Removal of procainamide and lidocaine on Amberlite XAD7HP resin and of As(V), Pb(II) and Cd(II) on the impregnated resin for water treatment

Marin, Nicoleta Mirela; Stanculescu, Ioana

Removal of procainamide and lidocaine on Amberlite XAD7HP resin and of As(V), Pb(II) and Cd(II) on the impregnated resin for water treatment

Nicoleta Mirela Marin [a,*], Ioana Stanculescu [b,c,d,**]

[a] National Research and Development Institute for Industrial Ecology ECOIND, Street Podu Dambovitei No. 71-73, District 6, 060652, Bucharest, Romania
[b] Department of Physical Chemistry, Faculty of Chemistry, University of Bucharest, 4-12 Regina Elisabeta Bd., 030018, Bucharest, Romania
[c] Horia Hulubei National Institute for Physics and Nuclear Engineering, Centre of Technological Irradiations IRASM, 30 Aleea Reactorului, 077125, Magurele, Romania
[d] Faculty of Applied Sciences, Reactor Institute Delft, TU Delft, Mekelweg 15, 2629, JB, Delft, the Netherlands

HIGHLIGHTS

- Polymeric adsorbent Amberlite **XAD7HP** removes procainamide and lidocaine from water.
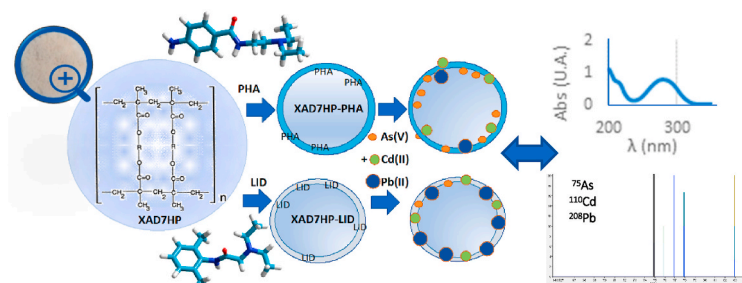- Langmuir model best fitted the adsorption isotherm for both pharmaceutics.
- Pseudo second order model best described the adsorption rate of **PHA** and **LID.**
- Resin regeneration is faster with Acetone than with 3% HCl and 10% NaOH.
- Pb(II) and As(V) are specifically removed by the **LID** form respectively **PHA** form of **XAD7HP.**

GRAPHICAL ABSTRACT

ARTICLE INFO

ABSTRACT

The purpose of the research consists of: i) development of a new specific adsorption method for two anesthetic drugs, procainamide (**PHA**) and lidocaine (**LID**) from aqueous solutions on Amberlite **XAD7HP** polyester resin and ii) obtaining a high-performance new material, **PHA** respectively **LID** loaded resin, for As(V), Cd(II) and Pb (II) metallic ions recovery. The influence of contact time, drugs concentration and the stability of the impregnated resin in presence of acetone, and also in acid (3% HCl) and basic (10% NaOH) solutions were followed by UV–Vis spectrometry. The intra-particle diffusion kinetic model best described the dominant stage of adsorption for **PHA**. Moreover, **PHA** and **LID** loaded resin proved efficient in selective hazardous metalic ions removal from synthetic waters as evaluated by ICP-MS and SEM analysis and inferred from the interplay between hydrophobicity and polarity of the two drugs structures. The resin in **PHA** form (**XAD7HP-PHA**) may be used specifically for As(V) removal up to 94% and selectively for Cd(II) and Pb(II) removal in 10–76% percentage range. Likewise, **XAD7HP** resin in **LID** form (**XAD7HP-LID**) removed the whole amount of Pb(II) and selectively Cd(II). Thus, **XAD7HP-LID** form has very high affinity for Pb(II) in all five solutions samples of metallic cations mixtures studied. Also, it was found that Pb(II) removal is not affected by the presence of As(V) and Cd(II), when sample concentration is 0.5 mg/L. Based on the adsorption study, two different materials i.e. **XAD7HP-PHA** and **XAD7HP-LID** for As(V) and Pb(II) removal from polluted water were developed. The rapid adsorption of the

* Corresponding author.
** Corresponding author. Department of Physical Chemistry, Faculty of Chemistry, University of Bucharest, 4-12 Regina Elisabeta Bd., 030018, Bucharest, Romania.
E-mail addresses: nicoleta.marin@incdecoind.ro (N.M. Marin), istanculescu@nipne.ro (I. Stanculescu).

PHA and **LID** on **XAD7HP** coupled with the good resin regeneration and excellent metallic ions recovery provide means for the expansion of polymer adsorbent applications to improve water treatment technologies.

1. Introduction

Nowadays, pharmaceutics among other organic compounds and toxic metallic ions are ubiquitous in aqueous media and their transfer between the geosphere and biosphere compartments is a current global level problem [1]. Adverse human health effects of As, Pb and Cd elements are well known: As is carcinogen even at extremely low levels of exposure and produces fever, anorexia, fluid and hair loss, etc.; Cd is a very toxic element, long-term exposure leads to buildup and possible kidney disease, fragile bones and lung damage, hypertension, arthritis, anemia, etc.; Pb is recognized as a major environmental health risk throughout the world, promoting serious adverse health effects, especially in young children, affecting the nervous, cardiovascular, renal and digestive systems [2]. Moreover, the occurrence of pharmaceutical compounds and of their degradation products even at very low concentrations leads to toxic effects on the biotic and abiotic environment [3,4]. In addition, pharmaceutical compounds may reach the environment through several pathways and different sources: industrial, household, hospital residual waste, etc., the wastewater treatment plants (**WWTPs**) being the main choice for their remediation in order to diminish the impact on various ecosystems [5]. The sludge produced in primary/secondary settling tanks decomposes the biodegradable organic matter via the present microorganisms before the final discharge [6]. Sometimes **WWTPs** are inefficient in pharmaceutical compounds degrading either during the primary or secondary treatment, not being able to specifically remove them. The legislation on the limits of discharge of pharmaceutical compounds is expected to appear in the near future [7]. In this regard, it is necessary to establish more efficient wastewater remediation technologies and the retention of pharmaceutical compounds on polymeric resins before the discharge in urban wastewater should be included among the adequate treatments [8]. From the multitude of options available due to the simplicity of application, the adsorption treatment could be used in this purpose with excellent selectivity [9]. In addition, the establishment of adsorbent treatment in current **WWTPs** is technologically feasible, polystyrene resins being the first choice for pharmaceutical compounds retention together with activated carbon [4,10–16].

Non-ionic macroreticular resins have several advantages over conventional activated carbon, among which: simple operation, low energy consumption, easy regeneration and the possibility of modeling control in different granules forms. In addition, the pore structure and the internal surface may be shaped by modifying the polymerization conditions [17]. Complexing resins may be obtained either by batch method or by column immobilization, their well-known use probing their effectiveness in separation and recovery of metal ions [18]. Literature review emphasizes non-ionic macroreticular resin Amberlite **XAD7HP** impregnated with different organic agents for metallic ions removal. Thus, **XAD7HP** resin was impregnated with Toluidine blue o [19] and Brilliant green [20] for Cr(VI) removal. The adsorption capacity of 20.62 mg/g and 5.45 mg/g respectively was found. Ciopec et al., 2012 investigated **XAD7HP** resin impregnation with di-(2-ethylhexyl)-phosphoric acid (DEHPA) for Cr(III) removal. By using the impregnated resin, 3 mg Cr(III)/g were adsorbed [21]. Also, 70 mg/g of Pd(II) was removed from acidic solutions by immobilized Cyphos IL-101 ionic liquid (IL; tetradecyl (trihexyl)phosphonium chloride) onto **XAD7HP** [22]. The use of chelating agent in enrichment and determination of Ni (II) from water samples was evaluated. The **XAD7HP** was used for retaining Ni-diamino-4-(4-nitro-phenylazo)-1H-pyrazole system. The detected adsorption capacity was 7.2 mg/g [23]. The chemical impregnation of **XAD7HP** with di-(2-ethylhexyl)phosphinic acid was applied for Lu(III) removal [24]. The determined value showed that the

modified resin retained 23.8 mg/g Lu(III).

The purpose of this paper is the research and development of new high selectivity adsorbent materials realized by immobilizing two anesthetics, **LID** (2-Diethylamino-N-(2,6-dimethylphenyl)acetamide), and **PHA** (4-amino-N-[2-(diethylamino)ethyl]benzamide) on **XAD7HP** resin beads, a scientific first to the best of our knowledge. Furthermore, the originality of this work comes from the use of the named immobilized compounds on the resin to selectively bind metal ions such as As(V), Pb (II) and Cd (II). The main objective of removing pollutant species from water is achieved through adsorption and kinetic studies using Langmuir and Freundlich isotherms and Lagergren, Morris-Weber and Pseudo second order models. **LID** and **PHA** bind through the aromatic groups and alkyl chains to the hydrocarbon matrix of the resin by π-π and hydrophobic interactions and to metal ions through donor atoms of amino and carbonyl functional groups. In terms of water quality, natural and synthetic materials probed to be effective in pre-concentrating and separating metal ions. However, the lack of selectivity of these materials has led to need of development of new materials containing functional groups such as **XAD7HP** impregnated resin that interacts strongly with metal ions and may form stable complex combinations. It is known that the modified resins may selectively retain a wide variety of metal ions by forming adducts of complexing agent and metal ion and that the stability of these complexes differs and depends on the experimental conditions [25]. Thus, from the analytical practice it is known that for complex composition wastewater treatment it is necessary to select technologies with very high selectivity to obtain maximum efficiency. The novelty and originality of this work consist of: i) the development of a new specific adsorption method for **PHA** and **LID** on **XAD7HP** resin and ii) the obtaining of high performance new materials, **PHA** and **LID XAD7HP** impregnated resin respectively, with excellent As(V), Cd(II) and Pb(II) metallic ions recovery properties.

2. Materials and methods

2.1. Chemicals

The following reagents from different chemical suppliers were used: HCl 37% for preparation of 4 M and 3% solutions and NaOH pellets for preparation of 10% solution by dilution with ultrapure water from Merck, Germany; procainamide hydrochloride (≥98%), produced in China, solid lidocaine hydrochloride monohydrate (≥98%), produced in Taiwan, Amberlite **XAD7HP** polymer resin produced in France from Sigma Aldrich. Acetone (**Ac**) (≥99.5%) of HPLC purity was purchased from Honeywell. The **XAD7HP** resin is an acrylic ester with affinity for pharmaceutical organic compounds that have high molecular weight and also for metal ions. The **XAD7HP** resin has: 20–60 mesh size, 1.14 mL/g mass resin pore volume, 1.24 g/mL density of dry mass and 1.05 g/mL for wet mass. The mean pore size is around 9 nm with 450 m^2/g surface area [26]. It can be used up to 149 °C and in the 0–14 pH range. The certified reference materials (**CRM**) of 1000 mg/L of H$_3$AsO$_4$, Cd (NO$_3$)$_2$ as well as Pb(NO$_3$)$_2$, used to prepare the analytical solutions in HNO$_3$ 0.5 mol/L were obtained from Merck, Darmstadt, Germany.

2.2. Equipment

The UV-VIS spectra of **PHA** and **LID** synthetic solutions were recorded using a DR/5000TM (Hach Lange, Germany) spectrophotometer using 1 cm quartz cells, in the 200–400 nm range, with 100 nm/min scanning speed, toward ultrapure water as reference. Metal ions from supernatant solutions before and after contact with **PHA** and **LID** loaded **XAD7HP** resin were evaluated with an Aurora M90 Bruker Inductively

Coupled Plasma- Mass Spectrometer (**ICP-MS**) (Bremen, Germany). Ultra-Clear system (Richfield, USA) was employed to obtain ultrapure water (18 MΩ/cm). Characterization of **XAD7HP** beads pre and post loading with **PHA** and **LID** in the first step and As(V), Pb(II), Cd(II) in the second step was done with the scanning electron microscope Quanta FEG 250 (Fei, Eindhoven, The Netherlands).

2.3. Preparation of working solutions

Stock solutions of 0.01 M concentration were prepared for each pharmaceutical compound as follows: the corresponding amount of **PHA** and **LID** was weighed on the analytical balance and passed quantitatively into 50 mL volumetric flasks and then filled up to mark with ultrapure water. Solutions of 10 mg/L Cd(II), Pb(II) and As(V) metal ions were obtained from 1000 mg/L CRM solutions. Afterwards from 10 mg/L solutions of 0.1; 0.2; 0.3; 0.4 and 0.5 mg/L using normality law were obtained.

2.4. Purification of the XAD7HP resin

A quantity of 10 g **XAD7HP** resin was weighed in a 100 mL Berzelius glass. The resin was washed several times with ultrapure water and after each wash the solution was decanted. Subsequently the resin was allowed to swell in ultrapure water for 24 h. Afterwards, the swollen resin was transferred in a glass column of 25 × 2.5 cm (height x internal diameter). After that, the resin was purified with 50 mL of 4 M HCl at 0.6 mL/min flow rate and subsequently was washed with ultrapure water until the pH became neutral. The purified resin was removed from the column and allowed to dry on filter paper for 24 h before being used in the adsorption studies.

2.5. Methodology for determining the optimum resin-pharmaceutical compounds contact time

The influence of the contact time between resin and **PHA** and **LID** studied compounds was tested at different moments. Thus, the mixtures obtained by combining 0.1 g **XAD7HP** resin and 10 mL **PHA** and **LID** aqueous solutions were mechanical stirred at 175 rotations per min (rpm) and spectrometrically evaluated at 30, 40, 50, 60, 70 and 80 min using the methodology described in section 2.9. Based on this experiment the optimum adsorption time was selected for the future steps of research. The evaluation of the reaction rate using kinetic adsorption models was done. The adsorption capacity that varies over time is calculated with the following relation:

$$Q_t = \frac{(C_i - C_t)V}{m} \tag{1}$$

where: C_i and C_t (mg/L) are the **PHA** and **LID** concentrations at the beginning of the experiment (i) and at time (t); m(g) is the mass of dry **XAD7HP**, V(L) is the volume of **PHA** and **LID** used. All experiments were done in duplicate and for Q_t calculation the average value was used.

2.6. Adsorption performance experiments by batch method in the system XAD7HP, PHA and LID

For this purpose, approximatively 0.1 g samples of **XAD7HP** resin, were weighed in Erlenmeyer flasks at analytical balance with an accuracy of 0.0002 g and the same volume (V) of 0.01 L **PHA** and **LID** of different concentrations was added. The samples obtained were stirred for 80 min, at 175 rpm scanning speed; afterwards the amount of pharmaceuticals in the filtrate of every solution was spectrometrically determined based on the methodology described in section 2.9. To evaluate the adsorbed quantity at equilibrium (Qe) for **PHA** and **LID** on **XAD7HP** mass (m) the following equation was used [27,28]:

$$Q_e = \frac{(C_i - C_e)V}{m} \tag{2}$$

All experiments were done in duplicate and for Q_e calculation the average value was used.

2.7. Methodology for regeneration of XAD7HP resin

For regeneration studies 10 mL of 10% NaOH, 3% HCl and **Ac** were added over 0.1 g of **PHA** and **LID** saturated resin considering the data sheet recommendations [29]. The mixtures were stirred for 1 h after which the supernatant solutions were recovered by filtration. All experiments were done in duplicate and for **PHA** and **LID** percentages removed from **XAD7HP** mass resin calculation the average value was used.

2.8. Methodology for adsorption of metal ions on XAD7HP resin in PHA and LID form

For this experiment, five samples of 0.5 g **XAD7HP** in **PHA** form, i.e. resin loaded with 50 mL of 54 mg/L solution and in **LID** form, i.e. resin loaded with 50 mL of 58 mg/L solution, were filtered and 0.01 L of metal ions solutions were added. The obtained mixtures were subjected to mechanical stirring for 3 h. The metal ions in supernatant solutions obtained at equilibrium were determined by ICP-MS method. The concentration interval for metallic ions determination was in the range 0.1–0.5 mg/L. The determination limit for each metallic ions on the equipment were 15 μg/L As(V), 7 μg/L Cd(II) and 9 μg/L Pb(II). Adsorption of metals as percentage of recovery (R%) on resin was calculated by the following equation:

$$R\% = \frac{C_i - C_e}{C_i} X100 \tag{3}$$

All experiments were done in duplicate and for *R%* calculation the average value was used.

2.9. UV-VIS determination of PHA and LID

Quantitative determination of **PHA** and **LID** from supernatant after adsorption studies was evaluated by calibration curves that were obtained from graphical representation of spectrum area (S_a) against concentration (C). Calibration curves determined by the least squares method were as follows: $S_{a\,PHA} = 3939.2C + 9.1109$; $R^2 = 0.9990$ in the range 13–50 mg/L for **PHA** and $S_{a\,LID} = 860.29C + 10.715$; $R^2 = 0.9988$, in linearity range 12–81 mg/L for **LID**. Furthermore, high values of correlation coefficient (R^2) suggest that the Lambert-Beer law was checked. Determination limit for **PHA** is quantified at 6 μg/L and 9 μg/mL for **LID** respectively.

3. Results and discussion

3.1. Influence of contact time between liquid and solid phase

The influence of contact time between the polymeric resin **XAD7HP** and the synthetic solutions of **PHA** and **LID** was determined experimentally. With this aim, adsorption of 83 mg/L **PHA** and respectively 80 mg/L **LID** in contact with 0.1 g resin mass was evaluated step by step for various periods totalizing 80 min and the results are presented in Fig. 1.

As expected, increasing the contact time between the liquid and solid phase increased the amount of **PHA** and **LID** retained by the resin mass. Thus, in the first 60 min the adsorption process is fast and becomes slow in the 60–80 min range where the percentages retained in the resin mass increased with only 0.7% for **PHA** and up to 2.96% for **LID** respectively, once the equilibrium was reached. Similar results on the contact time influence on **XAD7HP** resin and oil were obtained by Albatrni et al., 2019 confirming the rapid adsorption taking place in the first 60 min for
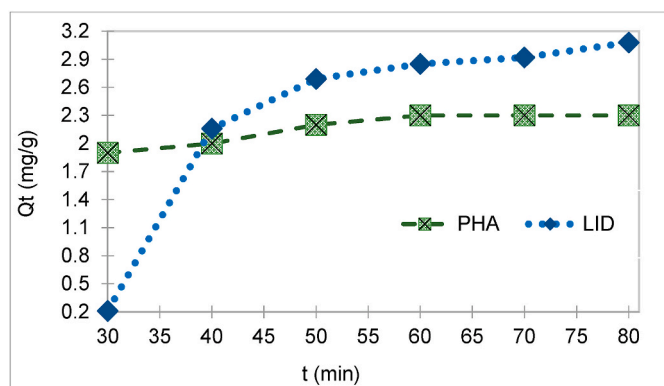
Fig. 1. Influence of **PHA** and **LID** contact time on adsorption on **XAD7HP** at T = 25 ± 2 °C; The value represents the mean of two duplicates studies with standard deviation (S_{dev}) below 3% for all measurements.

both drugs [30]. The ability to remove lignin, in 4 h, from alkali black liquor using **XAD7HP** resin was studied. The maximum adsorption capacity on the **XAD7HP** resin mass was determined in 2.5 h when 32% of the existing lignin in the sample was retained on the **XAD7HP** resin [31]. Anaia et al., 2014 studied the kinetics of 1-(2-Thiazolylazo)-2-Naphthol (**TAN**) adsorption using **XAD7HP** resin [32]. For this purpose, equilibrium was studied at different time intervals from 1 to 250 min. The best time to reach equilibrium was 35 min.

3.2. Influence of the PHA and LID initial concentration

The influence of concentrations ranges from 10 to 96 mg/L for **PHA** and from 6 to 96 mg/L for **LID** was checked using 0.1 g of **XAD7HP** resin mass and a volume of 0.01 L adsorbates solutions. The effect of initial concentration of **PHA** and **LID** on the adsorption behavior of **XAD7HP** resin is shown in Fig. 2.

The amount of pharmaceutical compounds in the resin was estimated spectrometrically determining the quantity found in supernatant based on the calibration curves previously determined, as explained in section 2.9. It was observed that the increase in the quantity of **PHA** and **LID** per **XAD7HP** mass increased their concentration in the analyzed supernatant solution. It is assumed that this process is due to the fact that the **PHA** and **LID** are retained on **XAD7HP** as a result of physical interactions that occur between the ester and hydrocarbon chains of the polymer substrate and aromatic and polar groups the **PHA** and **LID** structures. On the other hand, thereof retention inside the voids of resin porous structure act as a molecular sieve capable to retain compounds with high molecular mass. **XAD7HP** adsorbs better **LID** than **PHA**. Similar results were obtained by Coimbra et al., 2018, where the

maximum retention capacity of acetaminophen and ibuprofen analgesics on polymeric resin SEPABEADS SP217 varied between 7 and 18 mg/g for an initial concentration of 100 mg/L of drugs [5]. The adsorption performance of **XAD7HP** was evaluated when 1-(2-Thiazolylazo)-2-Naphthol (**TAN**) is removed from aqueous medium onto resin mass. The quantity detected was 4.05×10^{-3} g/g for 1.10×10^{-4} mol/L [32]. Adsorption behavior of **XAD7HP** resin was tested for pharmaceutical compounds nalidixic acid (**NAL**) and acetaminophen (**ACE**). Experimental conditions were carved out using batch method by mixing 0.01 g **XAD7HP** for **NAL** and 0.2 g **XAD7HP** for **ACE** with 0.02 L solution for 24 h at 180 rpm in the concentration range 5 up to 50 mg/L. The adsorption capacities were 16.98 mg/g for **ACE** and 51.02 mg/g for **NAL** [33].

3.3. Regeneration of XAD7HP resin

In the following step the resin loaded with **PHA** and **LID** was subjected to the regeneration experiment using the batch method with solutions of 10% NaOH, 3% HCl and **Ac** (see. Table 1) taking into account the recommendations from the technical sheet of the **XAD7HP** resin [29].

Based on the obtained data, it was noticed that the **XAD7HP** resin is regenerated with good yield when Ac is used. Practically, the efficiency of desorption agents on resin regeneration decreases in the order: Ac > 10% NaOH >3% HCl according to the results presented in Table 1. Similar studies on regeneration of XAD7HP resin have been done using HCl and NaOH (0.1–0.2 M), H_2O_2 (10–80 v/v) and ethanol (50 and 80 v/v) to desorb Reactive Blue - 13 dye [34]. Also, Bisgin et al., 2016 used for the Allura Red (**E129**) **AR** molecules desorption from the **XAD7HP** resin mass the following solvents: methanol, ethanol, acetone and acetonitrile [35]. When methanol and acetone were used the **AR** removal percentages were up to 100% from the **XAD7HP** resin. At the same time, when using ethanol and acetonitrile 98% and 96% of **AR** in the desorbed solution was detected. Anaia et al., 2014 studied the desorption of **TAN** from **XAD7HP** resin using 0.1 and 0.5 mol/L HNO_3 and 0.1 mol/L hexamine buffer [32]. According to the results obtained, 1.25% were desorbed when 0.5 mol/L HNO_3 was used and 0.54% when hexamine buffer was used. This behavior may be associated with the acid-base balances involved. Thus, **TAN** becomes more soluble in acidic environment due to the formation of the positive species **HTAN**$^+$ compared to **TAN** in neutral form in hexamine buffer medium when the desorption was low. Another study for polyphenol desorption from **XAD7HP** resin shows good desorption ratio when 70% ethanol was used [36]. As presented by Van Nguyen et al., Au(III) was recovered from **XAD7HP** resin with pure acetone, 99.33% being detected in eluent [37]. It can be concluded that the compounds presented in the literature as well as in this study may be desorbed from the **XAD7HP** resin with good yields using organic solvents in different proportions.

3.4. Adsorption mechanism studies

The adsorption mechanism is most often modeled by the Langmuir and Freundlich isotherms study [38–43]. Thus, the distribution of **PHA** and **LID** on the **XAD7HP** resin mass was characterized using the mathematical models of the Langmuir (4) and Freundlich (5) isotherms:
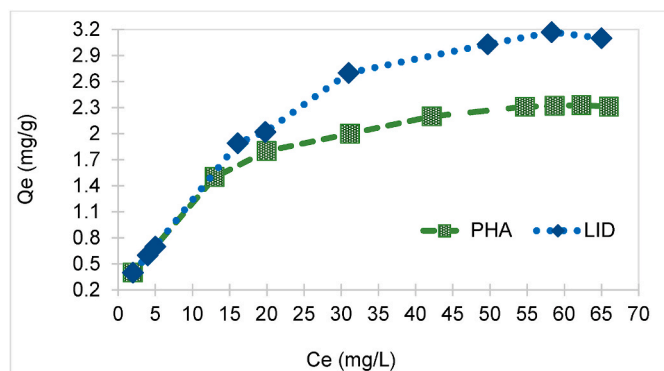

Fig. 2. Experimental isotherms obtained for adsorption of **PHA** and **LID** on **XAD7HP** resin; The value represents the mean of two duplicates studies with S_{dev} below 3% for all measurements.

Table 1
Percentages of **PHA** and **LID** desorbed of **XAD7HP** polymer resin.

Desorption agent	PHA$_{removed}$%[a]	LID$_{removed}$%[a]
Ac	82	75
10% NaOH	43	50
3% HCl	19.1	21.4

[a] The value represents the mean of two duplicates studies with St. dev. below 3% for all measurements.

$$\frac{C_e}{Q_e} = \frac{1}{bQ_0} + \frac{C_e}{Q_0} \qquad (4)$$

$$lnQ_e = lnK_f + \frac{1}{n}lnC_e \qquad (5)$$

where: Q_0 - maximum adsorption of XAD7HP resin, b – Langmuir constant correlated with the sorption capacity, K_f – Freundlich constant, n - constant correlated with the energetic heterogeneity of the adsorption sites.

Linear regression was used to determine the most appropriate isotherm model of the adsorption process. The applicability of isotherm equations was estimated with R^2 value. Linearized representations form of the Langmuir isotherm for adsorption of **LID** and **PHA** on **XAD7HP** resin are shown in Fig. 3.

The isotherm is linear over the whole range of concentrations studied with very good values of R^2. The isotherm parameters values obtained from the linearized as well as the nonlinearized Langmuir and Freundlich models for the **PHA** and **LID** adsorption on **XAD7HP** resin are presented in Table 2. Nonlinear experimental data fit is presented in Fig. 1S of Supplementary data.

Taking into account the R^2 values one may observe that the Langmuir isotherm fits very well the experimental data confirming the establishment of a saturated monolayer on the homogeneous surface of the **XAD7HP** resin when **PHA** and **LID** are removed from the liquid phase. According to the Langmuir model, the adsorption capacity, Q_o was 2.74 mg/g for **PHA**, lower than that for **LID** of 4.32 mg/g. The other Langmuir constant, b also indicates the lower degree of affinity for the **XAD7HP** resin of **PHA** compared to **LID**. The value of R_L in 0–1 range indicates a favorable adsorption of **XAD7HP** resin for **PHA** and **LID**. Thus, the value of R_L determined for **LID** indicates a stronger interaction with the **XAD7HP** resin compared with **PHA**. These experimental results could be correlated with two physical chemical characteristics: octanol water distribution coefficient (**log P**) and Polar Surface Area (**PSA**) of the two drugs in order to explain the higher retention of **LID** on **XAD7HP**. Using PubChem values of PSA of 32.3 respectively 58.4 Å and of log P of 2.44 respectively 0.88 for **LID** and **PHA** one may observe that the lower polarity and higher hydrophobicity of **LID** is related with higher adsorption on **XAD7HP**, a moderately polar substrate. Most probably the retention mechanism is based on van der Waals interactions and formation of physical bonds between the hydrocarbon network and ester group of the resin and aromatic, alkyl and polar structure of the two drugs. The values of R^2 determined from the application of Freundlich model are lower than those for the Langmuir isotherm model. Thus, it can be said that the Freundlich model cannot predict the degree of saturation of the heterogenic surface of **XAD7HP** resin.
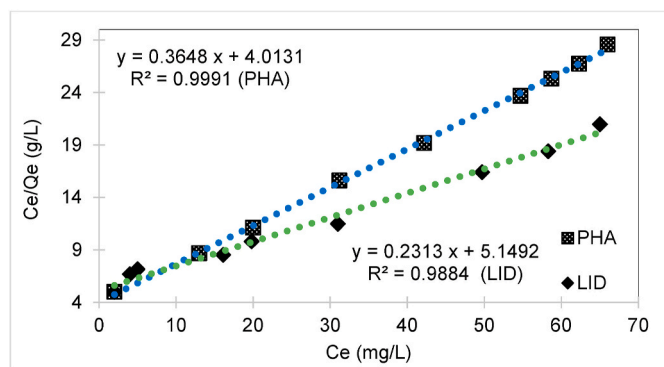
Table 2
Langmuir and Freundlich isotherm parameters.

	PHA		LID	
Langmuir	linear	nonlinear	linear	nonlinear
Q_o (mg/g)	2.74	2.82	4.32	4.31
b (L/mg)	0.10	0.08	0.04	0.04
R^2	0.9991	0.8801	0.9884	0.99
R_L	0.83	0.84	0.87	0.87
Freundlich				
K_f (mg/g)	1.63	1.39	3.68	1.65
1/n	1.07	0.58	0.63	0.42
N	0.94	1.72	1.60	2.41
R^2	0.9353	0.7701	0.9746	0.9501

3.5. Kinetic studies

To better understand the dynamics of the adsorption process mechanism and to calculate the kinetic parameters of **PHA** and **LID** adsorption on **XAD7HP** resin, three kinetics models were used [38,39]. Thus, kinetic studies based on the results of adsorption parameters obtained under the influence of contact time were performed using: the first order kinetic model [44] based on the Lagergren (1898) equation (see Table 3):

$$log(Q_e - Q_t) = logQ_e - \left(\frac{k_1}{2,303}\right)t \qquad (6)$$

the intra-particle diffusion model proposed by Weber Morris and described by the following equation:

$$Q_t = k_{id}(t)^{0,5} + C \qquad (7)$$

as well as the second-order kinetic model proposed by Ho and McKay (1998):

$$\frac{t}{Q_t} = \frac{1}{k_2 Q_e^2} + \frac{t}{Q_e} \qquad (8)$$

where: k_1 (min^{-1}) - rate constant of the **XAD7HP** adsorption process; Qe and Qt - amount of the two drugs (**PHA** and **LID**) retained at equilibrium (e) and at time (t) on **XAD7HP**; C - dimensionless constant determined from the intercept and provides information related to the film thickness and relates to the concentration of **PHA** and **LID** on the **XAD7HP** particle resin surface; k_{id} (min^{-1}) - the intraparticle diffusion constant; k_2 (g/(mg·min)) - rate constant of the second order kinetic adsorption model. The k_1 and $Q_{e\ calc.}$ constants were calculated from the linear regression curve log (Q_e-Q_t) vs t, k_{id} and C were obtained from the variation of Q_t vs t and the constants k_2 and $Q_{e\ calc.}$ were determined from the dependence of t/Qt in function of t. The best data fit, with the highest R^2 regression value, obtained by using the second order kinetic model is shown in Fig. S2 of Supplementary material.

Table 3
Kinetic parameters of adsorption process.

Kinetic model	PHA	LID
Lagergren		
k_1 (min^{-1})	0.066	0.070
$Q_{e\ calc.}$ (mg/g)	3.87	17.7
[a]$Q_{e\ exp.}$ (mg/g)	2.29	3.08
R^2	0.9347	0.9472
Morris–Weber		
k_{id} (min^{-1})	0.13	0.72
C	1.22	2.96
R^2	0.9208	0.7486
Pseudo-second order		
k_2 (g/(mg•min))	0.030	0.004
Q_e calc (mg/g)	2.68	5.08
R^2	0.9965	0.9637

[a] Values determined from the influence of contact time in section 3.1.

Fig. 3. Representation of the linearized form of the Langmuir isotherm for **PHA** and **LID** adsorption on **XAD7HP** resin.

As can be seen from Table 3 the values of calculated adsorption capacities of **XAD7HP** at equilibrium (Q_e) for **PHA** and **LID** were close to the results determined experimentally in section 3.1, when the second order kinetic model is applied. Similar values of the kinetic parameters for the adsorption of reagent TAN on **XAD7HP** were found in a study by Anaia et al. [32].

Also, the R^2 values are highest for the second order kinetic model linear regression fit for both drugs. Analyzing the values of R^2 (see Table 2) when applying the Morris Weber model, one may observe that the intraparticle diffusion controls the adsorption process of **PHA**. The lower value of $R^2 = 0.7486$ determined for **LID** indicated the fact that the intraparticle diffusion it is not the only process that controls the adsorption.

3.6. Selective removal of metal ions on XAD7HP resin loaded with PHA and LID

The two anesthetic drugs have amide and amine groups that may interact with metal ions frequently found in water such as Cd(II), As(V) and Pb(II) involving the non-participating electrons pair of nitrogen and the carbonyl bond [20,45–52].

In this final step, the retention of metal ions As(V), Cd(II) and Pb(II) on the **XAD7HP** resin loaded with **PHA (XAD7HP-PHA)** and **LID (XAD7HP-LID)** was verified using five synthetic solutions as explained in section 2.8. Quantitative determination of metal ions was done using the ICP-MS method. The results are showed in Fig. 4.

From Fig. 4a it is observed that the resin in **XAD7HP-PHA** form has very high affinity (R%), of 88% for As(V) and 40% for Cd(II) while Pb(II) is not retained from S1, where the initial concentration of metal ions in the mixture solution was 0.1 mg/L. From S2 solution (0.2 mg/L), the

a)

b)

Fig. 4. Metal ions removed on a) **XAD7HP-PHA** b) **XAD7HP-LID** from synthetic solutions (**S**); The value represents the mean of two duplicates studies with St. dev. below 3% for all measurements.

XAD7HP-PHA removed approximately 90% As(V), while Cd(II) and Pb (II) were retained in proportion of 50% and 10%, respectively. Following the adsorption experiments, it was observed that from S3 (0.3 mg/L) metal ions were retained in proportions ranging between 15% and 86%. Thus As(V), Cd(II) and Pb(II) were removed in proportion of 86.3%, 62% and 15.3%, respectively. In the S4 case solution (0.4 mg/L) the degree of retention was higher, 37% for Pb(II) if we refer to all five samples analyzed. For S5 (0.5 mg/L) the most retained ions were As(V) and Cd(II) in proportion of 94% and 76% respectively. Also, the **XAD7HP-LID** resin form retained As(V), Cd(II) and Pb(II) from synthetic solutions (Fig. 4b). It is observed that the resin in **LID** form has high affinity: 94% for Pb(II) and 81% for Cd(II) while the retention degree of As(V) was very low for S1 when 0.1 mg/L mixture solution was assessed. For S2 solution **XAD7HP-LID** removed 99% Pb(II), 77.5% Cd(II) and As (V) was lowly retained. For S3 solution the percentages of metal ions varied from 47% to 100%. Thus, Pb(II), Cd(II) and As(V) were retained in the following percentages: 99, 77.5 and 47.3% respectively. Analyzing S4 solution it was observed that As(V) was weakly adsorbed, approximately 13%, and the most retained were Pb(II) and Cd(II), 97% and 48%, respectively. Thus, the resin in **LID** form can be used as a specific material for wastewater containing Pb(II) remediation and selective for Cd(II) while As(V) was weakly retained, this behavior being highlighted in the case of the study of the most concentrated S5 solution. Comparable studies on the use of impregnated **XAD7HP** resin in the adsorption of: Au(III) [37], Cd(II) and Zn(II) [53] respectively Sc(III) [54] have been done showing good results in metal retention. Van Nguyen et al., 2013 impregnated **XAD7HP** resin with Cyanex 923 [55] and the impregnated resin was tested for removal of Cr(VI) from acidic medium. The adsorption mechanism of Cr(VI) on the modified resin may be explained by the interaction between the protonated oxygen atoms of the ester group of the **XAD7HP** resin structure and the solvation of Cyanex 923 extractant with the trioxochloromate complex (CrO_3Cl^-). It was also found that the impregnated resin retained 28 mg Cr(VI)/g impregnate compared to 16 mg Cr(VI)/g retained by the unmodified resin.

3.7. Surface morphology analysis by SEM

A selection of SEM microphotographs of **XAD7HP** resin beads pre and post adsorption of **PHA** and **LID** and As(V), Pb(II) and Cd(II) are shown in Fig. 5.

The analysis of the of the genuine **XAD7HP** surface beads morphology shows some fine rectangular voids with straight contours (Fig. 5b) visible in the high-resolution SEM image. The **PHA** and **LID** impregnated beads surface become smoother, most of the voids disappear or have rounded contours due to the drugs retention. In the case of the adsorption of metallic ions the surface morphology become finer, only very fine cavities being observed (Fig. 5d). Similar results on the AB13 dye retention on **XAD7HP** were obtained by Awasthi and Datta 2019 [34].

4. Conclusions

In this two parts organized study, the evaluation of the efficiency of **LID** and **PHA** retention on the **XAD7HP** resin was done in the first step, followed by the selective removal of metal ions As(V), Cd(II) and Pb(II) in presence of impregnated **XAD7HP** resin. The distribution of the compounds between phases was evaluated from the adsorption isotherms, obtained by fitting the amount of pharmaceutical compounds adsorbed as a function of their equilibrium concentration in the aqueous phase. The experimental results showed that when the initial pharmaceutics concentration was 96 mg/L, **XAD7HP** resin retained up to 24.1% **PHA** and 32.3% **LID**. After fitting the experimental data for each model, the characteristic parameters of the Langmuir and Freundlich isotherms were determined and the efficiency of the adsorption process was evaluated. Assigning the Langmuir adsorption model that best describes
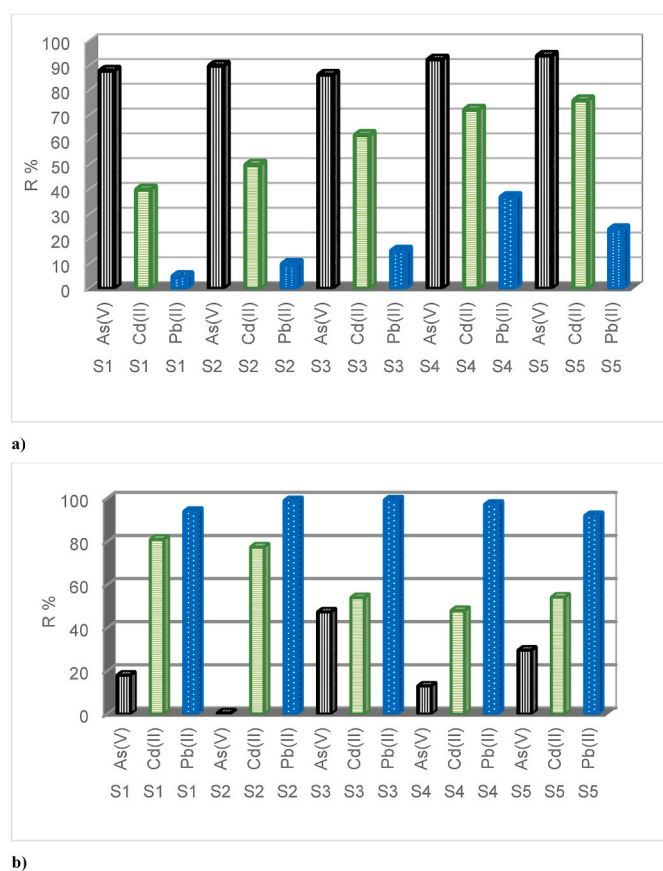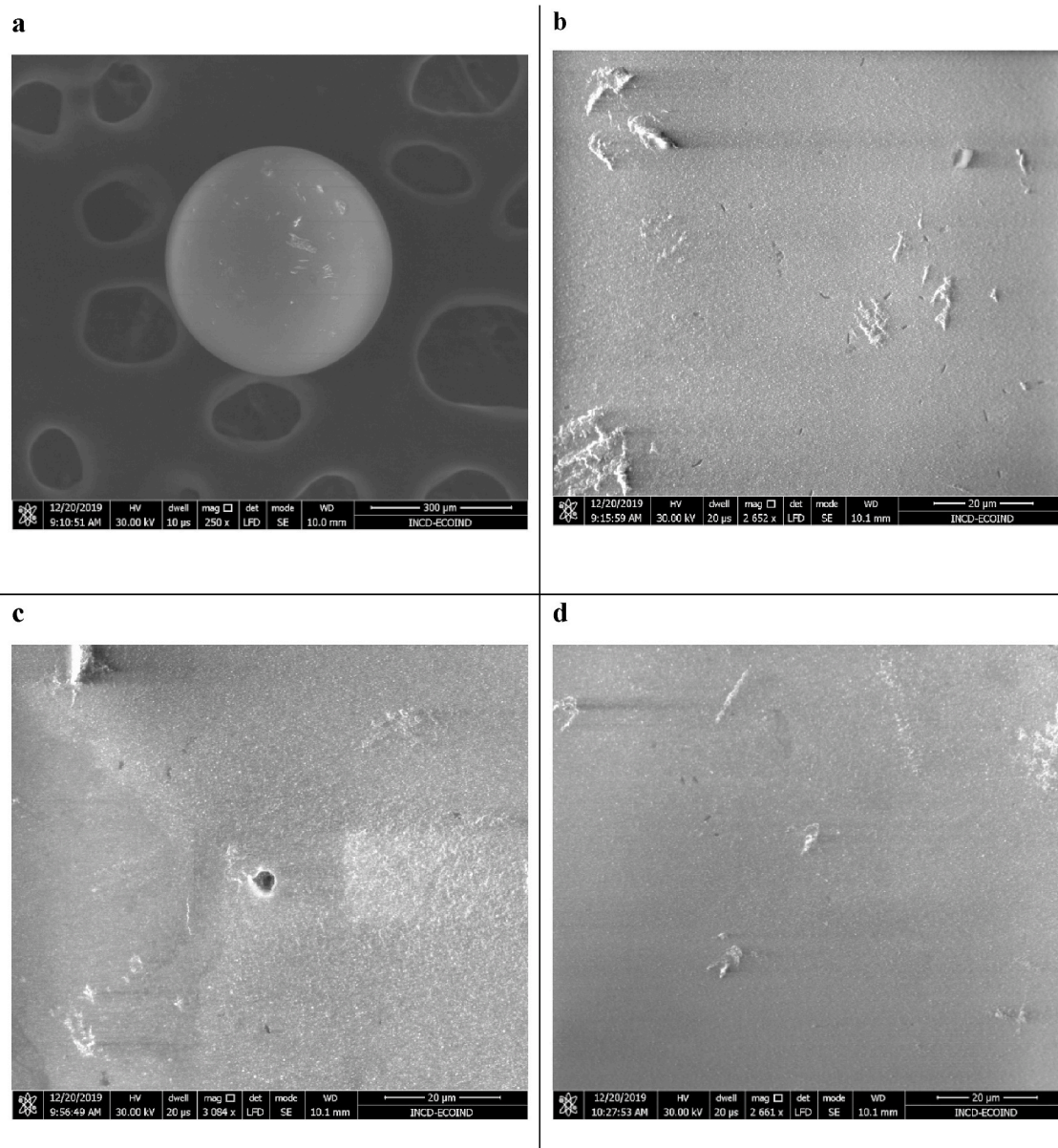
Fig. 5. SEM micrographs of a) polymer resin bead **XAD7HP,** magnification 250x; b) **XAD7HP** surface at magnification 2652x; c) **XAD7HP** loaded with **LID** magnification 3084x d) **XAD7HP** loaded with **PHA** and As(V), Pb(II), Cd(II) metal ions magnification 2661x.

the process was based on the calculated correlation coefficients: $R^2 = 0.9991$ for **PHA** and 0.9884 for **LID**. The slight difference in the **PHA** and **LID** adsorption performance on **XAD7HP** is owed to the difference in hydrophobicity and polarity of the two drugs. **LID** is less polar and more hydrophobic establishing stronger physical interactions with the hydrocarbon network of the polyester **XAD7HP** resin. The experimental data on the influence of the contact time were fitted based on Lagergren, Morris-Weber and pseudo second order kinetic models. It was found that the pseudo second order kinetic model best describes the system behavior. The dependence t/Qt vs t has given the regression equations over the entire 0–80 min time interval for both **PHA** and **LID**. The kinetical parameters obtained had values close with the ones found in the literature for similar studies on **XAD7HP** retention of other organic compounds. The selective removal of metal ions As(V), Cd(II) and Pb(II) on the **XAD7HP** resin loaded with **PHA** and **LID** showed that the resin in **LID** form is a specific material for wastewater containing Pb(II) remediation and selective for Cd(II) while As(V) was specifically retained and Cd(II) and Pb(II) were selectively removed on the resin in **PHA** form. The

rapid adsorption on **XAD7HP** of the two pharmaceuticals coupled with the good regeneration capacity and selective retention of the metal ions makes place to new resin material application in water depollution and metallic ions recovery.

CRediT authorship contribution statement

Nicoleta Mirela Marin: Writing – original draft, Writing – review & editing, Conceptualization, Data curation, Funding acquisition, Investigation, Methodology, Project administration, Resources, Supervision, Validation. **Ioana Stanculescu:** Conceptualization, Writing – review & editing, Formal analysis, Software, Visualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.matchemphys.2021.125582.

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