UNIVERSITY OF BUCHAREST
FACULTY OF CHEMISTRY
DOCTORAL SCHOOL OF CHEMISTRY

DOCTORAL THESIS

CLASSIC AND NON-CONVENTIONAL ION EXCHANGERS WITH APPLICATIONS IN ENVIRONMENTAL QUALITY CONTROL METHODS

(Summary of PhD Thesis)

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(corresponding to the doctoral thesis)

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INTRODUCTION

The environmental protection and especially the aquatic ecosystems have become a major concern for authorities and local communities. Chemical contamination of water with metallic cations and organic compounds from the synthetic dyes category is a serious problem for the environment and human health. Therefore, the current legislation imposes even more restrictive rules on the quality of waste water discharged in urban sewage networks and in natural receptors, respectively.

In general, before being discharged the waste water treatment is done using ion exchangers. Ion exchangers are used to retain chemical, inorganic or organic chemicals that are in the ionic form in solution. For this purpose there are used columns filled up with either anion exchangers or cation exchangers or a mix of them. However, the selectivity of commercial resins for different ions in the solution is limited. For this reason, recent studies have been carried out to increase the selectivity of classical ion exchangers.

Ion exchange resins have been modified by chemical synthesis and ion exchange equilibrium. These resins contain analytical reagents immobilized in the hydrocarbon structure, which have complexing groups which will selectively retain certain ions from the solution. In general, methodologies that use ion exchange resins are chemically modified by synthesis and have higher costs than those based on ion exchange resins modified by ion exchange equilibrium. Most studies have as object of research the retention of metallic cations using ion exchangers. However, the aims are various: depollution, concentration for a detection goal, recovery followed by reduction for reevaluation of rare-earth metals. The organic compounds can be retained by ion exchange if they have in their structure ionizable groups or can be retained using adsorption and by weak interactions that which be established between the hydrocarbon backbone of the resin and the organic compound. The class of compounds which can be used for these conditions is the azo dyes. In addition, very toxic compounds to the environment could be obtained by dyes biodegradation.

They are many exhaustive studies in the literature that described results obtained with ion exchangers involved in the dyes recovery from industrial effluent. A valuable alternative of the classical and modified ion exchangers is to use the stationary phases from vegetable and animal origin. The most commonly plant materials used for this purpose are cellulose and lignin or chitosan from animal origin.

These materials have hydroxyl groups of the alcohol type (cellulose, lignin, chitosan) or phenol (lignin) and they can participate in ionic exchange equilibria, in certain conditions, as weak cation exchangers. This type of biomaterial is mainly used for the retention of metallic cations in waste water and it has the great advantage of being cheap and easy to use.

Chemically modified ion exchange resins (to increase selectivity) and plant materials (to reduce costs) could be used as alternatives to classical ion exchange resins to remove organic dyes, but only the biological methods have proven their effectiveness. Biological methods were used for both toxicity and biodegradation assessment, respectively. In recent years, ecotoxicology studies have grown at European level because (i) there is a significant number of chemicals present in the environment and only a limited number of them are continuously monitored, (ii) there is limited data, in recent years, on the possible negative effects of chemicals on the individual, population or community organisms from the environment (iii) a pollutant may produce toxic effects below its chemical detection limit in the environmental, (iv) chemical analyzes can give information about the concentration of a pollutant in the environment but they do not provide data on the degree of bioaccumulation and long-term effects on ecosystems, (v) there are needed information on combined toxicity caused by the coexistence of several pollutants chemical agents from the environment (synergism and/or antagonism).

Based on the above-mentioned aspects, the research described in this doctoral thesis has as follows:

MAIN GOAL

Study the behavior of classical and unconventional ion exchangers in the presence of pollutants, inorganic and organic chemical species such as metallic cations and azo dyes.

OBJECTIVES

Characterization of ion exchange equilibria by a kinetic and sorption isotherm studies as well as evaluation of the exchange capacity of investigated materials;

Determination the performance of ion-exchange and biological methods for two azo-dyes selected for this study.

In the original experimental part of this doctoral thesis are presented and analyzed the results of the studies performed in the following directions, which are described in chapters 2, 3, 4 and 5.

THE EXPERIMENTAL ORIGINAL PART OF THE THESIS

CHAPTER II

ASSESSMENT OF PERFORMANCE PARAMETERS FOR THE SPECTROMETRIC METHODS

II.1. Determination of dye concentrations by UV-VIS molecular absorption spectrometry

The spectrometric methods described in chapters 3 and 4 of this PhD thesis were used to estimate the dye concentrations in ion exchange studies. For this purpose, the linearity of the Lambert-Beer law was verified on different ranges of concentration.

The dye concentrations of the supernatant solutions, obtained from the ion exchange experiments between resin and the dyes, were analyzed using equations of the linear regression line in Chapter 3 (ion exchange experiments between Amberlite IRA 400 resin and Acid Orange 10 (AOG 10)) and in Chapter 4 (ion exchange experiments between Amberlite IRA 400 resin and Gryfalan Navy Blue RL (GNB)).

II.2. In house validation for the determination of metallic cations methods

In-house validation of ICP-OES method (SR EN ISO 11885/2009-Detection of selected elements by inductively coupled plasma optical emission spectrometry (ICP-OES)) for measurement of the following metallic cations: Cu, Cr, Fe, Mn, Mo, Se, Ti, As, Li, V, Mo, Co, Cd, Be and Zn from waste water samples was evaluated.

Linear regression lines were used to detect the concentrations of synthetic solutions, waste water or leaching samples from mining sediment to the metallic elements. Under those circumstances, the linear regression lines were obtained by graphic representation of the peaks area of the analyzed samples for each calibration solutions to the reference material that contained 21 metallic elements. For this purpose, the following validation parameters of the analytical method were determined such as: linearity, detection and quantification limit, precision (assessed by repeatability), and accuracy (which was studied through retrieval yield).

CHAPTER III

REMOVAL OF THE ACID ORANGE 10 FROM AQUEOUS SOLUTIONS BY AMBERLITE IRA 400 RESIN AND MICROBIOLOGICAL BACTERIAL METHODS

In this chapter, Acid Orange 10 was removal by ion exchange and microbiological methods. For this purpose, a strongly basic anion exchange resin Amberlite IRA 400 was used to retained the Acid Orange 10 (AOG 10) and also for further biodegradation studies in the presence of following bacteria: *Escherichia coli* (gram negative bacteria), *Salmonella enterica* (gram negative bacteria) and *Citrobacter freundii* (gram negative bacteria) which are further notated to as *E. coli*, *S. enterica* and *C. freundii.* The chemical structure of AOG 10 presented itself under a disodium salt form. In water solution, it is completely dissociated to an anionic form with two negatives charges. Taking into account these considerations, AOG 10 can be fixed by an ion exchange equilibrium in the anion exchange resin. Also, the existence of the naphthalene and benzene hydrocarbon structure provides significant electronic density and the possibility of sorption AOG 10 on the Amberlite IRA 400 anion exchange resin not only through ion exchange equilibrium but also by π-π interactions that are established between the aromatic structure of resins and the studied dye [1].

III.1. Study of the parameters that modulates the ion exchange process

III.1.1. The effect of contact time between Acid Orange 10 sorption and strongly basic anionic resin Amberlite IRA 400

First of all, the sorption capacity of the Amberlite IRA 400 anion exchange resin was calculated against AOG 10 studied. The AOG 10 dye has three groups in its structure where was completely ionized in solution at a pH greater than 9. The exchange capacity was calculated as 1.38 meq/mL, result that are close to the theoretically calculated value when AOG 10 was fixed to a single sulphonic group ($-SO_3^-$). Thus, ion exchange can retained up to 2262 mg/L AOG 10, if all active groups of the Amberlite IRA 400 anion exchange resin were involved.

The influence of contact time to AOG 10 sorption on the anion exchange resin was studied at *t* 25 °C by detected the quantity of AOG 10 loaded on the resin using the procedure described in *Chapter II.*

The experimental data presented in figure 3.1, showed different values of sorption capacity obtained in the first 35 minutes, but after this time, a plateau tendency was observed due to reaching a chemical equilibrium. From now on, the subsequent studies were performed at any time values greater than 35 minutes.

Taking into consideration structure, geometry and volume of the AOG 10 dye, it can be assumed that it becomes more difficult to approach ionizable groups of the Amberlite IRA 400 on structure resin. Therefore, a time of 65 minutes was enough to establish the chemical equilibrium.

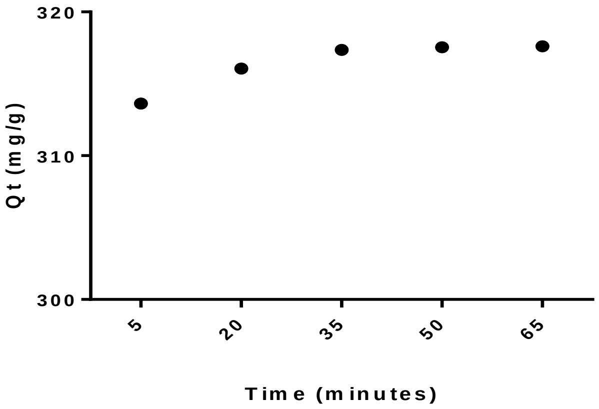


Figure 3.1. Effect of the contact time on the sorption of AOG 10 onto strong basic anion-exchange resin Amberlite IRA 400 (experimental conditions: 2262 mg/L AOG 10 with 0.1 g of Amberlite IRA 400 highly strongly anion exchange resin in the Cl^- form, 175 rpm and at t °= 25 ± 2 °C)

III.1.2 Study the influence of temperature for AOG 10 sorption

For this study, the experiments were carried out by dynamic method at different temperatures ranging from 25, 35, 45 and 65 °C. The data obtained in this experiment (figure 3.2) showed that the sorption capacity has the same tendency as described in figure 3.1, but with a slightly higher increase of the values, proportional to the temperature.

The increase in sorption could be explained by the increased number of active centers from the sorbent and also by the increase of the porosity and pore volume and by the geometry of the organic compound, too [2]. Therefore, there was a very slow increase in sorption between 25 and 35°C, but no difference when operating at 35°C or 45°C, in consequence, the further experiments were carried out at 25°C. The sorption capacity of Amberlite IRA 400 toward AOG 10 detected at 25°C and 65 minutes was 317.6 mg/g.

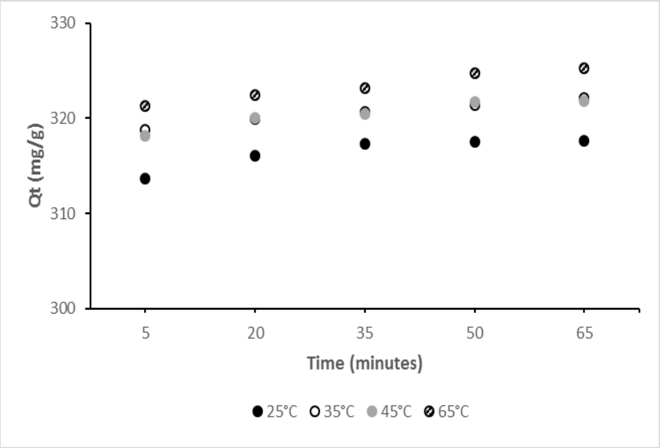


Figure 3.2. Effect of the temperature on the sorption of AOG 10 onto Amberlite IRA 400

III. 1.3. Study the Acid Orange 10 desorption from the Amberlite IRA 400

The desorption process of AOG 10 from the resin can be explained as follows: with increasing of HCl concentration, the high concentration of Cl^- ions in the solution are fixed on the resin instead of the dye. In the figure 3.3, was graphically showed a representation of the AOG 10 percentage variation desorbed are proportionally with the HCl concentration used as a desorption agent. The results showed that if 7.65 M HCl solution was used, more than 81% of the AOG 10 retained on the resin can be desorbed in only 30 minutes of agitation. Therefore, with the increase of contact time, the whole quantity of the dye can be desorbed and the resin will be reused. These results show that the resin loaded with AOG 10 is quite stable in acidic solution (not more than 1 M). In addition, a chloride ion concentration less than 1 M does not affect the ion-exchange equilibrium between AOG 10 and Amberlite IRA 400 resin. The strong linkage between AOG 10 and the resins leads us to consider, besides the ion-exchange equilibrium, a physical interaction involving the π electrons of hydrocarbon moiety of both AOG 10 and ion-exchange resin.

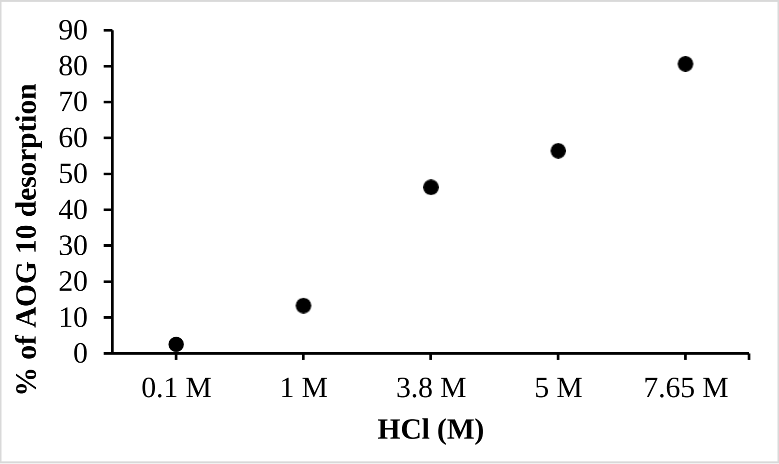


Figure 3.3. Influence of the acidity solution on the desorption AOG 10 from the strongly basic anionic resin Amberlite IRA 400

III. 1.4. Study the influence of pH for AOG 10 sorption on strongly basic anion-exchange resin Amberlite IRA 400

Often, the pH induces structural changes on the AOG10 structure, especially at pH>9, where the phenolic group, which is a weak acid, is ionized. This new anionic changes could influence the sorption process of dye on Amberlite IRA 400 resin. In the presence of different buffer solutions, the percentages of AOG10 retained from the solution were 99.9, 99.9, 99.9, 99.6, 99.4, 99.6, 99.6 and 99.7%. The buffer solutions used (1.02, 1.65, 2.01, 3.56, 4.76, 6.67, 8.28 and 10.3) do not affect the sorption of the dye in the resin. These results confirm that no matter the pH value, AOG 10 is retained by the Amberlite IRA 400 anion exchange resin, which represent an advantage in using those resin for this purpose.

III.2. Study of sorption isotherms

The relationship between the quantity retained per mass of adsorbent and the corresponding concentration of solute at equilibrium represents the sorption isotherm. The mathematical models of the Langmuir, Freundlich, Temkin and Dubinin-Raduschevich isotherms were used to evaluate the data obtained at equilibrium and the efficiency of the sorption process [2-3].

Taking into account the correlation coefficients, it was possible to describe the sorption of AOG 10 dye on the strongly basic anion exchange resin. By modeling experimental data using the mathematical models of sorption isotherms, the following information is obtained when using those models. The Langmuir isotherm, can describe the sorption process on homogeneous surfaces by forming a monolayer to the external surface of the resin. The Freundlich isotherm describes the sorption process that occurs on heterogeneous and multilayer surfaces. Dubinin-Raduschevich isotherm provides information about the type of interaction that characterizes the sorption process by assessing the average sorption energy and finally the heat of the sorption process was evaluated based on the Temkin-Pyzhev model.

The parameters of the Langmuir isotherm were determined graphically from the slope and intercept of linear regression line $Ce/Qe = f\,(Ce)$. The maximum adsorption capacity of monolayer Q_o(mg/g) for the high strength anion exchange resin Amberlite IRA 400 determined was 556 mg/g. The second Langmuir parameter b (L/mg) studied, reflects the affinity of the anion exchanger for AOG 10 dye. The experimentally value determined was 0.30 (L/mg) one can suggests a strong binding between AOG 10 dye on the anion exchanger. The R_L value determined is 0.02 that ranged between 0 and 1, with confirming that the ion exchange equilibrium and physical adsorption of AOG 10 in the resin are favorable. High value of correlation coefficient suggests that the AOG 10 is described by the Langmuir isotherm theory can described sorption of dye on homogeneous surfaces to the outside of the resin particles until is formed a saturated monolayer of dye molecules.

Freundlich constant value $1/n$=0.19 was less than 1 can suggests that the AOG 10 is retained by anionic resin. The Freundlich constant K_F for the anionic resin Amberlite IRA 400 was 14 mg/g. This value suggests a sorption capacity of AOG 10 dye on the heterogeneous monolayer of resin is less favorable, hypothesis sustained by the low correlation coefficient $R^2 = 0.6736$.

The heat of sorption b_T was calculated using Temkin equation. The value obtained is 45 (J/mol), which suggests strong interactions between the AOG 10 dye and the Amberlite IRA 400 anion exchange resin. A good correlation described by the Temkin model for the resin studied is sustainable by the value of the correlation coefficient $R^2 = 0.8296$.

The value of average sorption energy was obtained by applying the Dubinin-Radushkevich isotherm model, which provides information about the nature of the interactions that characterize the sorption process. The high energy value, E>16 KJ/mol for the resin studied can indicated that, there are strong interactions of both ion exchange and physical type π-π.

III.3. Kinetic studies

The sorption of AOG 10 on the resin Amberlite IRA 400 was analyzed by studying four consecrated kinetic models, namely: Morris-Weber, Lagergren, Elovich and the second kinetic order [4-5]. The characteristic constants of each kinetic model were determined from linear regression.

According to the Morris-Weber kinetic model from the graphical representation of *qt* versus $t^{0.5}$, it was obtained a value of correlation coefficient R^2 = 0,8996. The results presented show that the value determined is less than for all other kinetic models. From the graphical representation of the *log (qe-qt)* versus to *t* from the slope and intercept were determined the experimental constants of this model.

The correlation coefficient obtained using the Lagergren kinetic model was R^2=0,9872, while the calculated *qe* value (*qe, calculated* = 7,77 mg/g) based on the Lagergren equation is not in concordances with the *qe* determined experimentally (*qe,exp*=317,6 mg/g) using the influence of contact time; these results suggest that the Lagergren model cannot be used to describing the sorption process.

The α and β constants of the Elovich kinetic model were calculated from the slope and intercept of the linear regression line represented graphically by $Q_t=f(lnt)$. The high correlation coefficient describes the kinetics of the dye on the anionic resin (R^2 = 0,9739).

The experimental data obtained at equilibrium were modeled using the second order kinetic model. Thus, the graphical representation of *t/qt* versus *t*(minutes) led to the determination of a straight line according to the range studied. In addition, the quantity at equilibrium *qe*(mg/g) value determined by this model is close to the experimental results obtained at influence of contact time and the correlation coefficients of the second kinetic model are close, to 1. In conclusion, the process is subject to this kinetic model.

III.4. Evaluation the AOG 10 toxic effect on the environment based the bacterial models

The ecotoxicity effect of AOG10 on the growth bacterial (strains of gram negative bacteria) was monitored spectrophotometrically for 3 hours at a wavelength of 600 nm. The 10^{-4}M AOG

10 had a limited toxic effect on *E. coli*, inducing a bacterial growth inhibition of 8% after 1h of incubation, then bacteria adapted to the new toxic condition and the growth inhibition declined to 0 compared to the control sample (bacteria incubation without AOG10) (figure 3.4A). The growth inhibition curve induced by 10^{-4}M AOG 10 had the same characteristics as for the 10^{-2}M AOG 10, but the inhibition peak was at 35 % for 1h of incubation and then decreased to 25% after 2-3h of incubation.

C. freundi was slow to respond to the toxic effect of the dye, because the maximum inhibition peak was reached after two hours of incubation in presence of 10^{-2}M AOG 10 (36% inhibition) and 10^{-4}M AOG 10 (19% inhibition). Overall, *C. freundi* followed the same adaptation trend as *E. coli* when the inhibition growth decreased during the incubation time (figure 3.4B).

S. enterica was the most sensitive bacterial strain to 10^{-2}M AOG 10, more than 50% inhibition after 1h of incubation. At smaller dye concentration (10^{-4}M AOG 10) the maximum inhibition peak was at 2h of incubation (figure 3.4C).

Overall, all bacterial strains used to monitor the toxic effect of the dye followed the same adaptation trend: a fast the growth inhibition followed by a constant growth recovery during the incubation time.

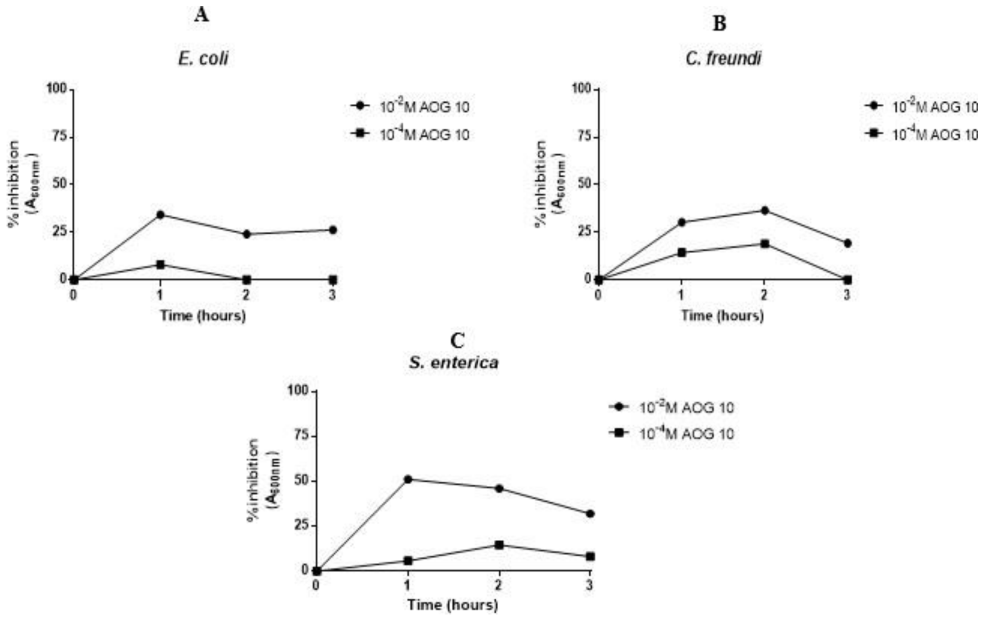


Figure. 3.4. Modulation of bacterial growth rate by various concentrations of AOG 10. *E. coli* (A),*C. freundi* (B) and *S. enterica* (C) were incubated at 37ºC in presence of 10^{-2}M or 10^{-4}M

AOG 10 and their inhibition growth rate was determined in function of the bacteria growth without dye treatment. All studies represent one of at least two independent experiments.

III.5. Monitoring the biodegradation of the AOG 10

The biodegradation effect of AOG10 on the environment was monitored for 3h at a wavelength of 478nm by bacterial growth (three gram negative bacteria strains).

In our assay, the concentration of AOG 10 (regardless of the concentration) incubated without bacteria showed no significant variation during 3h. In presence of *E. coli*, the 10^{-2}M AOG10 showed a very fast (1h of incubation) degradation, up to 25%, but no significant degradation was detected for 10^{-4}M AOG 10 (figure 3.5A), may be due to the dilution close to the detection range. During the incubation time, the degradation rate increased up to 75% for 10^{-4}M AOG 10 or 50 % 10^{-2}M AOG 10.

The AOG 10 degradation by *C. freundi* followed the same pattern as for *E. coli*, with a noticeable delay (2h) for 10^{-4}M AOG 10 degradation (figure 3.5B). Both bacterial strains induced a degradation rate for 10^{-2}M AOG 10 which seemed to reach a plateau after two hours. On the opposite side, *S. enterica* showed a linear degradation pattern for AOG 10 degradation (figure 3.5C).

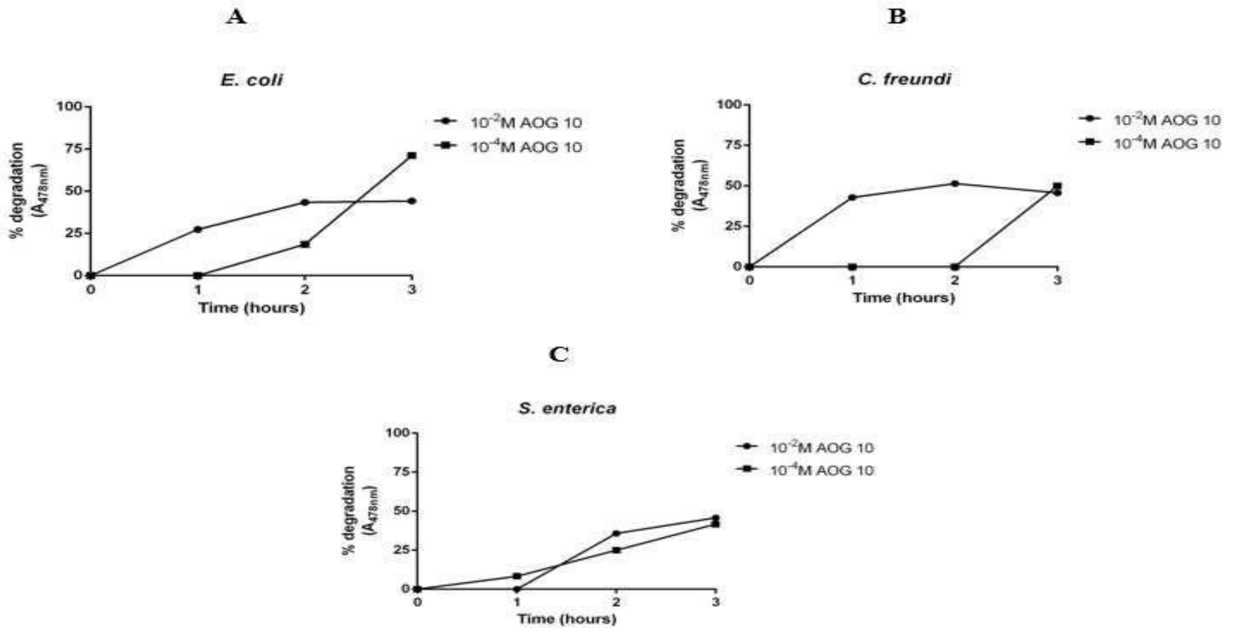


Figure. 3.5. The influence of bacteria on AOG 10 concentration. *E. coli* (A), *C. freundi* (B) and *S.*

enterica (C) were incubated 3h at 37ºC in presence of 10^{-2}M or 10^{-4}M AOG 10 and the dye concentration was monitored at 478nm. The data was analyzed in report to the A_{478nm} value of each AOG 10 concentration at the time 0h.

The correlation between the bacterial growth and the AOG 10 degradation showed that the azo dye was toxic for the bacterial population and its growth inhibition was directly linked with the pollutant concentrations. The remaining bacterial population seemed to recover due to their capability for AOG 10 degradation, therefore by only three hours the AOG 10 degradation ranged between 25% and 70%.

CHAPTER IV

COMPLEX SEQUENTIAL METHODOLOGY BASED ON ION EXCHANGE AND BIODEGRADATION MECHANISMS FOR GRYFALAN NAVY BLUE RL DYE REMOVAL FROM AQUEOUS SOLUTIONS

The experiments investigated in this chapter were based on a consecutive sequential methodology for the dye removal Acid Blue 193 as known Gryfalan Navy Blue RL (noted GNB) from synthetic solutions. For this purpose, a strongly basic anion exchange resin with quaternary ammonium functional groups in the Cl^- form Amberlite IRA 400 was used for ion exchange experiments and the degradation of the dye was accomplished using laccase, an enzyme isolated from the white-rot fungus [6].

IV.1. Study the parameters that influences the ion exchange mechanism

IV.1.1. Study the influence of the contact time

The contact time required to reach the ion exchange equilibrium was evaluated using the batch method with varied in the range 0-90 minutes. Thus, according to the experimental results obtained, the quantities of dye retained in the resin increases with the contact time in the first 50 minutes and remain constant after 65 minutes when the equilibrium is reached. In figure 4.1 is shown the variation of the amount of dye retained on the mass of resin in function of time.

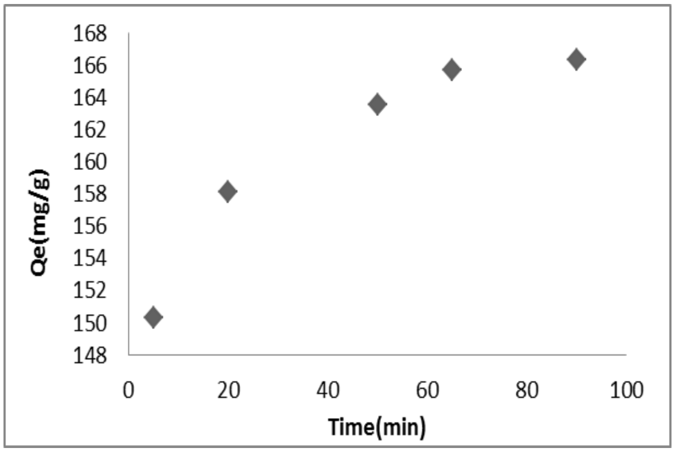


Figure 4.1. Effect of contact time on the sorption of GNB dye on the Amberlite IRA 400

IV.1.2. Sorption of the initial dye concentration on the resin

From the experimental data obtained at equilibrium, it was observed the following aspects in the case of sorption GNB in the Amberlite IRA 400, the quantity of dye retained on the resin increased with the initial concentration. This behavior can be explained by the fact that, quantity retained is influenced on the increased initial concentration of GNB. Based on the experimental data, the isotherm form at equilibrium is shown in figure 4.2.

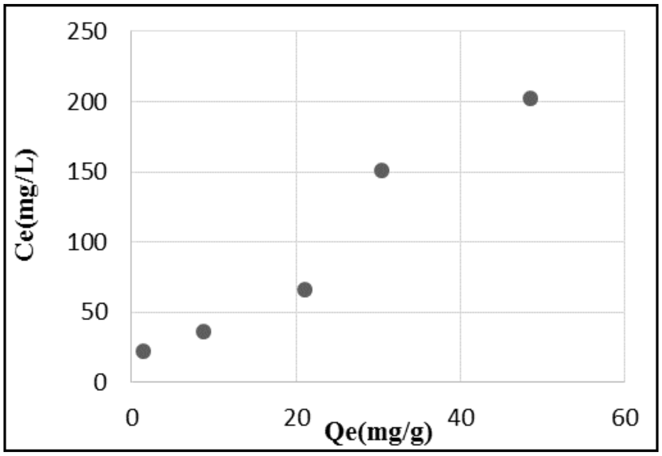


Figure 4.2. Graphical representation of the experimental isotherm for sorption GNB on the Amberlite IRA 400 strongly basic anion exchange resin

IV.2. Study the sorption isotherms

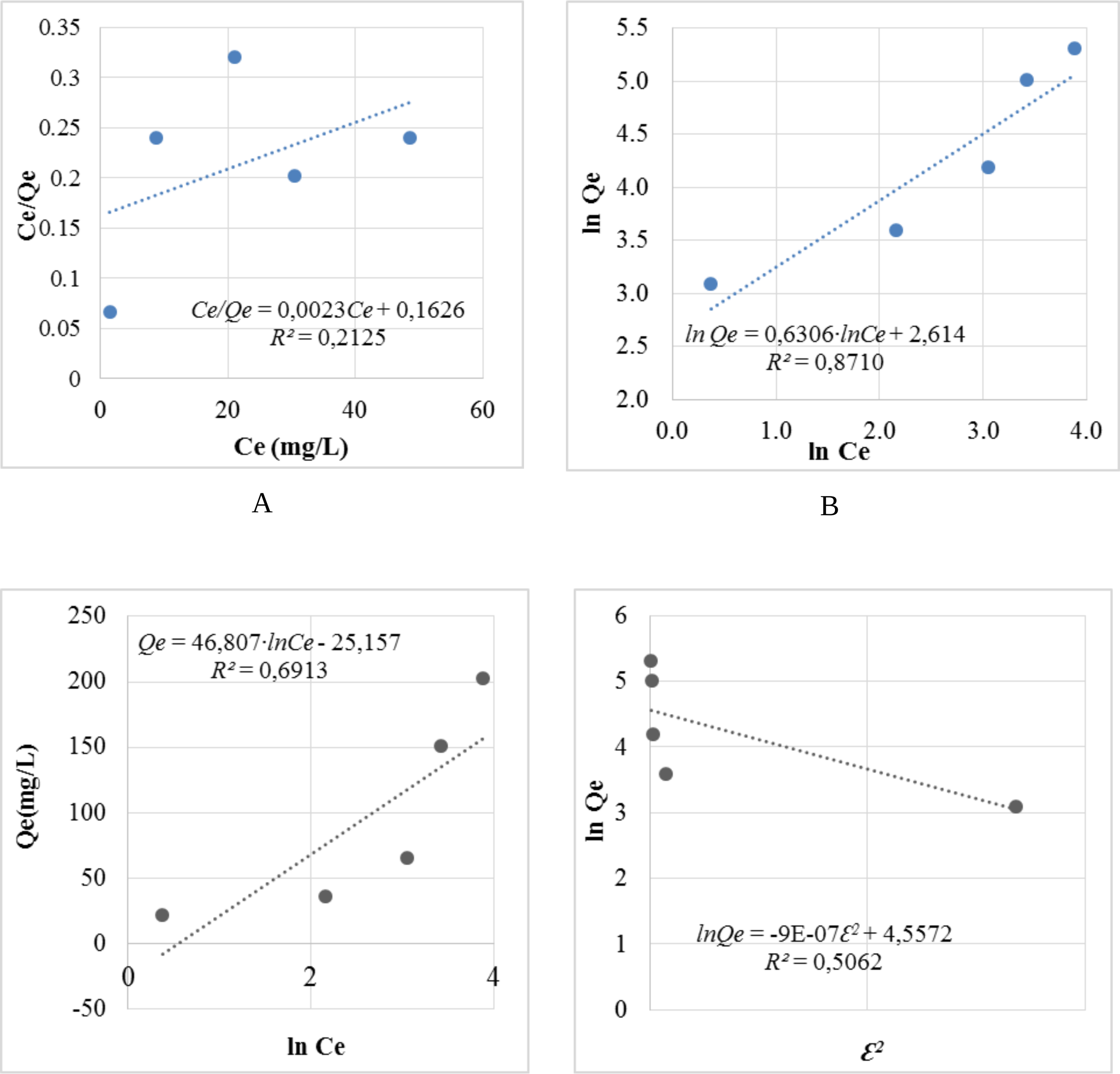
The results obtained experimentally at equilibrium were analyzed using the sorption isotherms described by the Langmuir, Freundlich, Temkin and Dubinin-Radushkevich [7]. These isotherms generate important information about the sorption process that describes the dye sorption on the strongly basic anion exchange resin Amberlite IRA 400. The parameters characteristic of each isotherm were obtained on the basis of linear regressions equations (figure 4.3A). The Langmuir isotherm describes the quantitatively formation of a saturated molecular monolayer on homogeneous surface of the resin. The low correlation coefficient $R^2 = 0.2125$ suggests that the sorption of GNB on the anion exchange resin is not performed on the surface of the adsorbent monolayer.

On the contrary, R_L value is 0.28, being in the range 0-1, which indicated a favorable sorption of GNB dye on the Amberlite IRA anion exchange resin.

The Freundlich isotherm model can be used to describe the sorption characteristics on a heterogeneous surface when is formed a multiple layers. In figure 4.3B is graphically represented the experimental form of the Freundlich isotherm. The high value of correlation coefficient $R^2 = 0.8710$ suggests that the sorption of the GNB dye on the strongly basic anion exchange resin is subject to the Freundich isotherm model. Thus, based on this hypothesis the sorption of the GNB is made on exchange centers of the heterogeneous surface in the resin.

The Temkin-Physev model was used primarily to describe interactions of sorbent-sorbit on the covered surface and to evaluate the hypothesis that, in this case, the heat of sorption would linearly decrease with the coverage of surface. The Temkin isotherm constants *A* (L/mg) and *B* were obtained by graphical representation of *Qe* versus *lnCe* from the linear equation. The graphical representation of experimental data of Temkin-Phyzev isotherm is shown in figure 4.3.C. The *b* value is 52 (J/mol) and indicated that the process is fastening and exothermic. In conclusion, the sorption of the GNB dye on the Amberlite IRA 400 highly strongly basic anion exchange resin is not influenced by the temperature.

The Dubinin-Radushkevich isotherm model was applied to obtained information about the type of sorption, whether the interactions between the GNB and the strongly basic anion exchange resin Amberlite IRA 400 are physical, chemical or ion exchange. If the value of *E* ranges between 8-16 KJ/mol, the type of sorption is characterized by ion exchange, if E is ≤ 8 KJ/mol the sorption is the physical type given by van der Waals and if $E>16$ KJ/mol the sorption is of the chemical type. The constants of the Dubinin-Radushkevich isotherm were calculated from the linear equation obtained from the graphical representation of ln *Qe* vs. $\mathcal{E}^2$. The linear Dubinin-Radushkevich isotherm obtained for the sorption of the GNB on the Amberlite IRA 400 resin is described in figure 4.3.D. The obtained value of *E* is 745 KJ/mol for this study, is more than 16 KJ/mol which indicated can we have a major ion exchange process followed by the interactions between the aromatic rings of the resin and between the naphthalene sulfonate structures of GNB.



A

B

C

D

Figure 4.3. Linear forms of isotherms: A, Langmuir; B, Freundlich; C, Temkin; D, Dubinin-Radusckhevich for the sorption of the GNB on the strongly basic anionic resin Amberlite IRA 400

IV.3. Enzymatic discoloration of GNB

IV.3.1. Study the influence of pH on the efficiency enzymatic reaction

To evaluate the influence of pH on the initial enzymatic efficiency, the optimum pH value was established to reach a maximum enzyme activity of the laccase. Following the experiments, were done at the most sustainable pH value for laccase activity and was determined at pH = 4 (figure 4.4). This result is also sustained by the fact that the optimal pH of dyes discoloration was usually found in the acid range [8]. However, we mention the GNB discoloration recorded a new peak of enzymatic activity under alkaline conditions at pH = 9 (figure 4.4).

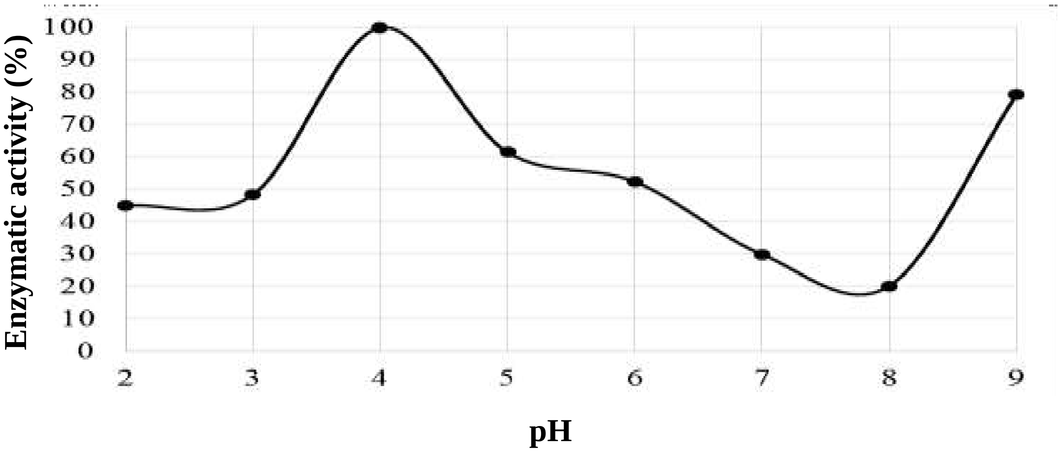


Figure 4.4. Influence of pH on the GNB dye discoloration using laccase

IV.3.2. Effect of GNB concentration on discoloration efficiency

The degradation conditions of the GNB by laccase were established for the optimal pH value of 4 and the 10^{-2} mM GNB concentration during 1440 minutes, incubation in the presence of 0.1 U/mL figure 4.5. The discoloration was monitored spectrometrically at wavelengths from 400-700 nm and the optimal range considered was from 550 to 650 nm (figure 4.5A). The results showed a rapid discoloration up to 400 minutes and the maximum efficiency (75.2%) was detected at 1440 minutes (figure 4.5B). The reaction of discoloration process followed a first order kinetics in accordance with the equation: $A = 0.2258C + 14.394$, $R^2 = 0.9912$, being performed to the reaction time up to 1440 minutes (figure 4.5C).

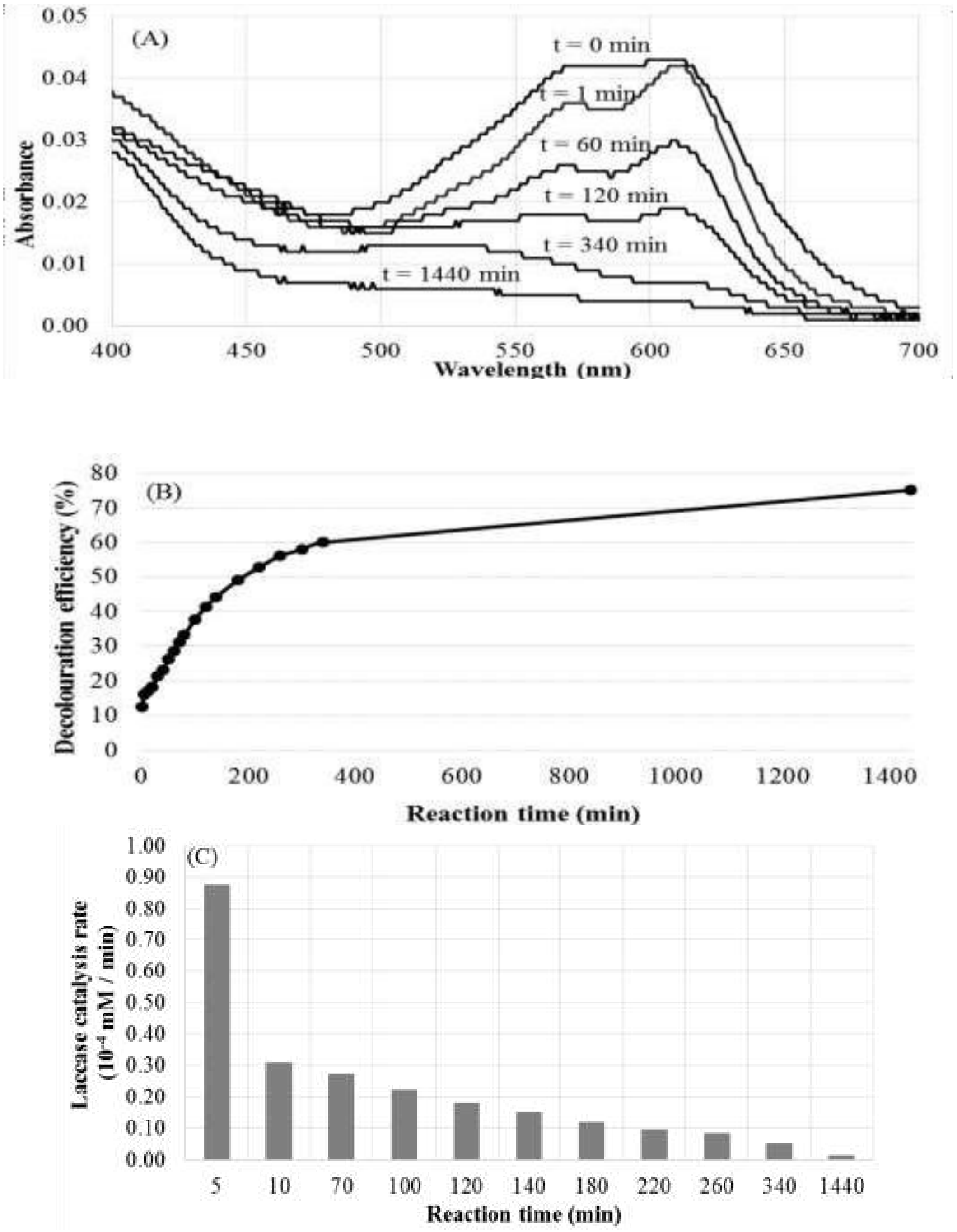


Fig. 4.5. Dynamics of the spectral curves recorded between 400 and 700 nm during GNB discoloration (10^{-2} mM) at pH 4.0 (A), the trend of discoloration efficiency (%) with fallowed to the reaction time(minutes) (B) and variation of the laccase catalysis rate (measured as decolored concentration per minute) during investigation time (C).

CHAPTER V

MAIZE STALK AS NATURAL ION EXCHANGER FOR METALLIC CATIONS

In this study, the ion exchange properties of maize stalk harvested at maturity were evaluated. The structure of this biomaterial is composed by lignin, cellulose, hemicellulose, vegetable proteins and sugars. Those compounds contain functional groups acting as weak cation exchanger for retention of metallic cations in the solution through ion exchange equilibrium.

Ion exchange equilibrium was evaluated using the influence of contact time (0-120 minutes), pH (maize stalk loaded on metallic cations was regenerated with solutions of 1M and 4M HCl) and the variation of initial metallic concentration (the interval range studied was 0.2 - 0.7mg/L).

The ion exchange equilibrium between metallic cations and the maize stalk was studied from a kinetic point of view and the sorption isotherms were evaluated.

In addition, surface of biomaterial was characterized by various techniques such as surface electron microscopy (SEM) and total attenuated IR absorption (FTIR-ATR). Subsequently, the maize stalk was tested for retention of metallic cations from waste water and sediments from tailings ponds [9]. In figure 5.1 are presented the image of maize stalk plant at maturity collected for the Western part of Romanian Plan (figure 5.1 A) and shredded of maize stalk used in ion exchange studies (figure 5.1 B).

Figure 5.1. Maize stalk at maturity (A) and shredded of maize stalk for ion exchange studies (B)

V.1. Removed of the metallic cations on maize stalk from synthetic solutions

Initially, evaluation of the activated maize stalk was performed using 0.02 mg/L solutions of 21 metallic elements. At this concentration, a strong affinity of activated maize stalk for the following metallic cations present in synthetic solutions were observed for: Mo(VI) 91%, Pb(II) 73.7%, Sb(III) 37.3%, while for the other cations, a poor retention was observed such as Se(IV) 19.5%, Cr(III) 15%, Tl(III) 11.6% and V(II) 4.60% while the following cations were not retained: As(III), Cd(III), Mn(II), Ni(II), Zn(II) and Li(I). The results obtained represent the average of two experimental assays.

Selectivity of maize stalk for Mo(VI), Pb(II) and Sb(III) (the most retained elements from synthetic solutions) was experimentally characterized by means of the sorption isotherms and kinetic models.

V.2. Study the parameters that influences the ion exchange equilibrium

V.2.1. Effect of contact time

The influence of contact time between synthetic solutions of Sb(III), Mo(VI) and Pb(II) and maize stalk was studied up to 120 minutes. As one can observe in figure 5.2, the ion exchange equilibrium was reached in 100 minutes, when sorption was faster. On the other hand, the additional time increased from 80 to 120 minutes and did not influenced significantly the quantity retained on maize stalk ranging between 0.280, 0.292 to 0.295 mg for Mo(VI). For Sb(III) the following quantities were retained and detected to as 0.260, 0.268 to 0.276 mg on the activated mass of maize stalk. For Pb(II) the next quantities of 0.110, 0.120 and 0.120 mg were retained. The quantities retained of Sb(III) and Mo(VI) on maize stalk were about twice high as for Pb(II), figure 5.2.

Taking into account the structure of the biomaterial, it can be assumed that the access of the metallic cations to ionizable groups would being made more difficult. In order to investigate applicability of this study a time of 100 minutes it was necessary to achieve the equilibrium.

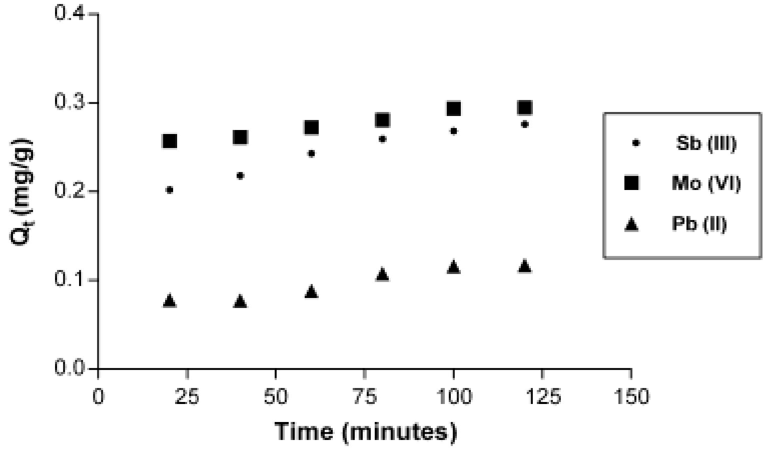


Figure 5.2. Experimental data of contact time for Sb(III), Mo(VI) and Pb(II) on the maize stalk

V.2.2. Study of the stability of cations retained on the maize stalk

As was shown in figure 5.3, the ion exchange equilibrium for Co(II) and Pb(II) is not affected by 1M HCl, whereas the 4M HCl solution removed all the cations except Mo(VI) and Tl(III); for other cations, the tendency of their removal from the maize stalk is subject to theoretical rules.

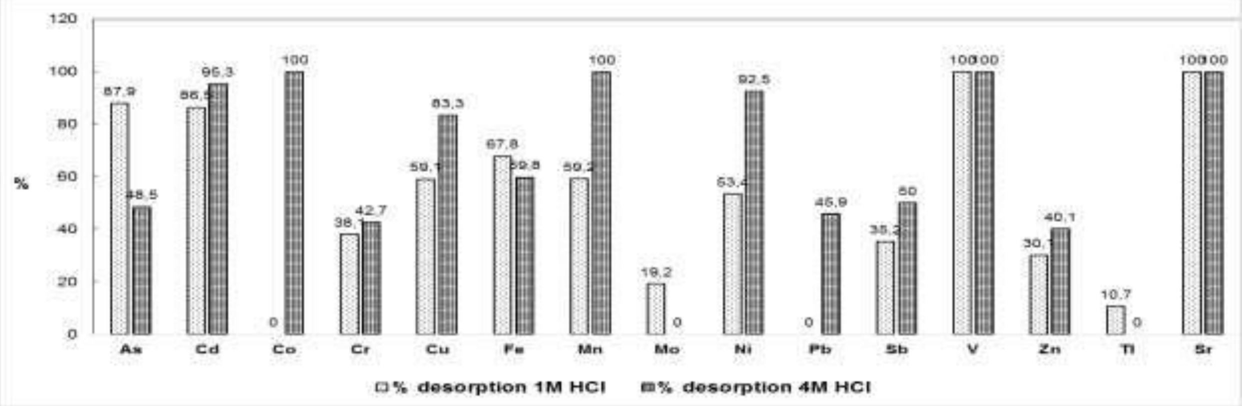


Figure 5.3. Desorption of metallic cations from maize stalk using 1M and 4M HCl

V.3. Study of sorption isotherms

The ion exchange equilibrium was characterized using the most studied isotherm such as: Langmuir, Freundlich, Temkin and Dubinin-Radushchevici [10], that can be used to evaluated the experimental data and to obtained information about the sorption process can involving the retention of metallic cations on the maize stalk. For the all models studied, the greater value of the correlation coefficient was obtained for Mo(VI) R^2 =0.9995 which was higher than for Sb(III) with R^2 = 0.9853 and Pb(II) with R^2 = 0.8660 for the Freundlich isotherm model.

On the other hand, the highest sorption capacity was 0.4475 mg/g for Sb(III), followed by Mo(VI) with 0.3804 mg/g and Pb(II) with 0.2807 mg/g using the Langmuir isotherm model. In addition, the R_L and n constants calculated for the Langmuir and Freundlich isotherms indicated a favorable sorption for Sb(III), Mo(VI) and Pb(II) on the biomaterial tested. Thus, the R_L values are: 0.3820; 0.6263 and 0.8601 obtained for Sb(III), Mo(VI) and Pb(II). The detected values were within the range (0-1) imposed for this constant. Moreover, Freundlich constants values n calculated using experimental data were 1.8293; 2.3674 and 1.3870 for Sb(III), Mo(VI) and Pb(II) being greater than 1, the condition imposed for this constant.

Moreover, the Dubinin-Radushkevich isotherm confirms the working hypothesis of this study that the metallic cations are retained on the maize stalk by ion exchange mechanism. The average energy of sorption (E) was higher than 16 KJ/mol, for all studied cations.

Finally, the heat of the ion exchange process b_T was calculated using the Temkin-Phyzev isotherm and the results obtained experimentally suggested a strong interaction between the cations and the maize stalk. The results of correlation coefficients determined were 0.9688, 0.9682 and 0.8362 for Sb(III), Mo(VI) and Pb(II) respectively. These results were lower comparison to the rest of the studied models; therefore this model cannot be used to describe the sorption of the studied metallic cations.

V.4. Kinetic studies of the ion exchange equilibrium

The kinetics of metallic cations retained in materials is an important parameter to predict the design of waste water treatment systems. In this case the configuration of the columns depends on the speed of the sorption process. A rapid kinetics will facilitate the design of column with a lower length, while a slow sorption rate will require long columns to maximize the sorption potential of the biomaterial.

In addition the sorption rate to the biomaterial depends on the several factors such as: the structural properties of the sorbent, the initial concentration and the interaction between the analyte and the active sites of sorbent.

The kinetic models studied were evaluated using: Lagergren, Morris-Weber, Elovich and the second kinetic model [11-12]. The applicability of these models has been assessed on the basis of correlation coefficients. The rate constants for Lagergren model $k(min^{-1})$ and the quantity of sorption at equilibrium $qe(mg/g)$ have been found based on the graphical representations of $log(qe-qt)$versus *time*, from slopes and intercept. The values $qe,_{calc.}$, obtained by applying the first kinetic model were not in agreement with the results of $qe_{exp.}$ 0.2769, 0.2947 and 0.1171 mg/g determined at influences of contact time. The obtained data of $qe,_{calc.}$ are 6.2187, 6.0632 and 5.4288 for Sb(III), Mo(VI) and Pb(II) calculated by Lagergren model.

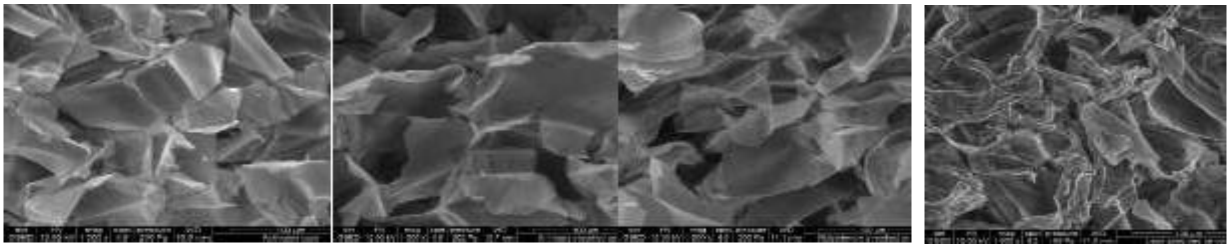
Morris-Weber kinetic model describes the sorption of Sb(III), Mo(VI) and Pb(II) when the linear line obtained from the graphical representation of *qt*(mg/g) versus $t^{0,5}$(min^{-1}) passing through zero. The quantities of Sb(III), Mo(VI) and Pb(II) retained on the surface of the maize stalk were obtained from the intercept of linear equation. The values detected for the intercept were different to zero and have been: 0.1432; 0.2239 and 0.0378 for Sb(III), Mo(VI) and Pb(II) respectively and is represented by the quantities retained on the surface of the biomaterial. The results calculated for correlation coefficients were lower than for the all of the studied models. These results indicate with this model doesn't describe the kinetics of sorption of the studied metallic cations.

Moreover the second order speed constants, k^2 (g/(mg·min.) of the sorption process as well as the maximum capacities $qe(mg/g)$ were determined from the graphical representation of the ratio t/qt according to *t*. The quantities determined for qe_{calc}. were 0.2976, 0.3044 and 0.1392 mg/g that are close to the experimental results and were 0.2769, 0.2947 and 0.1171 mg/g for

Sb(III), Mo(VI) and Pb(II), respectively. In addition the values of correlation coefficients obtained have the highest values compared to the all of the studied models. It can be concluded as the sorption process is subject to the second order kinetics theory which is based on the hypothesis that the rate at which metallic cations are retained on the maize stalk is controlled by ion exchange process. Low values of correlation coefficients determined using the Elovich kinetic model suggested can this model does not describe the kinetic of the metallic cations studied on the maize stalk.

V.5. Maize stalk characterization by surface electron microscopy (SEM) studies

For this purpose the biomaterial samples loaded with Mo(VI), Sb(III) and Pb(II) were analyzed by checking the morphological changes against the activated biomass used as a control sample. The images obtained using SEM (microscopy) is shown in figure 5.4. These analyzes highlight the existence of Mo(VI) by quantification of 2.12% and for Sb(III) with 2.94% values above the base-line.



control Sb(III) Mo(VI) Pb(II)

Figure 5.4. The morphological image of the samples studied

V.6. Studies with total attenuated IR (FTIR-ATR)

Spectral studies were performed by IR spectrometry using the FTIR-ATR technique. The spectra are presented in figure 5.5. It is very much the same except for the 1730 cm^{-1} band belong to the $-COO^-$ group, which upon interaction with different cations that decreases in intensity. In addition, new peaks were observed at about 1692 cm^{-1}. The most significant spectral differences were noticeable when interacting with Pb(II), this being in concordance with the morphological changes observed in the SEM images.

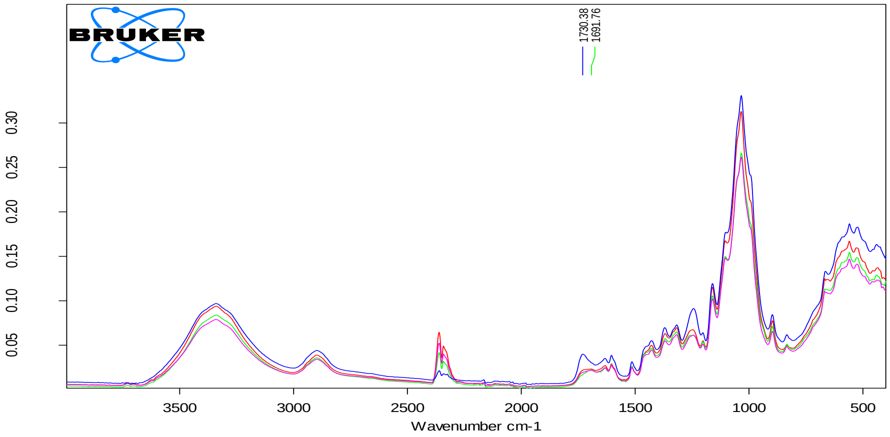


Figure 5.5. FTIR-ATR spectra of maize stalk, maize stalk+Mo(VI), maize stalk+ Sb(III), maize stalk +Pb(II)

V.7. Retained the metallic cations from waste water and from the mining waste sediments samples on the maize stalk

In our study, this biomaterial has been used for waste water purification because it has the ability to remove, in different percentages, almost all investigated metallic cations. It is worth to notice the capacity for the removal of Sb(III), together with Mo(VI) and V(II) from very acidic waste water samples.

Depending on concentration of the metallic cations in leaching samples, different percentages are removed by the structure of maize stalk plant material (figures 5.6÷5.9).

It is known that the cation exchange resin has high affinity for concentrated solutions irrespective of the charge and volume of the metallic cations, this behavior is also evidenced in these experiments based on the results showed in figures 5.6, 5.7, 5.8 and 5.9.

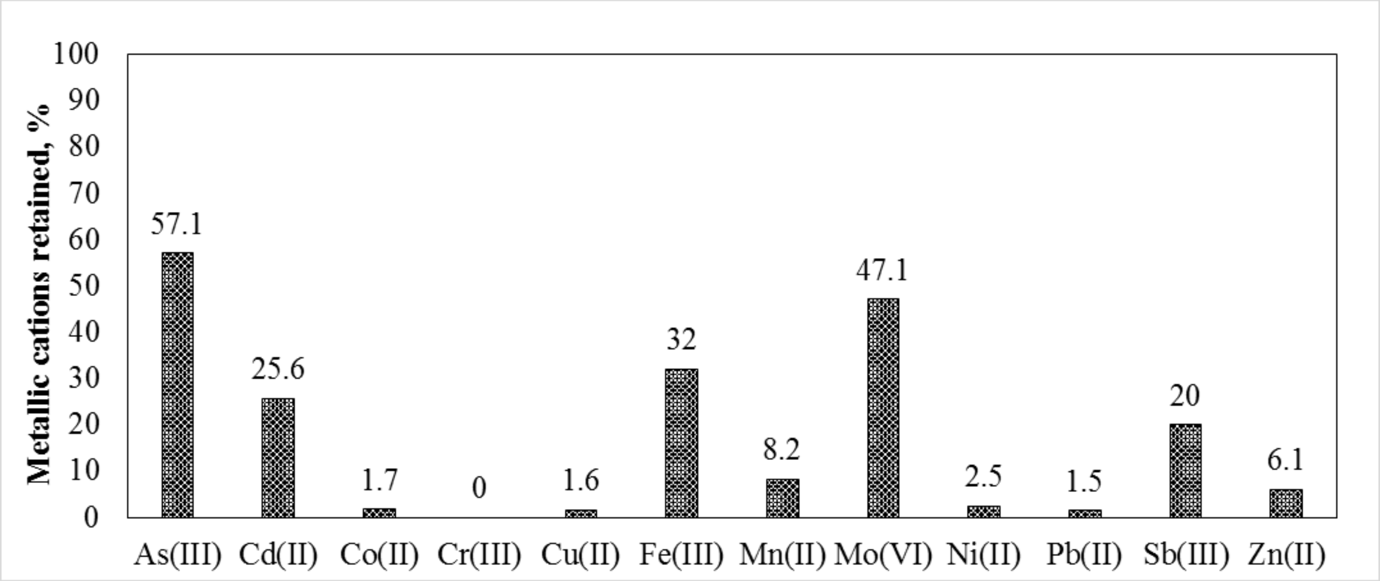


Figure 5.6. Percentages of metallic cations retained from the leaching solution on maize stalk using the ion exchange process for sample 1

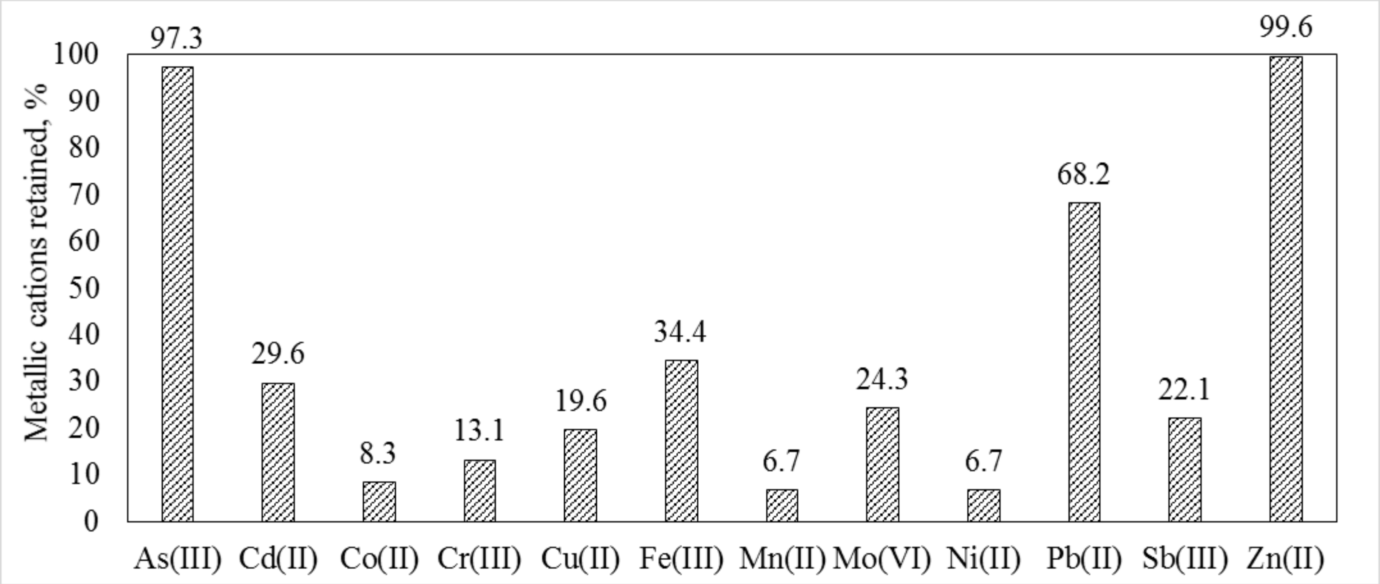


Figure 5.7. Percentages of metallic cations retained from the leaching solution on maize stalk using the ion exchange process for sample 2

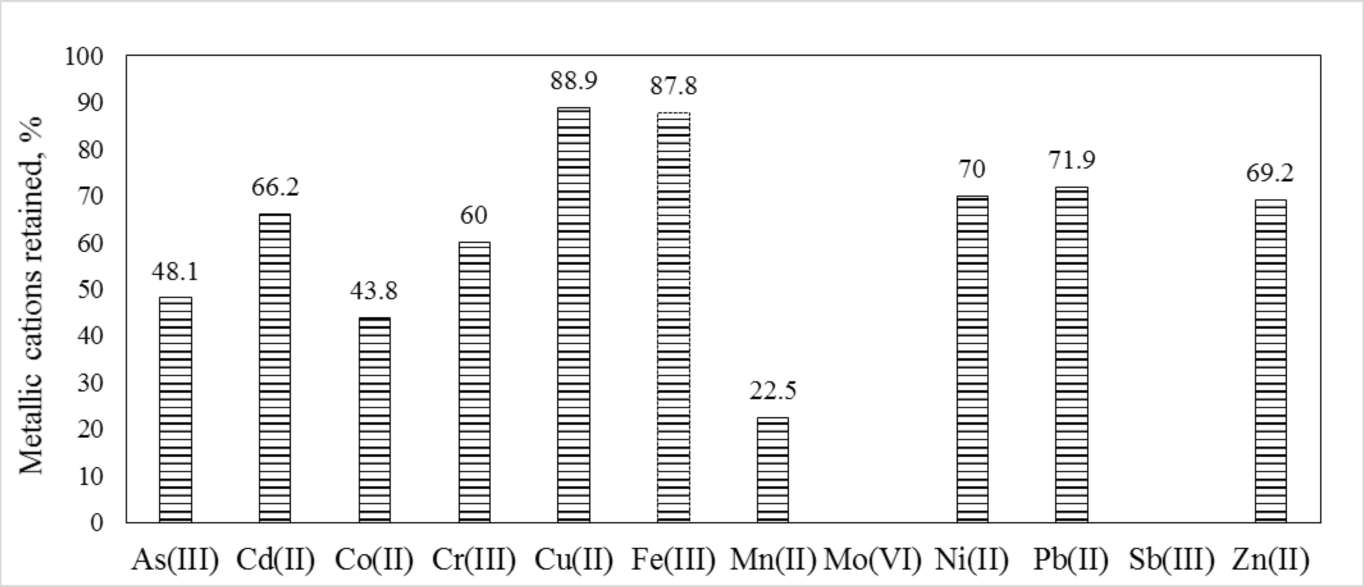


Figure 5.8. Percentages of metallic cations retained from the leaching solution on maize stalk using the ion exchange process for sample 3

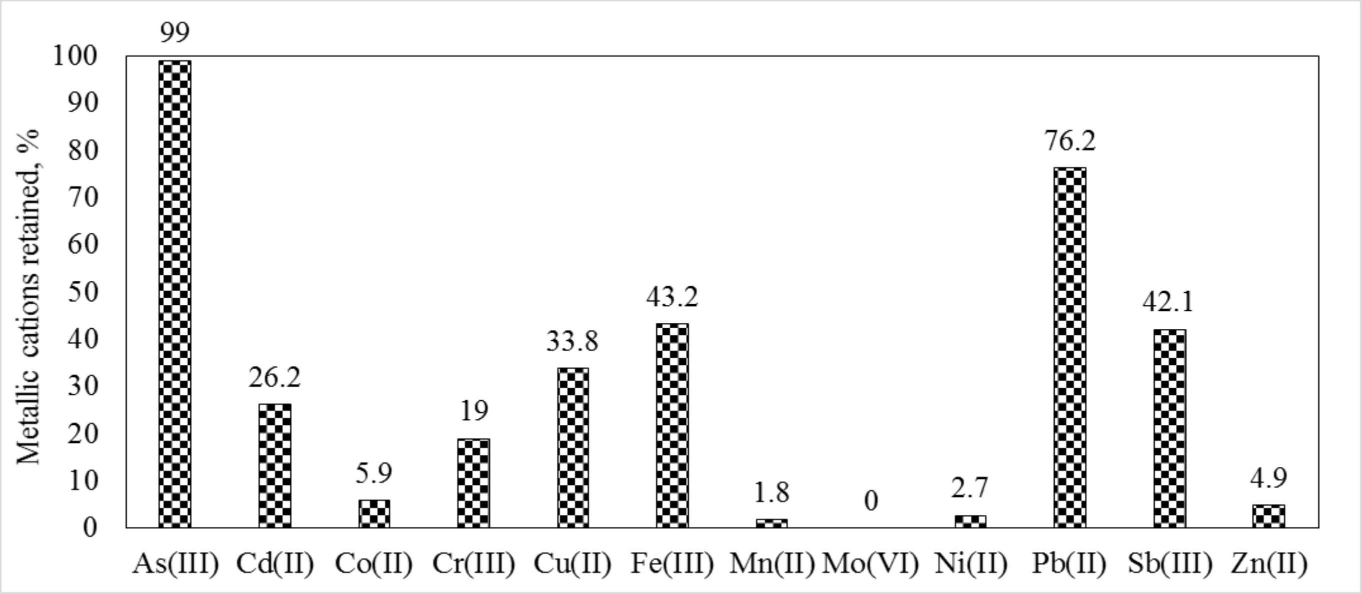


Figure 5.9. Percentages of metallic cations retained from the leaching solution on maize stalk using the ion exchange process for sample 4

Thus, as a result of sorption studies, activated maize stalk retained up to 57.1% As(III), 47.1% Mo(VI), 32% Fe(III), 25.6% Cd(II) and 20% Sb(III) for initial concentrations presents in analysis of 941; 1.70; 53715; 86.6 and 5.50 mg/L respectively, for leaching sample 1.

For sample 2, the metallic cations were retained as follows on maize stalk: Zn(II) 99.6%, As(III) 97.3%, Pb(II) 68.2%, Fe(III) 34.4, Cd(II) 29.6%, Mo(VI) 24.3% and Sb(III) 22.1% while a lower rate of sorption was observed for Cu(II) 19.6%, Cr(III) 13.3%, Co(II) 8.3%, Mn(II) and Ni(II) 6.7%.

The maize stalk activated retained the following cations: Cu(II) 88.9%, Fe(III) 87.8%, Pb(II) 71.9%, Ni(II) 70%, Zn(II) 69.2, Cd(II) 66.2% and Cr(III) 60% for to initial concentrations of 9.0; 2338; 38.1; 6.0; 1309; 15.1 and 1.50 mg/L respectively for the leaching sample 3.

While for the sample 4, the cationic species were retained as follows: As(III) 99% and Pb(II) 76.2% to the initial concentrations of 995 and 50.9 mg/L respectively.

In order to quantification the results obtained according to the literature data, the metallic species existing in solution to different chemical forms: in the simple cations form but also in the organometallic combinations form [13-14].

For ion exchange process only the metallic cations from solution can be retained by the maize stalk using ion exchange equilibrium (which is obtained between metallic cations and the H^+ ions from the hydroxyl groups of the plant material structure).

Arsenic elements exists in the inorganic form, such as H_3AsO_3 arsenic acid (slightly dissociated in solution) and H_3AsO_4 arsenious acid. The results obtained for the arsenic element can be explained by the fact that exists in nature and in the organo-metal cation form [15], which can also participate at ion exchange equilibrium. Taking into consideration these aspects and the fact that, it is a difficult metallic cation, we propose the maize stalk as a selective biomaterial for this metallic element.

GENERAL CONCLUSIONS

Both the aim of the thesis and its objectives have been fulfilled, with articles, published for the first time in literature, on the Amberlite IRA 400 a highly strongly basic anion exchange resin for sorption of two hazardous azo dyestuffs from the environment. In addition, the maize stalk can be used as an inexpensive and efficient natural ion exchange for retained of the metallic cations or as an additional barrier to prevent leakage of pollutants, especially from mining tailings ponds or it could be used in the waste water treatment.

In addition the results obtained in the experimental part led the following consideration. The physico-chemical methods using classical and unconventional ionic exchangers as well as the biological methods can synergistic contribute to the reduction of the toxic impact of some organic and inorganic pollutants.

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