺	K _F	17386	
	n	1.51	

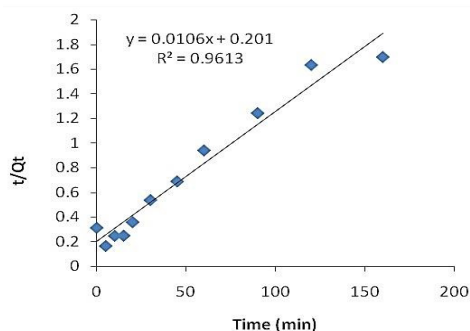


Figure 5: Second order kinetics plot for the adsorption of Cd²⁺ on commercial charcoal

The kinetics of cadmium adsorption onto the commercial charcoal fitted much better the second order kinetic equation (Fig. 5). This model is based on the assumption that the step preceding the chemisorption is the adsorption. This phenomenon involves forces and exchange of electrons between the adsorbent and the sorbate.¹⁸

Adsorption isotherms

The adsorption isotherm is fundamental in studying the adsorption aptitude of the substrates and helps to establish the most appropriate conditions for the adsorption under continuous flow. The adsorption isotherms of metals having different ionic radius size on LC and CC are shown in Fig. 6. For the two types of charcoal, the adsorption capacity values ranged from 200 to 600 $\mu\text{mol/g}$, depending on the metal ions under investigation. For both charcoals, the highest

capacity was reached with Cd²⁺ (about 600 $\mu\text{mol/g}$).

These isotherms are used to establish the maximum adsorption capacity of the adsorbate on the adsorbents in $\mu\text{mol/g}$. As mentioned before, 4 metals (Pb²⁺, Cd²⁺, Hg²⁺ and Ni²⁺) and two solid substrates (lignin-based and commercial charcoals) were used (Fig. 6). These isotherms were modeled according to Langmuir and Freundlich equations.

Electrokinetic properties of charcoal

To study the adsorption mechanism, the zeta potential of the charcoals in the presence or absence of metal ions was investigated. The variation of the zeta potential with pH, which reflects the change in the surface charge with pH, for the CL and CC, is shown in Fig. 7. The CL and CC had a point of zero charge (PZC) around a pH of 2, became negatively charged above a pH

value of 2.5-3, and reached a plateau over a pH of 5. These charges arose from ionisable and ionic groups present on the surface of the charcoal formed during the pyrolysis process. Among these chemical functions, the carboxylic, sulfate, quinone, lactone and phenol are to be mentioned. However, the magnitude of the zeta potential at the plateau was much lower for CL compared to that of CC (i.e., -35 mV for the former against -8 mV for the latter). This is indicative of higher surface density in the negatively charged groups of CL, compared with its CC counterpart. These ionized or ionic negative charges constituted a

binding site for the adsorption of metal ions *via* electrostatic interactions and/or ionic exchange mechanisms.

At pH 5, the addition of metal cations to the charcoal, CL, led to a steady growth in the zeta potential until a plateau from around -5 to -10 mV was reached (Fig. 8), indicating a decrease in the density of negative charges. This result confirmed that the adsorption of metal ions by the charcoal from lignin was driven by electrostatic attraction between the negative charge on the charcoal and the positive metal cations.

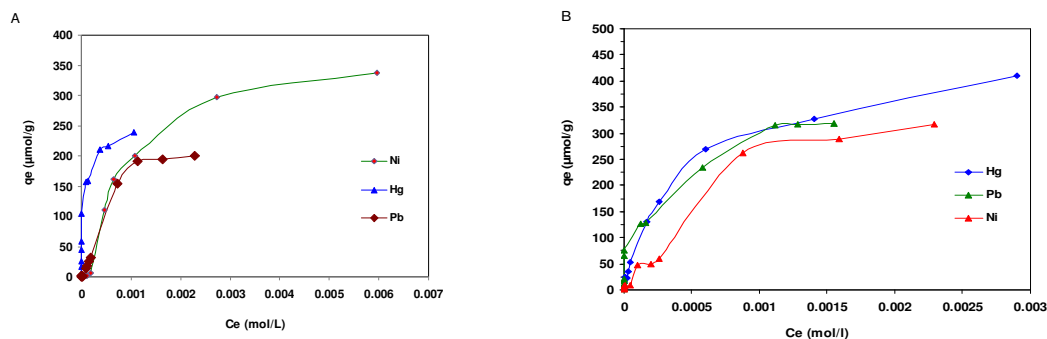


Figure 6: Adsorption isotherms of heavy metal ions (Pb^{2+} , Hg^{2+} and Ni^{2+}) onto (A) lignin-based and (B) commercial charcoals

Table 5

Thermodynamic parameters of the adsorption for the 4 metallic cations on lignin-based and commercial charcoals

Adsorbent	Metal	Temperature (K)	ΔG° (KJ.mol ⁻¹)	ΔH° (KJ.mol ⁻¹)	ΔS° (KJ.mol ⁻¹ .K ⁻¹)	Adsorption capacity (mg.g ⁻¹)
CL	Pb^{2+}	308	-4.74			43.20
		318	-8.04	96.90	0.33	22.58
		328	-11.34			26.98
	Cd^{2+}	308	-16.63			72.90
		318	-18.13	29.57	0.15	88.72
		328	-19.63			101.48
	Ni^{2+}	308	-16.72			83.90
		318	-19.26	54.11	0.23	106.65
		328	-21.32			131.57
	Hg^{2+}	308	-16.73			72.93
		318	-18.86	48.87	0.21	85.14
		328	-20.90			118.16
Commercial coal	Ni^{2+}	308	-14.40			136.30
		318	-16.07	37.03	0.16	179.34
		328	-17.74			248.16
	Hg^{2+}	308	-13.48			59.65
		318	-15.08	35.80	0.16	84.31
		328	-16.68			92.01

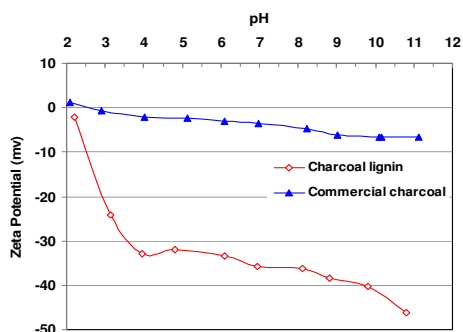


Figure 7: Variation of zeta potential of CL and CC at different pH

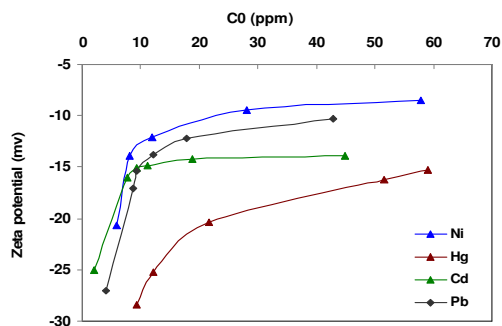


Figure 8: Variation of zeta potential of CL vs metal ion concentration for Pb²⁺, Ni²⁺, Cd²⁺ and Hg²⁺ at pH 5

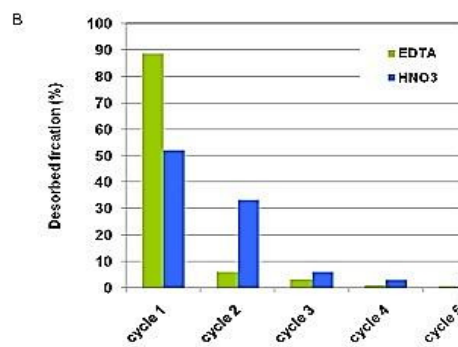
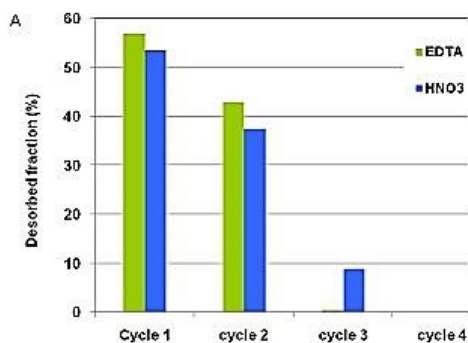


Figure 9: Desorbed amount using EDTA and HNO₃ stripping solutions for metal ions on (A) charcoal lignin, and (B) commercial charcoal (initial concentration = 200 ppm; adsorbent dosage: 50 mg in 50 ml; pH 5; EDTA and HNO₃ solutions: 10⁻³ M)

Thermodynamic parameters

The thermodynamic parameters, free energy of adsorption ΔG° , entropy ΔS° , and enthalpy ΔH° for the adsorption process by the coal were determined using the Van't Hoff equation (Eq. 4):

$$\ln K_c = \ln \frac{q_e}{C_e} = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (4)$$

where K_c is the equilibrium distribution coefficient ($K_c = q_e/C_e$), q_e and C_e – the adsorbed amounts at equilibrium and the equilibrium concentration, respectively, R – the gas constant (8.314 J mol⁻¹ K⁻¹) and T – the temperature (K).

The enthalpy change was obtained by calculating the slope of a plot correlating $\ln K_c$ versus $1/T$. The obtained parameters for Pb are listed in Table 5.

The adsorption free energy (ΔG°) was negative under all the tested conditions, their solvating water molecules were stripped off. This dehydration process requires energy and presumably it exceeded the exothermic heat

produced by the metal ions attaching to the adsorbent surface. The ΔS° was also positive, indicating an increased randomness at the solid/solution interface during the adsorption process, even though the metal ions were immobilized on the adsorbate. This was probably due to the higher mobility gained by water molecules lost by the adsorbate ions, thus allowing the increase in the randomness in the system.

The adsorption capacity of Pb, Cd, Hg and Ni enhances by increasing the temperature from 35 to 55 °C. The thermodynamic adsorption parameters: free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°), were determined and are given in Table 5. These data explain the mechanism of the adsorption process of different metals by the lignin-based and commercial charcoals.

Generally, the value of ΔG° for an ion exchange mechanism is in the range of 8 kJ/mol to -16 kJ/mol.¹⁹ According to Weng *et al.*,²⁰ these values indicate that the adsorption mechanism is

due to the attraction of anions to the electropositive surface of the acidic sites of lignin.

Adsorbent regeneration

The desorption of the adsorbed metal ions from the exhausted coal was also studied by a batch equilibrium method, using HNO₃ and EDTA solutions. The obtained results showed that the EDTA solution gave the best performance with desorption efficiencies approaching 100% after two desorption cycles in a 10⁻³ M EDTA solution, while in the HNO₃ solution, the desorption efficiency was limited to about 90% of the adsorbed metal after four desorption cycles (Fig. 9). The change in the metal ions and in the adsorbed amount did not lead to a meaningful change in the result. The low efficiency of the acid solution to release the adsorbed metal ions is presumably the result of the high binding capacity of the ionic and acid surface sites *via* electrostatic binding interaction. Hence, to release the adsorbed cations, it is necessary to use a strong chelating agent with high complexing capacity to the metal ions. The EDTA coordinated metal is no longer capable to interact with the negatively charged groups on the surface of the adsorbent. After the regeneration of the charcoal, no appreciable loss of the adsorption capacity was noted.

CONCLUSION

Charcoal was successfully produced from lignin precipitated from black liquor, a by-product arising from the pulping industry of alfa grass (*Stipa tenacissima*). The produced charcoal was carefully characterized and used as an adsorbent for four heavy metal cations. The adsorption kinetics were established and found to fit very well with first-order and second-order kinetic models and the kinetic parameters were deduced. The adsorption isotherms were also studied and found to obey the commonly used Langmuir and Freundlich models. Finally, batch and column adsorption processes were used to test the capacity of adsorption and the ability of regeneration of these adsorbents and gave very promising results. Zeta potential measurements suggested that the adsorption was driven by an ion exchange process and by the electrostatic interaction between the negatively charged sites on the coal surface and the metallic cations.

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