

Maize Stalk as Natural Ion Exchanger for Hazardous Pollutants

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This paper recommends maize stalk as a cheap natural ion exchanger. Ion exchange equilibrium was studied using thermodynamic and kinetic models. The results showed a high selectivity towards cationic species of antimony (III), molybdenum (VI), lead (II) and arsenium (III). Waste waters and sediments from tailing ponds samples were analysed.

Keywords: maize stalk, natural ion exchanger, heavy metals, waste, mining, tailing pond

In recent years, various chemical compounds such as organic and inorganic micropollutants have been detected in high concentrations in waste water, including hazardous metals with a high toxic effect to human health and the environment [1-3]. It has been known that the hazardous metals in low concentrations were toxic and had a tendency to bio accumulate both in the environment and in the human body, affecting functions of the central nervous system, blood composition, liver, kidney of the lungs and it could ultimately cause death [4-9]. In the present, the developments of new environment-friendly technologies used for water purification and protection of the population have been both economically and ecologically necessary [10, 11]. Initially, the underground waste storage method was used, but the rainfall leaching could migrate the toxic compounds to the ground, the subsoil, the surface water and to the groundwater where they could accumulate in high concentration through adsorption process [12-14]. As a new environmental friendly alternatives, a variety of technologies are available to remove hazardous metals for wastewater purification, including reverse osmosis, coagulation/flocculation, precipitation, ion exchange, electrochemical process, solvent extraction, and membrane technology have been developed but their operational costs were high compared to the adsorption process, which is a good alternative to wastewater treatment [15-20].

Corn, one of the most important agricultural crops in the world, could be a viable technological and economical matrix for adsorption processes. It was used mainly as corn flour for food preparation and as corn stump for animal feed. Being one of the most versatile plants as all its parts could be used for various purposes it became an important raw material in many industries. Thus corn silk has found applications in traditional medicine and cosmetics, corn starch in food and pharmacy, sugar and oil industry and in the production of ethanol. The major problem related to these activities is represented by the corn waste management. One can find all over the world stalks and

stems in the field or discarded by-products from industries [21, 22]. To prevent pollution associated with these activities, in the last decades an increasing consideration has been done to the valorisation of this biomass in the direction of new materials. We have noticed, studying the scientific literature that there is an increased tendency in use of natural bio sorbents for reducing pollution damages or for bioremediation [23-28].

Therefore, our research was focused in a new direction that involves the valorisation of corn biomass as natural ion-exchangers for inorganic cations. Basically, lignin, cellulose, semi cellulose, vegetable protein and sugars contain functional group acting as weak cationic exchangers. First, we have investigated at laboratory scale the retention of inorganic cations in corn derived material and second we have applied the model to a natural environment.

Experimental part

Materials and methods

Chemicals

All reagents were analytical grade and were purchased from Merck: 37% HCl, 65% HNO₃, KBr solid and ICP multi-element standard CertiPUR® containing 21 elements 100 mg/L (in diluted nitric acid): As, Be, Cd, Ca, Cr, Co, Cu, Fe, Pb, Li, Mg, Mn, Mo, Ni, Sb, Se, Sr, Tl, Ti, V and Zn.

Equipment

The ICP- EOS Spectrometer (OPTIMA 5300 DV Perkin Elmer equipment) was used to determine the concentration of the elements in effluents.

SEM analyses were carried out on a Quanta 200, FEI, Scanning Electron Microscope (FEI), with GSED detector, chamber pressure of 200 Pa, spot size 4.5 and 12.50 kV voltage. All treated samples were analysed for morphological modifications, compared with control.

The diamond crystal ATR analysis was performed with a FT-IR/Raman Bruker Vertex 70 instrument. Spectra were recorded between 400 - 4000 cm⁻¹ with 64 scans and spectral resolution of 4 cm⁻¹.

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Determination of elements by ICP-EOS

The CertiPUR® solution containing 21 elements was used in ICP-EOS experiments. The linearity was evaluated and a linear regression analysis was made for each element in a concentration range between 0.1 mg/L and 0.5 mg/L. The equations computed in this study were used to evaluate the concentration of each element at equilibrium. When necessary dilutions were made and the linearity checked again.

Sampling and shredding of maize stalk

In this study, corn crops harvested from Olt County, located on the Western part of Romanian Plain, have been used. The sampling was done according to statistic rules, various maize stalk being collected at maturity in autumn. Internodes for all parts of the stem have been cut in pieces of 15 cm, washed with water and dried in laboratory. Dried stems samples were further cut in smaller pieces then grounded with an electrical mill and sieved using a standardized sieve of 10 mesh.

Activation of maize stalk

This biomaterial has been activated in a column using a solution of 4N HCl. After activation, the biomaterial was dried in laboratory for 48 h.

Ion exchange experiments

All experiments have been done using the batch procedure. A quantity of 0.1 g of activated biomaterial was shaken at 175 rpm for 2 h at room temperature with various solutions of one or more elements that contained a volume of 10 mL. At the end of the experiment the samples were filtered through Whatman filter paper and the effluent was collected and quantitatively transferred in 25 mL volumetric flasks and the elements determined by ICP-EOS.

Stability of the cations loaded by biomaterial

The same procedure was applied but the samples were shaken with HCl having different concentrations ranging from 1 to 4 mol/L.

Thermodynamic studies

Ion exchange equilibrium was characterised by means of Langmuir, Freundlich, Temkin and Dubinin-Radushkevich isotherms. The concentration of the analyte at equilibrium was calculated using the following equation:

$$Q_e = \frac{(C_o - C_e)V}{m} \quad (1)$$

where:

Q_e is the concentration of the analyte in maize stalk phase, C_o and C_e are the initial concentrations and at equilibrium, respectively, expressed in mg/L, m is the mass of dry maize stalk (g), while V is the volume (L).

Kinetic studies

These investigations were performed at the following $25 \pm 2^\circ\text{C}$ temperatures using the same batch procedure described above.

The sorption capacity at time t , was determine with the equation:

$$Q_t = \frac{(C_i - C_t)V}{m} \quad (2)$$

where:

C_i and C_t are the metallic cations concentrations (mg/L) initially and at the time t (mg/L); m is the mass of dry maize stalk (g), V is the metallic cations volumes initially used (L).

Sorption of metallic cations from different waste waters on maize stalk

A quantity of 0.1 g of maize stalk was mechanically shacked for 100 minutes at 175 rpm with 0.01L of different waste water taken from Ilfov region, subsequently the samples were filtered and the filtrate was collected in 50 mL volumetric flask.

Sampling of waste waters and sediment samples

Firstly, different waste waters taken from Ilfov region, have been used in this study.

Secondly, the tailing pond having the GPC coordinates Lat: $45^\circ 57' 38.97''\text{N}$, Long: $22^\circ 58' 55.39''\text{E}$ is situated on Valea Mealului, tributary to the Cartej river, about 3 km downstream of the Certej preparation plant, near Certejul de Sus, in the south of the Metaliferi Mountains. This tailing pond has a total surface area of 42,33ha, a canopy of 59 meters and a volume of 5,8 mil m^3 (fig. 1). The waste deposited in the pond consists of the sterile slurry resulting from the preparation of the polymetallic and gold-silver ore. The sediment capacity to transfer the metallic cations towards the environment (soil, plants, surface water and the underground water) was evaluated using leaching test [30]. The sediment samples were dried and sieved followed by the leaching test (1:10 mass per volume, sediment: ultra-pure water) for the particles less than $63\mu\text{m}$ in order to detect the cationic exchange ratio. Samples were collected according to the SR ISO 5667/12 [29].



a



b

Fig. 1. Tailing pond a. GPS localisation; b. Image/picture of the site

Results and discussions

Our preliminary studies were performed using a solution of 21 elements in which each of them represents 0.02 mg/L. At this dilution we have observed a very strong retention on the maize stalk cationic exchanger for Mo(VI) 91%, Pb(II) 73.7% and Sb(III) 37.3%, while the others were loaded less such as Se(IV) 19.5%, Cr(III) 15%, Tl(III) 11.6% and V(II) 4.6% or not retained such as As(III), Cd(II) Mn(II), Ni(II), Zn(II) and Li(I). Under these circumstances the further investigations were made for solutions containing the cations of the three above mentioned elements: Mo(VI), Pb(II), Sb(III).

The ICP-EOS method used in this study has been verified in our laboratory in term of linearity, limit of detection and limit of quantification for all 21 investigated elements. The results presented in table 1 shows the validation

Table 1
VERIFICATION OF ICP-EOS METHOD USED FOR THE DETERMINATION OF Sb(III), Mo(VI) AND Pb(II)

Metallic cation	Concentration range (mg/L)	Calibration curve	R ²	LOD (mg/L)	LOQ (mg/L)
Sb(III)	0.1-0.5	y = 11429x - 32.53	0.9995	0.0020	0.0065
Mo(VI)	0.1-0.5	y = 51412x - 300.4	0.9991	0.0004	0.0012
Pb(II)	0.1-0.5	y = 27170x - 27.14	0.9999	0.0005	0.0015

parameters of ICP-EOS method for the three above mentioned elements.

Thermodynamic studies

The ion exchange equilibrium were characterised by means of four isotherms computed on experimental data presented in figure 2. As one can observe the equilibrium is reached after 80 min. For this reason we have chosen 100 min as optimal time for all further studies.

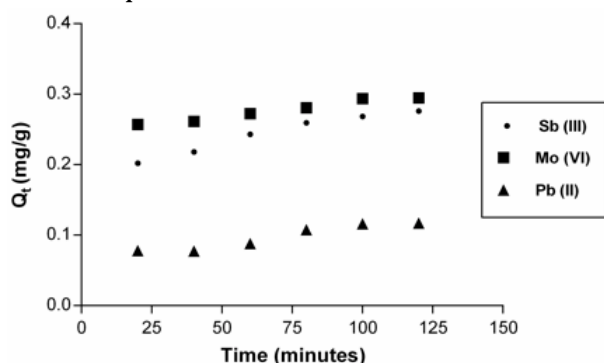


Fig. 2. Experimental isotherms for Sb(III), Mo(VI) and Pb(II) loaded by the activated maize stalk

The isotherms of Langmuir, Freundlich, Temkin and Dubinin-Radushkevick were used to analyse the experimental data and to obtain information about the mechanism involved in this process [31]. The equations of these isotherms are presented below:

Langmuir equation

$$\frac{C_e}{Q_e} = \frac{1}{bQ_0} + \frac{C_e}{Q_0} \quad (3)$$

Freundlich equation

$$\ln Q_e = \ln K_f + \frac{1}{n} \ln C_e \quad (4)$$

Temkin equation

$$Q_e = \frac{RT}{b\tau} \ln(AC_e) \quad (5)$$

and can be linearized as:

$$Q_e = B \ln A + B \ln C_e \quad (5.1)$$

Dubinin-Radushkevick equation

$$\ln Q_e = \ln q_m - \beta \varepsilon^2 \quad (6)$$

$$E = \frac{1}{\sqrt{2\beta}} \quad (6.1)$$

where: Q_e is the quantity of Sb(III), Mo(VI) and Pb(II) at equilibrium (mg/g); C_e is the final concentration of Sb(III), Mo(VI) and Pb(II) at equilibrium (mg/L); Q_0 , the monolayer sorption capacity of the activated maize stalk (mg/g); b , is the Langmuir constant (L/mg); K_f is the Freundlich constant that evaluate sorption capacity of the activated maize stalk (L/g); $1/n$, heterogeneity factor determined and indicates sorption intensity, that is adimensional; β , is the constant related of the mean free energy of sorption (mol^2/KJ^2); q_m , represents theoretical saturation capacity of maize stalk; ε , is the Polanyi potential, $\varepsilon = RT \ln(1 + (1/C_e))$, R ($\text{J mol}^{-1} \text{K}^{-1}$) is the gas constant, T (K) is the absolute temperature and $b\tau$, is constant of Temkin isotherm, (J/mol).

Results obtained in the thermodynamic investigation of ion-exchange equilibrium are presented in table 2.

These results showed that all four models fit the experimental data with a correlation coefficient R^2 greater than 0.9650 for Sb(III) and Mo(VI). Among the studied isotherms the highest R^2 value 0.9995 was obtained for Freundlich model describing Mo(VI) sorption. On the other hand, the maximum sorption capacity of the monolayer calculated by means of Langmuir isotherm was obtained for Sb(III), 0.4475 mg/g. In addition, both Langmuir and Freundlich models indicated a favourable sorption of Sb(III), Mo(VI) and Pb(II) on this biosorbent. Moreover, Dubinin-Radushkevich isotherm confirm an ion-exchange model for the sorption of these elements (in all studied cases the sorption energy is greater than 16 KJ/mol). Finally, the heat of sorption process was calculated by means of Temkin-

Thermodynamic model	Sb(III)	Mo(VI)	Pb(II)
Langmuir			
$Q_0(\text{mg/g})$	0.4475	0.3804	0.2807
$b(\text{L/mg})$	5.1151	1.8400	1.2910
R^2	0.9734	0.9752	0.5262
R_L	0.3820	0.6263	0.8601
Freundlich			
K_f	1.9652	1.9699	5.4905
$1/n$	0.5437	0.4224	0.7210
n	1.8392	2.3674	1.3870
R^2	0.9853	0.9995	0.8660
Dubinin -Radushkevich			
$X_m(\text{mg/g})$	2.7815	2.9067	6
$\beta(\text{mol}^2/\text{kJ}^2)$	4.00E-08	2.00E-08	5.00E-08
$E(\text{KJ/mol})$	5000	7071	3162
R^2	0.9677	0.9713	0.8514
Temkin-Phyzev			
$A_\tau(\text{L/mg})$	51	157	16
b_τ	24820	31704	44270
B	0.0981	0.0768	0.0550
R^2	0.9688	0.9682	0.8362

Table 2
PARAMETERS CALCULATED FOR LANGMUIR, FREUNDLICH, DUBININ-RADUSHKEVICK AND TEMKIN ISOTHERMS

Phyzev isotherm and the values obtained indicated a strong interaction between ions and biosorbent.

Kinetic studies

Experimental results were evaluated using various kinetic models in order to obtain information about the ion exchange equilibrium involving the cations Sb(III), Mo(VI) and Pb(II) on maize stalk. Models such as Lagergren, Morris-Weber, Elovich and Pseudo-second order have been used in this study [32]. The equations of kinetic models are presented below:

Morris-Weber equation

$$q_t = k_{id} (t)^{0.5} \quad (7)$$

Lagergren equation

$$\log(q_e - q_t) = \log q_e - \left(\frac{k}{2.303}\right) t \quad (8)$$

Elovich equation

$$q_t = \ln(\alpha\beta) + \frac{1}{\beta} \ln t \quad (9)$$

The Pseudo-second order equation

$$\frac{t}{q_t} = \frac{1}{k_2 (q_e - q_0)} + \frac{t}{q_e} \quad (10)$$

where:

q_e and q_t represents the sorption capacities of activated maize stalk at equilibrium and at time, t (min.); k_{id} is the internal particle diffusion constant; k (min^{-1}) is the rate constant for the Lagergren model; α ($\text{mg/g} \cdot \text{min}$) is the initial sorption rate; β (g/mg) the desorption constant and k_2 ($\text{g}/(\text{mg} \cdot \text{min})$) is the rate constant of Pseudo-second order model. Results obtained in using the above mentioned models are presented in table 3.

As one can see in table 3 the ion exchange equilibrium involving of Sb(III) is well described by means of the four kinetic models and among them, the Pseudo-second order kinetic model provided the best R^2 value 0.9958.

Stability of the ions loaded on maize stalk

We have investigated the stability of the ions fixed in the biosorbent material using two different concentrations 1M and 4M HCl. On the one hand, we expect to have a good stability in a solution of HCl 1 mol/L as the real samples are usually highly acidic, and on the other hand we wanted to recover some of the valuable cations and we need an eluent able to do this. In addition, the selectivity of an ion exchange resin towards cations has been taken into consideration when we have chosen these two concentrations.

Figure 3 shows that the ion exchange equilibrium involving ions such as Co(II) and Pb(II) is not influenced by a solution of 1M HCl, while a solution of 4M HCl removed almost all cations, except Mo(VI) and Tl(III). For the other cations the tendency followed the theoretical rules the more concentrated hydrochloric acid is, the more cation is removed.

Maize stalk characterization

SEM analyses were carried out. All treated samples were analysed for morphological modifications, compared with control (activated biomaterial) and the pictures are presented in figure 4.

Elemental composition was quantified using EDAX module at 1000x magnification and ADC1 detector on acquisition matrix of 512x400. These analyses emphasize existence of Mo(VI) quantification of 2.12% and Sb(III) quantification of 2.94%, values over the base-line.

Kinetic model	Sb(III)	Mo(VI)	Pb(II)
Lagergren model			
k (min^{-1})	0.0290	0.0431	0.0438
q_e (mg/g)	6.2187	6.0632	5.4288
R^2	0.9689	0.7266	0.7873
Morris-Weber model			
k_{id} (min^{-1})	0.0127	0.0066	0.0074
R^2	0.9845	0.9311	0.8475
Elovich model			
($\text{mg/g} \cdot \text{min}$)	0.0459	0.0261	1.0017
β (g/mg)	23	46	41
R^2	0.9617	0.8616	0.7597
Pseudo-second order model			
k_2 ($\text{g}/(\text{mg} \cdot \text{min})$)	0.2798	0.5944	0.2867
q_e (mg/g)	0.2976	0.3044	0.1392
R^2	0.9958	0.9970	0.9383

Table 3
RESULTS OBTAINED FOR THE FOUR KINETIC MODELS

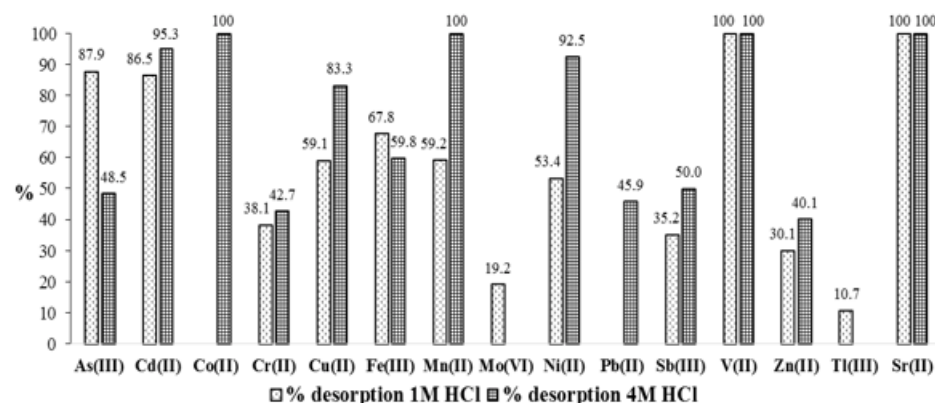


Fig. 3. Desorption of metallic cations from the maize stalk at two different concentration of HCl

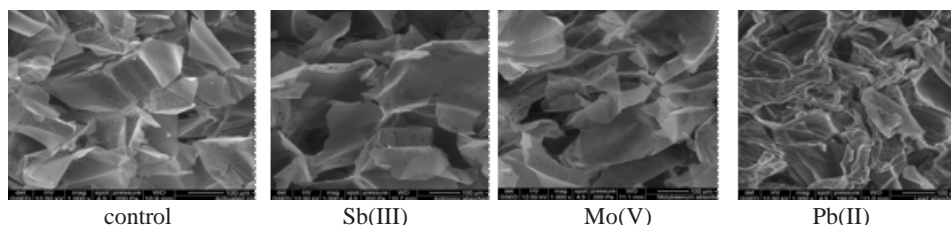


Fig. 4. Morphology comparison of analysed samples

ATR technique

ATR spectra of maize stalk pre and post sorption of cations of molybdenum (VI), antimony (III) and lead (II) were carried out. The shape of the spectra is very much the same except the 1730 cm^{-1} band of $-\text{COO}^-$ group that upon interaction with different ions decrease in intensity. In addition, new maxima at about 1692 cm^{-1} was observed. The most noticeable spectral differences was observed for lead(II) ion interaction, this being in agreement with the changes of morphology observed in the SEM micrographs.

Analysis of river and tailing pond samples

Results obtained for the four waste waters and for the four sediment samples are presented in table 4 and 5, respectively.

As one can observe in table 4 the biomaterial has the capacity to remove in various percent almost all the investigated cations. It is worth to notice the complete removal of Sb(III) no matter the pH of the sample, together with that of Mo(VI) and V(II) from highly acidic waste water samples.

For sediments the removal of cationic species (table 5) is nearly completely for arsenic, which represents the major asset for this new biomaterial.

Table 4
PERCENT OF METALLIC CATIONS REMOVED FROM WASTE WATER USING ACTIVATED MAIZE STALK

Metallic cations	Sample 1 pH (0.5-1) (%)	Sample 1 pH (6.5-7) (%)	Sample 2 pH (0.5-1) (%)	Sample 2 pH (6.5-7) (%)	Sample 3 pH (0.5-1) (%)	Sample 3 pH (6.5-7) (%)	Sample 4 pH (0.5-1) (%)	Sample 4 pH (6.5-7) (%)
Cd(II)	n.d.	n.d.	30.0	n.d.	36.4	n.d.	n.d.	n.d.
Co(II)	n.d.	n.d.	27.6	23.5	n.d.	46.2	100	45.5
Cr(III)	n.d.	n.d.	1.50	9.70	n.d.	4.30	n.d.	26.7
Cu(II)	n.d.	n.d.	14.8	94.6	n.d.	21.7	55.2	29.9
Fe(III)	9.76	67.3	6.30	15.7	n.d.	18.3	n.d.	25.0
Mn(II)	14.7	42.5	4.10	13.4	n.d.	9.40	1.60	14.0
Mo(VI)	1.39	13.9	25.9	21.7	27.1	32.4	68.6	18.0
Ni(II)	n.d.	n.d.	n.d.	1.40	n.d.	6.30	n.d.	n.d.
Pb(II)	39.6	73.6	77.3	n.d.	91.5	38.9	93.0	n.d.
Sb(III)	n.d.	n.d.	45.9	40.0	52.9	100	100	n.d.
Se(IV)	n.d.	n.d.	85.9	n.d.	80.3	n.d.	50	n.d.
Ti(IV)	n.d.	n.d.	27.8	n.d.	85.6	19.8	10.8	15.9
V(II)	n.d.	n.d.	100	n.d.	100	33.3	71.2	37.5
Zn(II)	43.6	70.7	4.80	7.40	n.d.	6.50	3.20	10.9
Tl(III)	66.7	2.08	29.6	n.d.	36.7	n.d.	n.d.	n.d.
Li(I)	5.41	2.70	3.00	n.d.	n.d.	3.60	4.00	10.0

n.d.: not determined

Metallic cations	Sediment 1 (%)	Sediment 2 (%)	Sediment 3 (%)	Sediment 4 (%)
As(III)	57.1	97.3	48.1	99.0
Cd(II)	25.6	29.6	66.2	26.2
Co(II)	1.70	8.30	43.8	5.90
Cr(III)	n.d.	13.1	60.0	19.0
Cu(II)	1.60	19.6	88.9	33.8
Fe(III)	32.0	34.4	87.8	43.2
Mn(II)	8.20	6.70	22.5	1.80
Mo(VI)	47.1	24.3	n.d.	n.d.
Ni(II)	2.50	6.70	70.0	2.70
Pb(II)	1.50	68.2	71.9	76.2
Sb(III)	20.0	22.1	n.d.	42.1
Zn(II)	6.10	99.6	69.2	4.90

n.d.: not determined

Table 5
PERCENT OF METALLIC CATIONS REMOVED FROM MINING WASTE LEACHING USING ADSORPTION PROCESS

Conclusions

The maize stalk represent a new material suitable for cation removal from various waste waters and mining sediments. Our study has revealed that this biomaterial acts as a highly efficient ion exchanger especially for cationic species of antimony(III), molybdenum(VI), lead(II) and arsenium(III). Therefore, we proposed this new material as a cheap and efficient natural ion-exchanger to be used as additional barrier to prevent leakage of pollutants especially from tailing ponds.

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