REMOVAL OF ACETYLSALICYLIC ACID FROM AQUEOUS SOLUTIONS USING POLYMERS CONTAINING AMINOPHOSPHINIC GROUPS

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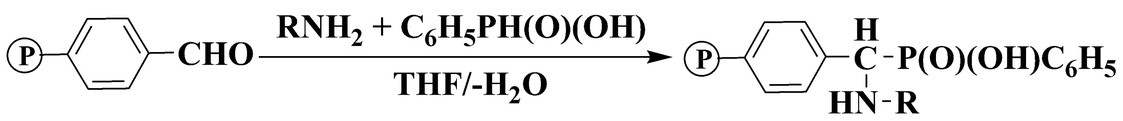
Introduction

Pharmaceuticals are persistent pollutants and cause a lot of damage to the environment [1-3]. Environmental protection is a matter of interest, in order to maintain ecological balance, and to improve the quality of life and working conditions suitable for current and future generations [2,4]. Modification of the polymers by the polymer-analogous reactions is one possible method of obtaining the functional groups grafted resins. These pendant groups introduced to the resins are capable of modifying the surface chemistry of the adsorbent allowing specific adsorbent-adsorbate interactions and also to improve adsorption procedures.

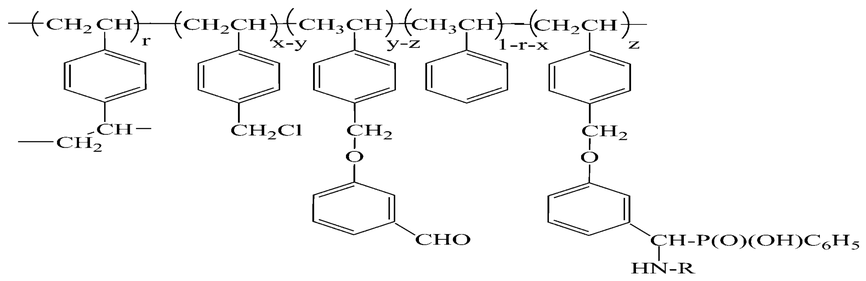
Aim

- Macroporous resins with 6.7% divinylbenzene cross-linking were used for functionalization with aminophosphonic functional groups.
- The adsorption technique was used to reduce concentration of acetylsalicylic acid in aqueous solutions. Their adsorption properties and performance toward pharmaceutical compound were tested.

Experimental



Scheme 1. The synthesis of aminophosphinic groups grafted on St-DVB copolymers.
Where: AAP1: R= $-C_3H_7$;
AAP2: R= $-CH_2-C_6H_5$;
AAP3: R= $-C_4H_9$.



Scheme 2. Statistical structure of the "macromolecular" copolymers .

Batch adsorption tests were carried out in 200-mL Erlenmeyer flasks. To start the experiment, 0.200 g of polymeric adsorbents (AAP1, AAP2 and AAP3) were mixed with 25 ml acetylsalicylic acid solution of 0.0275mM concentration. The experiment was carried out at 3 different temperatures: 298 K, 308 K and 323 K. The contents of the flask were mixed using a shaker. The solution was tested hourly. Every hour an amount of 2 ml solution was sampled from the flask to analyze the acetylsalicylic acid uptake on the adsorbent. A final test was carried out after 24 hours when the adsorbtion equilibrium has been reached. Similar batch experiments were performed to study the influence of the concentration of acetylsalicylic acid solutions (0.025 mmoles/L, 0.02 mmoles/L, 0.0175 mmoles/L and 0.015 mmoles/L) on the adsorption process, using the same adsorbent dosage and a 24 h contact time.

Results and Discussion

Table 1. The characteristics of pendant groups in functionalized copolymers.

Adsorbent Code	mmoles pendant groups/g of copolymer
AAP1: R = $-C_3H_7$	0.33
AAP2: R = $-CH_2-C_6H_5$	0.56
AAP3: R=$-C_4H_9$	0.34

Table 2. The adsorption capacity of pharmaceutical compounds on the AAP1, AAP2 and AAP3 adsorbents after 24 hours

Pharmaceuticals	Equilibrium adsorption capacity		
	AAP1	AAP2	AAP3
acetylsalicylic acid	0.124	0.120	0.122

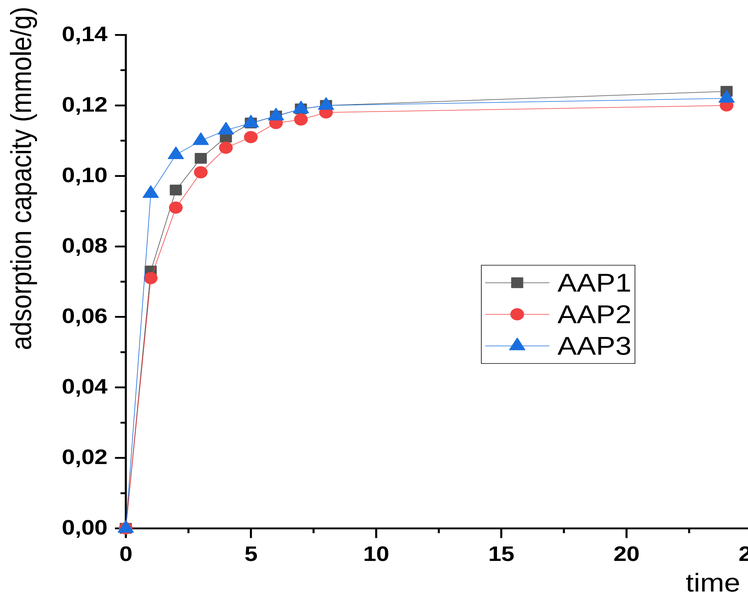


Figure 2. Effect of contact time on the adsorption capacity of acetylsalicylic acid on the functionalized copolymers.

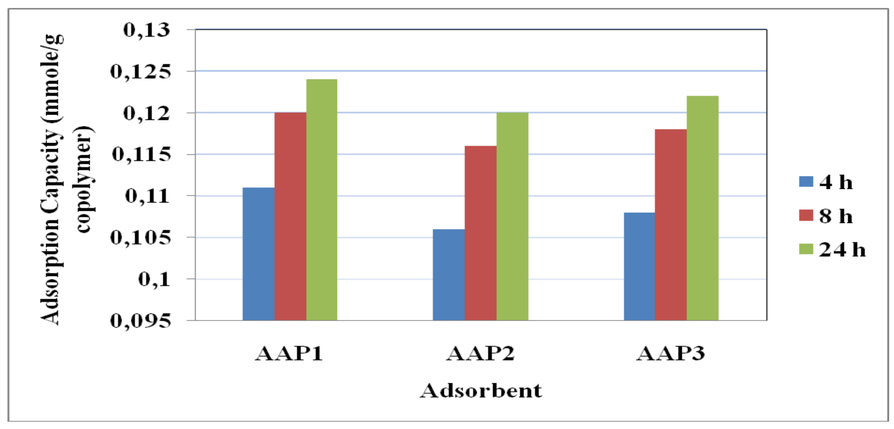
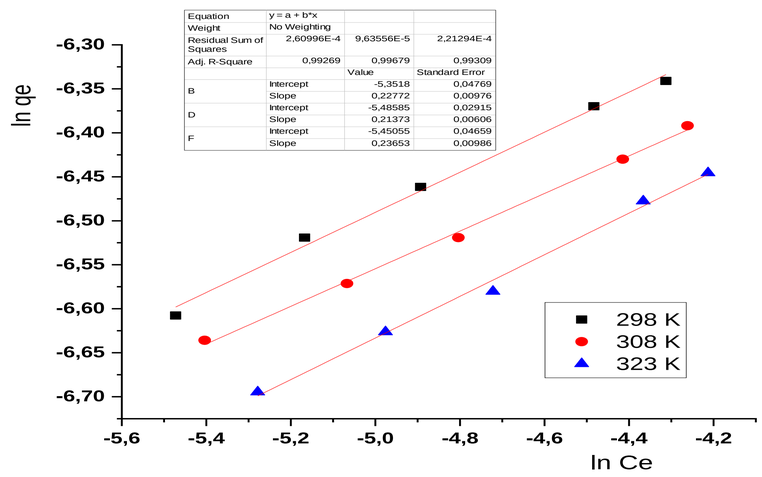


Figure 3. Comparative representation of the amount of acetylsalicylic acid adsorbed after 4, 8 and 24 hours respectively, at 298 K.

- The resins with the different pendant groups in the structure of the macromolecular copolymers, see Table 1.
- Equilibrium adsorption capacities at 298 K for the three polymeric adsorbents tested are presented in Table 2.
- The adsorption technique is used for reducing pharmaceutical compound oncentration and their adsorption properties toward acetylsalicylic acid are presented in Fig 2 and Fig. 3.
- The Freundlich adsorption isotherm is represented graphically for the process of adsorption of acetylsalicylic acid from aqueous solution on adsorbent AAP1, at 3 different temperatures: 298 K, 308 K and 323 K.
- The residual concentrations of acetylsalicylic acid solutions were determined using a UV-VIS spectrophotometer, measuring the absorption at a wavelength of 225 nm.

Figure 4. The Freundlich adsorption isotherm in case of adsorption of acetylsalicylic acid on adsorbent AAP1



References

1. Puckowski, A., et. all, Journal of Pharmaceutical and Biomedical Analysis 127 (2016) 232–255;
2. Khetan, S.K., Collins, T.J., Chem. Rev. 107 (2007) 2319e2364;
3. Hun-Soo Byun, Young-Nam Youn, Yeon-Hum Yun, Soon-Do Yoon, Separation and Purification Technology 74 (2010) 144–153;
4. C.H. Hennekens, Curr. Atheroscler. Rep. 9 (2007) 409–416.

Conclusions

The efficiency of the 3 adsorbents tested, in terms of acetylsalicylic acid adsorption varies in the following sequence: AAP1> AAP3> AAP2 The most effective for the adsorption of acetylsalicylic acid from aqueous solution is the adsorbent AAP1 in which propylamine was used in the functionalization reaction and the least effective is AAP2 in which the functionalization was performed using benzylamine, a larger radical that can determine a lower adsorption capacity. The adsorption process was studied thermodynamically using the Langmuir and Freundlich adsorption isotherms. It is found that the process of adsorption of acetylsalicylic acid on the 3 adsorbents is described more accurately using Freundlich isotherm, hence the conclusion that the adsorption of acetylsalicylic acid is not a monomolecular adsorption.