

A COMPARATIVE STUDY ON ADSORPTION OF GALLIC ACID ONTO POLYMERIC ADSORBENTS WITH AMINE FUNCTIONAL GROUPS

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The paper studies the adsorption of gallic acid from kinetic and thermodynamic perspectives, using several synthesized polymers with amine functional groups. These compounds, defined as P1, P115, P-Ba 2 and PHH, and obtained by appropriate chemical transformation reactions on crosslinked pyridine and acrylic copolymers, were characterized by weight and volume exchange capacities, their values being of $2.70 \text{ meq} \times \text{g}^{-1} / 1.26 \text{ meq} \times \text{mL}^{-1}$; $5.736 \text{ meq} \times \text{g}^{-1} / 0.187 \text{ meq} \times \text{mL}^{-1}$; $9.510 \text{ meq} \times \text{g}^{-1} / 0.510 \text{ meq} \times \text{mL}^{-1}$; $1.304 \text{ meq} \times \text{g}^{-1} / 0.523 \text{ meq} \times \text{mL}^{-1}$, respectively. The obtained results indicated their adsorption capacities in the following order: P115 > P1 > P-Ba-2 > PHH. A study of the adsorption kinetics and thermodynamics of gallic acid was carried out on the most efficient resin. The adsorption isotherms were fitted to Langmuir and Freundlich models and the thermodynamics parameters were calculated for comparing the total adsorption capacities. The results obtained will be used to develop future procedures for the separation of natural polyphenolic compounds.

Keywords: polyphenols, adsorption, polymeric adsorbents, kinetics, Langmuir isotherm, Freundlich isotherm

INTRODUCTION

Phenolic compounds, ubiquitous in plants, are of considerable interest and, due to their bioactive functions, have received more and more attention in recent years. These compounds possess an aromatic ring bearing one or more hydroxyl groups, while their structures may range from that of a simple phenolic molecule to that of a complex high-molecular mass polymer.¹

Natural phenols have been reported to possess excellent properties as food preservatives,² as well as for their important protective role against several pathological disturbances, such as atherosclerosis, brain disfunction and cancer.³ Moreover, polyphenols have many industrial applications, for example, they may be used as natural colorants and preservatives for

foods, or in the production of paints, paper, and cosmetics.

Consequently, efforts have been made at providing a highly sensitive and selective analytical method for the isolation and characterization of polyphenols present in different plant tissues.⁴

Thus, initial pre-concentration and purification of polyphenols from the complex matrix is crucial prior to instrumental analysis. The aim of pre-concentration is to simplify the chromatograms obtained, in view of their reliable identification and quantification. The purification stage is the critical part of a method, the removal of potentially interfering components varying according to the vegetal matrix to be analyzed.

The procedure includes liquid-liquid partitioning with a non-miscible solvent and open column chromatography, performed on a Sephadex LH-20, polyamide, Amberlite, prep-HPLC, and solid phase extraction (SPE), using commercially available cartridges.

Polyphenols can be usually purified by adsorption-desorption processes with highly efficient sorbents, among which C18 and highly crosslinked styrene-divinylbenzene (S-DVB) copolymers are very popular.⁵

Adsorption based on polymeric adsorbents could be the most prominent technique for the separation of phenolic compounds, as due to their favorable stability, large adsorption capacity, good selectivity and structural diversity. To attain a higher adsorption capacity and better selectivity for a specific organic compound, chemical modification of ordinary polymeric adsorbents is often adopted, by introducing some special functional groups onto the matrix of the adsorbents. Such functional groups should modify the chemical composition of the adsorbent, and hence improve the adsorption behavior of the organic compounds. The structures of these groups are very different and generally complex. The primary, secondary and

tertiary amine groups are probably the simplest ones.

The present paper tests the efficiency of several polymeric adsorbents with amine functional groups in adsorption studies using gallic acid as a reference product for polyphenolic compounds. The results obtained after a 24 h adsorption indicated that the adsorption capacities of the resins are in the following order: P115 > P1 > P-Ba-2 > PHH. The study of adsorption kinetics and thermodynamics of gallic acid were carried out on the most efficient resin, namely P115.

MATERIALS AND METHOD

The main characteristics of the adsorbents used in the study (functional groups, volume weight and exchange capacity) are presented in Table 1. The synthesis is presented only for sample P115, which has exhibited the highest retention capacity value of the gallic acid.

Synthesis of etylacrylate/acrylonitrile/divinylbenzene (EA/AN/DVB) copolymer

The crosslinked acrylic copolymer was obtained by water suspension radical polymerization of DVB (2 wt%), AN (20 wt%) and EA (78 wt%), in the presence of toluene as an inert component ($D = 0.4$).

Table 1
Characteristics of polymeric adsorbents

Sample	Functional groups	Volume weight (g/mL)	Exchange capacity, meq/mL	
				meq/g
P-115		0.03256	0.187	5.735
P-BA-2		0.0534	0.510	9.55
P-HH		0.2284	0.523	1.304
P1		0.4814	2.70	1.30

The ammonium salt of poly(styrene-co-maleic anhydride) was used as a polymeric stabilizer in the aqueous phase (0.5 wt%).

Benzoyl peroxide was used as an initiator in all polymerization processes (1 wt%).

An aqueous/organic phase ratio of 3:1 (v/v) was used in the copolymerization processes. The reaction was allowed to proceed for 4 h at 65 °C, 6 h at 75 °C, and 8 h at 85 °C, respectively. Following polymerization, the copolymer beads were washed with warm water and then extracted with dichloroethane, in a Soxhlet apparatus, to remove the traces of residual monomers, linear oligomers and diluent. Finally, they were vacuum-dried at 50 °C for 48 h.

The content of DVB units in the copolymers was assumed to be the same as the monomer content in the feed. The samples (0.3-0.8 mm in diameter) were characterized according to the uptake coefficients of methanol and toluene, by the centrifugation method.

The aminolysis reaction was performed at 110-115 °C using ethylenediamine (EDA), under reflux for 14 h, in a glass round-bottomed flask equipped with stirrer, reflux condenser and thermometer. The copolymer:amine ratio was of 1:5.5 for the copolymer with a crosslinking degree of 2%.

After the reaction, the synthesized compound was separated by filtration, washed with water and then regenerated with a 4% NaOH aqueous solution. The weak base ion exchanger was characterized by the following features: volume weight (WV, g/mL) – determined by measuring the weight loss of a known volume of fully hydrated sample in free base form, up to constant weight; volume (CV, meq/mL) and weight (CWt, meq/g) weak base exchange capacities, and transformation degree of the aminolysis reaction. The CV weak base anion exchange capacity was determined according to the following method: a known volume of ion exchange resin was treated with a specific volume of 1 N HCl solution of a known concentration and the excess of hydrochloric acid was removed by passing the mixture solution of water:methanol 1:2 (v/v) through the resin. The eluent was measured by titration to the mixed indicator end point with a 1 N NaOH solution.

CV was calculated according to the equation:

$$CV = (V_1 \cdot f_1 - V_2 \cdot f_2) / V$$

where:

V_1 – volume of 1 N HCl solution, mL;

V_2 – volume of 1 N NaOH, mL;

V – volume of resin, mL;

f_1 – factor of 1 N HCl solution;

f_2 – factor of 1 N NaOH solution.

CWt was determined by drying a known volume of weak base anion exchanger at 110 °C, up to constant weight. CWt was calculated according to the following equation:

$$CWt = (V_1 \cdot f_1 - V_2 \cdot f_2) / m$$

where V_1 , V_2 , f_1 , f_2 have the same meaning as in the above-mentioned equation and m is resin weight, g.

Sorption experiments

The influence of the amount of gallic acid (GA) upon sorption was investigated by using 104-400 mg/L gallic acid solutions. For the measurements, 0.1 g of each resin, in a dry state, were equilibrated with a 25 mL GA solution of different concentrations (104-400 mg/L) at room temperature (25 °C) in the dark, for 24 h.

Kinetic measurements were conducted on samples of adsorbent (P115) in a dry state (0.1 g), in contact with two concentrations of gallic acid solutions – of 104 mg/L and 160 mg/L, respectively. The concentration of GA in solution was determined at known time intervals.

The effect of temperature on the adsorption capacity was studied at three different temperatures (4, 25 and 45 °C) for GA concentrations of 104, 160, 192, 240, 320 and 400 mg/L, respectively.

In all experiments, the resin was separated through filtration and the filtrate was analyzed by UV-VIS spectrometry, measuring the O.D. at 280 nm. Prior to UV determination of the samples, a calibration curve was established, at different concentrations of gallic acid. The regression equation allowed the calculation of GA concentrations after adsorption.

The amounts of gallic acid adsorbed at time t , q_t (mg/g), were calculated by the following the mass-balance equation:⁶

$$q_t = \frac{(C_0 - C_t)V}{m}$$

where: C_0 and C_t are the initial and final gallic acid concentrations at time t (mg/L), respectively; V is the total volume of solution (L) and m is the mass of the adsorbent used (g).

The efficiency of the adsorbent in gallic acid recovery was estimated by the recovery yield, R (%), calculated as:⁷

$$R = \frac{C_0 - C}{C_0} \times 100$$

where C_0 and C are the initial and equilibrium gallic concentrations in solution (mg/L).

RESULTS AND DISCUSSION

Effect of initial concentration

Sorption studies of gallic acid considered the potential application of adsorbents in both separation and recovery of natural polyphenolic compounds from different vegetal resources. The sorption capacity of the investigated adsorbents with amine functional groups was investigated in a monocomponent solution. Increasing the initial concentration of gallic acid led to the increase of the sorption capacity and decrease of the recovery yield. Table 2 lists

the recovery yield values for the synthesized polymers.

The best sorption capacity of GA was evidenced by sample P115. Therefore, kinetic and thermodynamic sorption experiments of GA were performed on the polymeric material obtained by the aminolysis–hydrolysis of EA:AN:DVB with EDA. Sample P1 also shows a high recovery yield, the disadvantage of this resin being that the adsorption process requires more than 8 h to reach equilibrium.

Effect of contact time of phases

Figure 1 shows the effect of contact time on the recovery of gallic acid with P115 adsorbent, for two concentrations of gallic acid: 104 and 160 mg/L.

For both concentrations applied in the experiments, the recovery capacities increased with time, reaching equilibrium within 2 h. In each case, the decreasing concentration of gallic acid remaining in the

solution indicates that this compound was strongly adsorbed on P115.

The sorption kinetics describing the solute retention rate which, in turn, governs the residence time of the sorption reaction, is one of the important characteristics defining sorption efficiency. Hence, the kinetics of GA adsorption has been carried out to understand the behavior of this adsorbent. To analyze the sorption rate, the kinetic data were modeled with a Lagergren pseudo-first-order equation:⁶

$$q_t = q_e(1 - e^{-k_1 t})$$

where q_t and q_e are the amounts of GA adsorbed (mg/g) at any time t and at equilibrium, respectively, and k_1 (min^{-1}) is the pseudo-first-order rate constant.

The kinetic parameters derived from the linear Lagergren plot of $\lg(q_e - q_t)$ against t , listed in Table 3, indicate the increase of the sorption rate with the increase in GA concentration.

Table 2
The recovery yield for gallic acid after 24 h of adsorption

C_0 (mg/L)	Recovery yield (%)			
	P115	P1	P Ba-2	PHH
104	98	93	90	71
160	98	92	89	70
192	97	91	89	65
240	97	91	87	60
320	96	90	83	53
400	94	87	80	50

Table 3
Kinetic parameters derived from Lagergren pseudo-first-order equation for GA adsorption

Initial concentration C_0 (mg/L)	Linear regression equation	Pseudo-first-order	
		k_1 (min^{-1})	R^2
160	$y = -0.002x + 1.240$	4.6×10^{-3}	0.982
320	$y = -0.003x + 1.674$	6.9×10^{-3}	0.983

Sorption modeling

The functional dependencies between the equilibrium concentration of GA in sorbent and solution phases, respectively, $q = f(c)$, are plotted by sorption isotherms.

The GA sorption isotherms on resin P115 at different temperatures are plotted in Figure 2.

The equilibrium sorption data were analyzed by Freundlich and Langmuir isotherm models, expressed by the following linear equations:

Freundlich isotherm: $\log q = \log K_F + 1/n \log c$

Langmuir isotherm: $c/q = c/q_0 + 1/K_L \cdot q_0$

where K_F is related to the sorption capacity, n is a measure of sorption energy, K_L is a parameter related to the strength of the sorbed GA-sorbent binding and q_0 is the saturation sorption capacity.

The sorption isotherm constants calculated from the intercepts and slopes of the corresponding plots for GA sorption, by the P115 resin, at different temperatures,

together with the correlation coefficients (R^2), are given in Table 4.

The values of the correlation coefficients from Table 4 show that the experimental GA sorption data for the temperatures under study were better fitted to the Langmuir model of monolayer coverage. The high values of the sorption constants suggest a strong interaction between GA and the amine functional groups, with the increase of temperature.

Based on Langmuir's constants, the thermodynamic parameters, such as free

energy (ΔG), enthalpy change (ΔH) and entropy change (ΔS), have been calculated with the equations:

$$\Delta G = -RT \ln K_L$$

$$\ln K_L = -\frac{\Delta H}{RT}$$

$$\Delta S = (\Delta H - \Delta G) \frac{1}{T}$$

where R is the general constant of gases and T is temperature. The thermodynamic parameters are shown in Table 5.

Table 4
Results of fittings to Freundlich and Langmuir models

T, K	Freundlich isotherm			Langmuir isotherm			
	K_F	n	R^2	q_0 (mmol/L)	q_0 (mg/g)	K_L (L/mol)	R^2
277	3.908	1.29	0.975	0.685	116.53	5195.2	0.997
298	6.9	1.377	0.951	0.759	129.17	8391.86	0.988
318	35.48	3.484	0.824	0.912	155.21	12183.23	0.987

Table 5
Thermodynamic parameters

T (K)	ΔG (KJ/mol)	ΔH (KJ/mol)	ΔS (J/mol·K)
277	-19.68	14.81	124.5
298	-21.98	14.81	125
318	-24.82	14.81	125

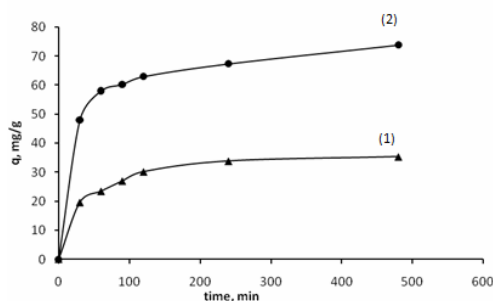


Figure 1: Effect of contact time on sorption of GA by P115 (adsorption conditions: initial concentrations of GA, 104 mg/L (1) and 160 mg/L (2); amount of adsorbent, 0.1 g; volume of adsorption medium, 25 mL; temperature, 25 °C)

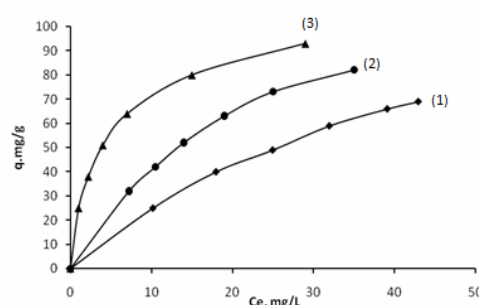


Figure 2: Sorption isotherms of GA on P115 (conditions: concentration of GA, 104-400 mg/L; amount of adsorbent, 0.05 g; volume of adsorption medium, 25 mL; temperature, 4 °C (1), 25 °C (2) and 45 °C (3); adsorption time, 6 h)

A negative ΔG value indicates that, for P115, the process is spontaneous as to the nature of adsorption, while a positive ΔH shows that the adsorption process is an exothermic reaction, as well as the strong interaction manifested between GA and the amine groups. The positive values of entropy

describe the more disordered state at the molecular level.

CONCLUSIONS

Several synthetic ion exchangers with amine functional groups were tested, for the separation of polyphenolic compounds from

different vegetal resources. Gallic acid was chosen as a representative compound, due to its presence in almost all plant species. The best sorption capacity of GA was evidenced in sample P115. Therefore, kinetic and thermodynamic sorption experiments of GA were performed on this polymeric material.

Kinetic studies showed that increasing the contact time increased adsorption, a constant value being recorded when equilibrium was reached within 2 h, for both concentrations.

The Langmuir model fits the adsorption equilibrium of GA on the P115 adsorbent, the high values of the sorption constants suggesting a strong interaction between gallic acid and the amine groups, with the increase of temperature.

The thermodynamic parameters indicated a spontaneous and exothermic adsorption, as well as a disordered state at the molecular level.

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