Sorption of Hg^{2+} and Pb^{2+} Ions from Aqueous Solutions on Corn Cobs Biomaterials

I. Study of sorption equilibrium of Hg^{2+} and Pb^{2+} cations on corn cobs

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The sorption capacities of grinded corn cobs for Hg^{2+} and Pb^{2+} cations from wastewaters were established for various particle dimensions and pH values. The (local) structure of Hg^{2+} and Pb^{2+} sorbed on corn cobs biomass has been investigated by secondary electron microscopy (SEM) and energy-dispersive X-ray analysis (EDX). The sorption isotherms indicate a slightly greater affinity for the Pb^{2+} cations, compared to the Hg^{2+} ones. The Langmuir model equation satisfactorily characterizes the experimental results. The values of calculated free energy changes correspond to physical actions, IR spectres and the structural modifications evidenced by electronic microscopy (SEM) analysis on biomass samples after Hg^{2+} or Pb^{2+} ions retention indicate that the heavy –metals binding mechanism is mainly a physical interaction and ion exchange process.

Keywords: copolymers, amide functional groups, mercury, lead, sorption, wastewaters

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Pollution due to heavy metals represents an important environmental problem due to their toxic effects towards humans, plants and animals. Heavy metals are non-degradable and present a tendency to accumulate throughout the food chain. Their chemistry is rather complex, and after some lands or aqueous basins are impregnated with heavy metals, their ions are released for long time intervals, even after pollution source elimination. Heavy metals contaminants exist in aqueous wastewaters of many industries, such as metal finishing, chemical manufacturing, mining operations and tanneries [1]. Lead(II) and mercury(II) are among the most dangerous. Lead forms complexes with oxo-groups in enzymes to affect virtually all steps in the process of hemoglobin synthesis and porphyry metabolism [2]. Mercury attacks brain, lungs, and kidneys and also causes skin cancer in most severe form [3].

Adsorption has been shown to be an economically feasible alternative method for removing heavy metals from wastewater and water supplies. Low cost adsorbents are preferred, and among them, many biomaterials found as natural products or as industrial or agricultural wastes were recommended. Biomass resulting from various natural or industrial sources may be used as sorbent material to remove heavy metals from wastewater [4, 5].

There are studies on the use of apple wastes[6], bacterial & algal biomass [7, 8], bark[9], chitosan[10], coconut fiber [11], corn cobs [12], feathers[13], fungal biomass [14], grape stalks[15], chitosan[16], leaves[17], maize cob and husk [18], marine algae [19], moss peat [20], polymerized orange skin and banana husk[21], residual lignin[22], sawdust [23], wool [24],etc.

The accumulation of those metals by biomass and the major interaction mechanisms are based on ionic interactions and complex formation between metal cations and active centers or groups contained in biomaterials [25].

In this paper study on the Hg^{2+} and Pb^{2+} sorption on corn cobs has been made. The corn cobs resulted as agricultural waste are among the less costly biomaterials available. The corn cobs composition was: 42.96% - cellulose, 13.73% - lignin, 21.50% - pentosan, 6.25% - waxes and resins, 4.01% - proteins, 4.75% - ash, 6.78% - humidity. The biomaterial physical characteristics were (as mean values): porosity 52.66%, specific surface 52.98 m^2/g, pore mean radius 173 Å, total adsorption capacity 0.75 mmol/g [26].

Experimental part

All the experiments have used as sorbent a cellulose-containing material produced by agriculture – corn cobs. The biomass was at first grounded and thereafter washed with distilled water until the organic substances content in the washing water (CCOMn) decreased below 2.5 mg O_2/L. The sorbent particles were subsequently dried at 105°C for 2 h and divided into fractions by sieving. The present study used the fractions with diameters d<1mm.

The monocation synthetic solution concentrations were: 0.86, 1.47, 2.02, 2.69, 3.65, 6.73, 12.88, 19.13mmol/L for Hg and respectively 0.12, 0.51, 0.98, 1.176, 2.65, 9.8, 14.32, 19.606 mmol/L for Pb^{2+}, covering the spectrum of the Hg^{2+} and Pb^{2+} ion concentrations in wastewaters resulting from different processes. The solutions were prepared using as ion source $HgCl_2$ and respectively $Pb(NO_3)$.

The batch experiments contacted the sorbent with the respective solutions at solid/liquid ratios C_B = 1g/L. According to preliminary tests, the necessary time for equilibrium attainment in the solid-liquid studied systems is about 200 min. In order to ensure the certitude of the real equilibrium attaining, the suspension was stirred by a magnetic rod for 24 h, and then filtered. The liquid phase was thereafter analysed for metal ions determination, using an SOLAAR 32 atomic absorption spectro-photometer. The working temperature was 20.0 ± 0.5°C. The pH was maintained at the value of 5.01 ± 0.02 units using Tritisol – Merck buffer solutions and its value was recorded by a Jenway 370 pH-meter.

The *p*H values vary in the interval 3÷6; at values less than 2 can observe biomass degradation, and at higher *p*H values Pb^{2+} ions precipitation can occur. The corn cobs particles used as biosorbent have the dimensions d<1mm.

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The procedure was similar to the one previously presented for sorption isotherms determination.

In order to identify the groups that may form bonds between the metal ion and the biosorbent, the solid-phase infrared spectre of the untreated biomass was determined, on a SP IR-620, JEASCO-2000 spectrophotometer, using anhydrous KBr as binding medium.

The electronic emission method (SEM) was used in order to identify the fine structure and the microstructure particularities of the biomass. An electronic microscope HITACHI S2600N with EDAX gauge was used.

Results and discussions

Biomass sorption isotherms for the Hg^{2+} and Pb^{2+} ions

The biosorbent adsorption capacity was determined by mass balance, as difference between the mass of metal ions existed initially in solution and the mass of metal ions in solution at equilibrium, reported to the biomass introduced in the system.

The calculation relationship was:

$$a = V(C_i - C_e)/m \quad (1)$$

Where:

a represents the quantity of metal ions retained by the mass unity of sorbent, mmol/g;

V – the volume of initial metal ion solution used, L;

C_i, C_e - the initial and respectively final (at equilibrium) concentration of metal ion in solution, mmol/L;

m - mass of dry adsorbent, g.

The experimental results obtained are presented in figures 1.

The maximal adsorption capacity value for the ions Hg^{2+} and Pb^{2+} are of about 0.65 mmol Hg^{2+}/g, and 0.98 mmol Pb^{2+}/g respectively. The sorption capacities for Pb^{2+} are higher than the ones for the ion Hg^{2+} at all *p*H values, which indicates a greater affinity for the Pb^{2+} ions.

In order to characterize the sorption equilibrium, the experimental data were fitted into equilibrium isotherm models elaborated by Langmuir and Freudlich.

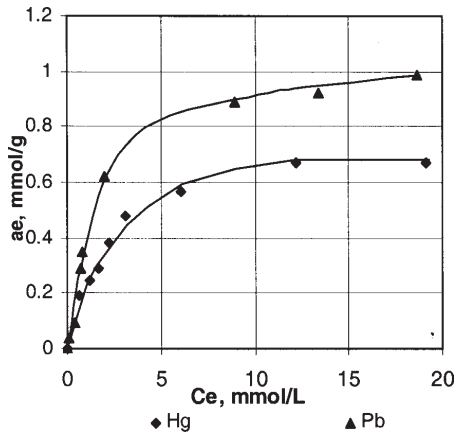

Fig. 1. Hg^{2+} and Pb^{2+}sorption isotherm
(T = 20.0 ± 0.5°C; *p*H = 5.01 ± 0.02, C_B = 1g/L)

Comparison of experimental isotherms with Langmuir model

The characteristic equation of the Langmuir isotherm model is:

$$a_e = \frac{ba_mC_e}{1+bC_e} \quad (2)$$

where:

a_e represents the adsorption capacity at equilibrium, mmol/g,

a_m - the maximal adsorption capacity at equilibrium, upon complete saturation of the mono-molecular layer, mmol/g;

C_e - the concentration of metal ion in solution at equilibrium, mmol/L;

b - equilibrium constant related to the adsorption/ desorption energy.

The liniarized form of Langmuir equation, after terms rearrangement is:

$$\frac{1}{a_e} = \frac{1}{a_m} + \frac{1}{ba_mCe} \quad (3)$$

The constant b and the maximal sorption capacity a_m can be determined from equation (3) writing $1/a_e$ values as function of $1/C_e$. The graphical representation of the liniarized Langmuir equation, $1/a_e = f(1/C_e)$, for the two ions are presented in figure 2.

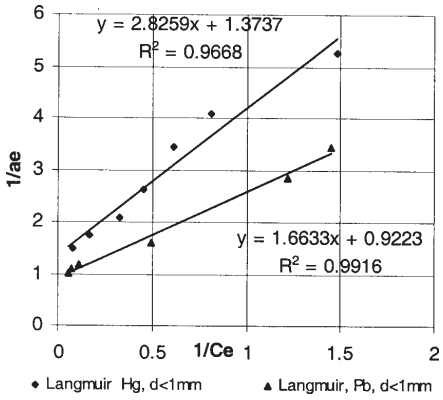

Fig. 2. Experimental data fitting into the liniarized Langmuir equation

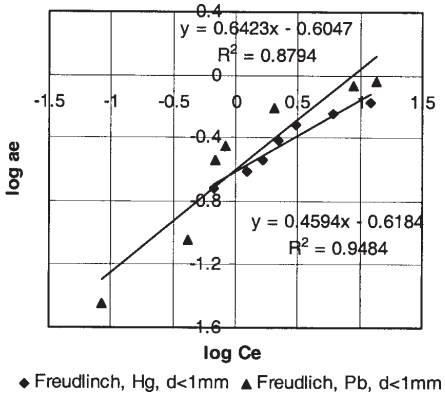

Fig. 3. Experimental data fitting into the liniarized Freudlich equation

The values of the maximal adsorption capacity „a_m", equilibrium constant „*b*" and regression coefficient R^2, characteristic to the Langmuir equation determined from the experimental data are presented in table 1.

Comparison of experimental isotherms with Freudlich model

The characteristic equation of the Freudlich isotherm model is:

$$a_e = KC_e^{1/n} \quad (4)$$

after linearization:

$$\log a_e = \log K + (1/n) \log C_e \quad (5)$$

where:

n and *K* represent constants specific to the system, depending on the working temperature.

Table 1
VALUES OF THE EQUILIBRIUM PARAMETERS CONSIDERING THE LANGMUIR AND FREUDLICH EQUATIONS FOR THE Hg^{2+} AND Pb^{2+} CATIONS SORBED ON CORN COBS

The cation	Langmuir isotherm			Freudlich isotherm		
	a_m	b	R^2	K	n	R^2
Hg^{2+}	0.7279	3.88	0.966	0.4.15	2.176	0.9484
Pb^{2+}	1.083	1.663	0.9916	0.402	1.5	0.8794

The graphical representation of the experimental data compared to the liniarized Freudlich equation is presented in figure 3.

The values of the equilibrium parameters *n* and *K* and of the regression coefficient R^2, corresponding to the Freudlich equation are presented in table 1.

Comparing the figures 2 and 3 and the value presented in table 1, one can affirm that the Langmuir model satisfactorily characterizes the sorption isotherms of Hg^{2+} and Pb^{2+} cations.

The pH influence on the adsorption capacity

The data presented in figure 4 evidences a slight amplification of the adsorption capacity as the pH value increases. At *p*H increase, the proton concentration inside the aqueous medium is lowering and the processes of hydroxyl and carboxyl active group dissociation are intensified. The Hg^{2+} and Pb^{2+} cations can be more easily bound on the biomass active centres.

At *p*H values higher than 5, the retained Pb^{2+} cation quantity is sharply increasing, due to the appearance of precipitation processes inside the system.

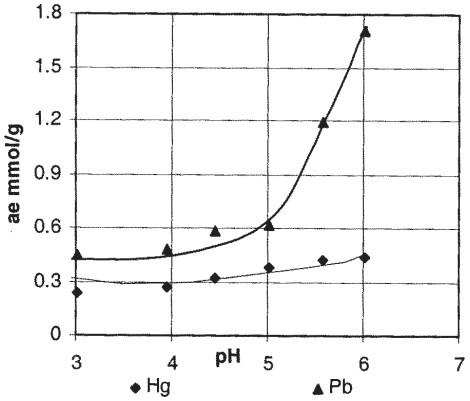

Fig. 4. The dependence of adsorption capacity for Hg^{2+} and Pb^{2+} on *p*H T = 20.0 ± 0.5°C; C_B = 1g/L; d <1mm, Ci_{Hg} = 2.69 mmol/L; Ci_{Pb} = 2.65 mmol/L

Thermodynamic analysis

The free energy change (ΔG.) was determined using the following equations

$$\Delta G = -RT \ln K_e \quad (6)$$

where:

Δ*G* is the change of the free energy, kJ/mol;

T - the absolute temperature, K;

R - the gas constant (8.314×10^{-3} J/Kmol K),

K_e - the equilibrium constant of adsorption, obtained by the relationship:

$$K_e = a_e/C_e = a_m * b \quad (7)$$

where:

a_e is the amount of the metal ion adsorbed on the adsorbent per litre of solution at equilibrium, mg/L;

C_e - the equilibrium concentration, mg/L;

a_m, b - parameters of the Langmuir equation.

The sorption experimental results lead to Δ*G* negative values, for both metal ions (table 2). According to the studied literature, a Δ*G* value up to -15 kJ/mol is connected with physical interactions between sorption sites and metal ion.

Spectrophotometric analysis

The figure 5 presents the comparative IR specters for the dread initial biomass, Hg-biomass and Pb –biomass in the range of 400-4800 nm, which may give information on the nature of the possible biomass-metal ion interaction, such as complex forming. Taken into account the similarities presented in the literature [27], one may identify the following functional groups for natural biomass that is presented in table 3.

The IR spectres of Pb-biomass and respectively Hg-biomass indicated no shifts or change in any of the characteristic absorbance bands results implied the possibility that biosorption could be performed through ion exchange or physical absorption processes rather than complex formation. This is in concordance with the results

Table 2
VALUES OF THE ΔG FOR THE ADSORPTION OF THE Hg^{2+} AND Pb^{2+} CATIONS (T = 20°C)

Cation	Hg^{2+}	Pb^{2+}
ΔG value (kJ/mol)	-2.533	-1.433

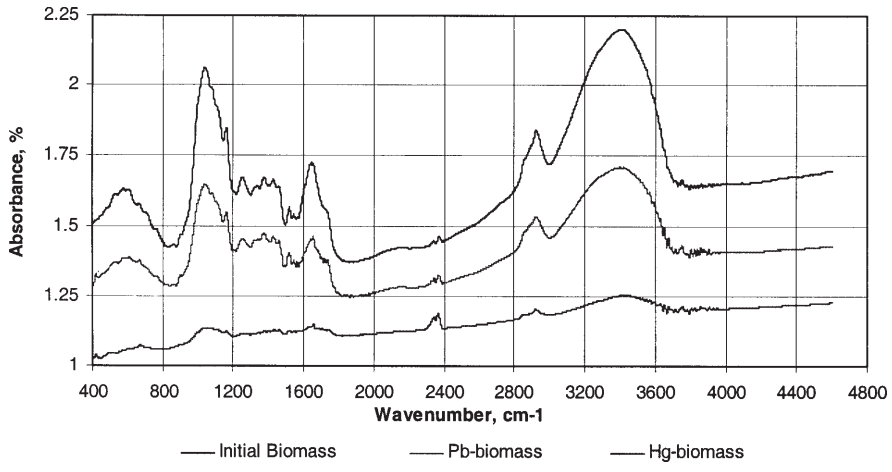

Fig. 5. The IR spectres for initial biomass and for biomass containing Hg^{2+} or Pb^{2+} ions, respectively

Table 3
THE FUNCTIONAL GROUP FOR THE NATURAL BIOMASS

Bond	Wavenumber, cm^{-1}	Notes
C-Cl, C-I	800-500	Difficult to interpret
C-O-C	1163	Glycoside group
C=O	1648	Amidic group
N=O	1371	Nitro compound
NH2	3500-3000 and 1250 - 1000	Amino
C-OH	1200-950 and 3400-3000	Alcohol a
C-OH	1255	Phenol
CH_3-CH_2- and CH_3	1460	Methyl and ethyl in lignin
C=C	3100-3000 or 1670-1600	Unsaturated alkenes or aromatic
C-H, –CH_2-	2930	Saturated organic compounds
-COOH	1720-1670	Carboxylic acids

obtained with the values of calculated free energy changes that correspond to physical actions or ion exchange processes. This conclusion is in accordance with the results reported by Guibal et al [28].

Electronic microscopy (SEM) analysis

The microscope analysis was performed using samples both from initial biomass and from the biomass after contact with Hg^{2+} or Pb^{2+} ions-containing solutions. The image was amplified by 700, respectively 2000 times, the discrimination capacity using biomass samples before and after contact with Hg^{2+} and Pb^{2+} containing solutions. Figure 6 presents the microscopic image of an initial biomass granule, at 2000 times amplification. The granule surface presents glomerulus's- being of of 10^{-8} cm order. The pores, present variable dimensions, and in the interval of 10-10000 Å have a ragged, non-uniform structure.

The figures 7 and 8 respectively present 250-times amplified images of biomass granules after contact with synthetic solutions containing Hg^{2+} and Pb^{2+} cations respectively. Compared to the initial biomass, one can observe significant structural modifications. The structure becomes round and uniform.

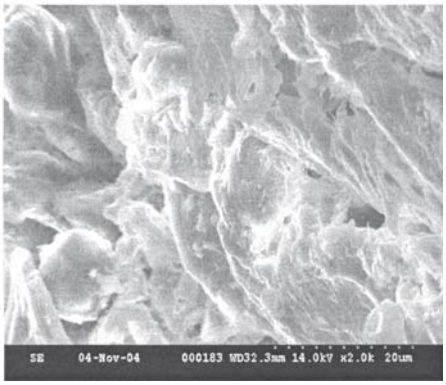

Fig. 6. Electronic microscope SEM analysis for the initial biomass, x2000

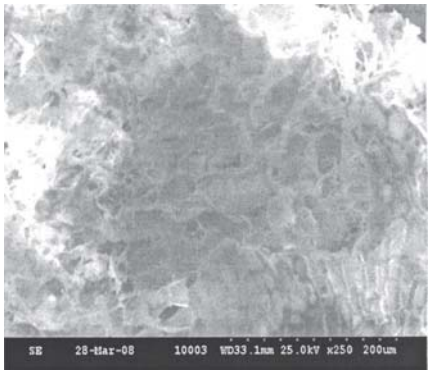

Fig.7. Electronic microscope SEM analysis for the biomass contacted with Hg2+, x250

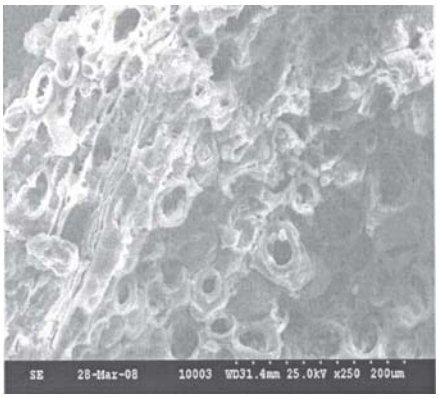

Fig.8 .Electronic microscope SEM analysis for the biomass contacted with Pb^{2+}, x 250

The biomass contacted with Hg^{2+} or Pb^{2+} cations was analyzed with EDAX gauge. The obtained images are presented in figures 9 and respectively 10. One can observe that the Hg^{2+} or Pb^{2+} ions do not form agglomerates and present a uniform distribution through the biomass surface. The retained quantities of metal ions are relatively large.

Figures 11 and 12 present the EDAX spectres of biomass contacted with Hg^{2+} and Pb^{2+} ions respectively. The

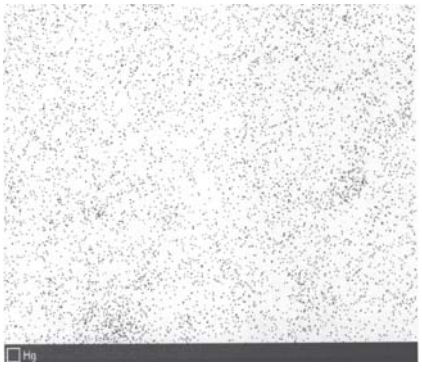

Fig. 9. Hg^{2+} distribution on a biomass granule

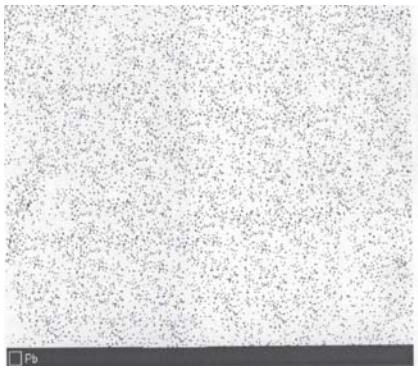

Fig. 10. Pb^{2+} distribution on a biomass granule

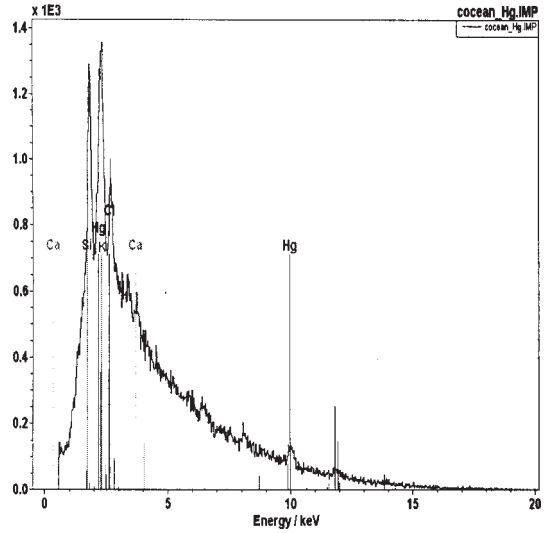

Fig. 11. EDAX spectrometric analysis of the biomass contacted with Hg^{2+}

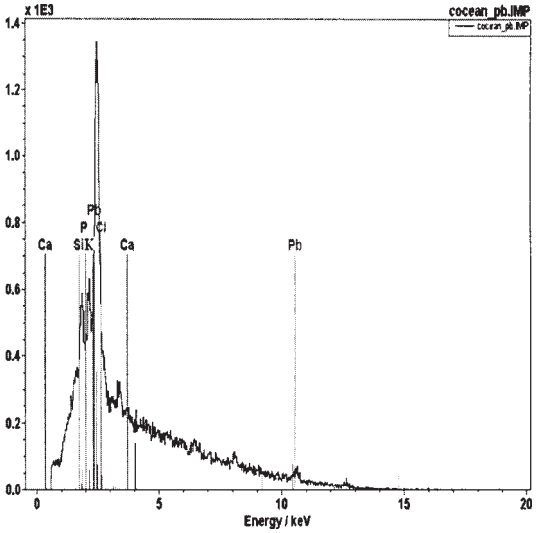

Fig. 12. EDAX spectrometric analysis of the biomass contacted with Pb^{2+}

structure is not crystalline, but quasi-amorphous. The base matrix include peaks corresponding to the elements Al, Si, P, K, Ca and Cl, Hg and Pb appear as non-specific elements and their presence represent a proof for a significant retention by biomass.

Conclusions

The sorption capacities for Hg^{2+} and Pb^{2+} cations from wastewaters were established for an available, low-cost cellulose-containing material - corn cobs.

The sorption isotherms indicate a slightly higher affinity for Pb^{2+} cations, compared to the Hg^{2+} ones. The Langmuir model equation satisfactorily characterizes the experimental results

The *p*H increase leads to the increase of the retained metal ion quantities.

The values of calculated free energy changes correspond to physical intractions; IR spectres and the structural modifications evidenced by electronic microscopy (SEM) analysis on biomass samples, after Hg^{2+} and Pb^{2+} ion retention, indicate physical interactions and ion exchange processes.

The EDAX spectrum for biomass contacted with heavy metals show that the $Hg^{2+}$and Pb^{2+} ions do not form agglomerates and present an uniform distribution on the biomass surface. The base matrix includes peaks corresponding to the elements Al, Si, P, K, Ca and Cl. Hg and Pb appear as unspecific elements and their presence represents a proof for a significant retention by biomass.

The subject was also studied by other researchers [29, 30].

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