

Adsorption of Phenol/tyrosol from Aqueous Solutions on Macro-reticular Aromatic and Macro-porous Polystyrene Cross-linked with Divinylbenzene Polymeric Resins

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The current work aims at separating by adsorption of low-molecular-weight organic compounds in a nanofiltration concentrate of the olive mill wastewaters. The experimental investigations on adsorption of phenol/tyrosol in single and binary systems were conducted in batch mode by using the commercially available macroporous resins FPX66 and MN202. The structures of such resins were examined by FTIR before and after adsorption. The operating parameters affecting the adsorption process such as resin dosage, contact time, pH, and initial concentration of phenol/tyrosol were investigated. Fast phenol and tyrosol uptakes were observed for both resins. It can be attributed to their physical properties, for instance high specific area and microporous area. The adsorption selectivity of phenol is larger than tyrosol when using FPX66 resin, but smaller if MN202 resin is used. Acidic pH appeared to be always favourable for the adsorption. A synergetic effect between solutes was observed since adsorption of phenol and tyrosol in the binary systems was faster than the individual sorption of each solute. Five isotherms namely Langmuir, Freundlich, Dubinin-Radushkevich, Temkin and Redlich-Peterson were selected to fit the obtained equilibrium experimental data. Finally, desorption of the examined compounds with ethanol (EtOH) allowed a maximum around 85 % of phenol, and equal to 94 % of tyrosol on FPX66 and MN202 resins.

1. Introduction

Olive mill wastewaters (OMW) represent an important environmental problem in Mediterranean areas where they are generated in huge quantities in short periods of time. The high concentration in phenolic compounds (4 -15g/L), lipid and organic acid makes them phytotoxic materials, but these wastes also contain valuable resources such as a large proportion of organic matter and a wide range of nutrients that could be recycled (Roig et al., 2006). The presence of these pollutants forces international agencies in charge of environmental protection to design regulations and set strict standards with respect to organic compounds together with their release into the environment. The problems caused by this procedure are pollution of groundwater layers and of terrains. For this reason, the procedure is considered illegal according to the EU Directive 91/271/EEC on urban wastewater treatment. This wastewater contains many polyphenols, mostly tyrosol and hydroxytyrosol, which may have a market value (Busca et al., 2008; De Martino et al., 2013). For many reasons, it is not easy to extract directly polyphenols from raw wastewater. The high suspended solids in the raw stream will quickly block the adsorption column, making the recovery process impossible. Moreover, many other interfering and undesired pollutants would interfere with the recovery process. There are important reasons for an adsorption investigation on phenol and polyphenols from OMW, in case of phenol for its elimination and for polyphenols for their recovery from OMW streams. Adsorption on activated carbon has been widely used for the removal of organic contaminants from OMWW (Soto et al., 2011). Compared with traditional adsorbents such as the silica gels, activated aluminate and activated carbons, polymeric resins are viewed as a more attractive alternative for the regeneration, control pore structures and the surface characteristics (Soto et al., 2011; Xu et al., 2003).

Adsorption and desorption by unchanged polymeric resins has been widely studied as an effective technique for removing organic compounds from OMWW. The efficient use of this technique depends on various factors such as temperature, pH, adsorbent dosage and characteristic such as micro-porosity and chemical properties (Xu et al., 2003).

To study the involved interactions during the adsorption/desorption process, a single adsorbate is normally chosen. However for many organic compounds as benzoic acids and its derivatives (gentisic, vanillic, gallic, syringic acids), cinnamic acids and derivatives (caffeic, ferulic, sinapic acids), phenolic alcohols, secoiridoides aglycones (oleuropein, ligstroside), flavonols, flavones and lignans, etc]] (Busca et al., 2008; Soto et al., 2011) coexisting frequently in OMWW, the necessity of elucidating the kinetic adsorption mechanism in binary or multi-component system is requested (Valderrama et al., 2007, 2010). As a matter of fact the interaction between the adsorbate species may be important, as shown by (Valderrama et al., 2010) with regard to the adsorption of the phenol/aniline from binary aqueous solutions.

The main aim of this study is to investigate the competitive adsorption between phenol and polyphenols by adopting tyrosol as representative of polyphenols and reducing the investigation to the binary interaction between phenol and tyrosol for sake of simplicity. In particular, in this work the adsorption/desorption of single and binary phenol/tyrosol in aqueous solutions onto macro-reticular aromatic (FPX66) and macro-porous polystyrene cross- linked with divinylbenzene (MN202) polymeric resins were investigated.

2. Materials and methods

2.1. Apparatus, reagents and adsorbents

Phenol (Hydroxybenzene) and tyrosol [4-(2-hydroxyethyl)] solutions were prepared by diluting 1g/L of stock phenol and tyrosol solutions, obtained by dissolving exact quantities of phenol (Fluka and Farnitalia Carlo Erba) and tyrosol (Sigma Aldrich) in bi-distilled and de-mineralized water. Before the adsorption runs, the pH of solution was adjusted to the fixed value by using H_2SO_4 (Carlo Erba) and NaOH (Carlo Erba) solutions. FPX66 and MN202 resin samples were provided by Rohm & Haas and Puro-lite Ltd., respectively. The physicochemical characteristics of these resins are summarized in Table 1.

Table 1: Physicochemical characteristics of the FPX 66 and MN202 resins.

Properties	FPX66 resin	MN202 resin
Physical form	White spherical beads	White spherical beads
Matrix	Macro-reticular aromatic polymer	Macroporous polystyrene cross-linked with divinylbenzene
Moisture holding capacity	60-80 %	50-60 %
Shipping weight	680 g/L	655-685 g/L
Specific gravity	1.015- 1.025	1.04
Surface area	$\geq 700 m^2/g$	$825 m^2/g$
Porosity	$\geq 1.4 cc/g$	1-1.1 mL/g
Mean diameter	Mean size 0.600 - 0.750 mm	$535 \pm 85 \mu m$
Particle size	≤ 2.0	d50, meso, d50, micro: 15 and macropores: 600-900

2.4. Adsorption and desorption procedure

First of all the resin to be used is swollen resin with EtOH and rinsed with de-mineralized water. Each adsorption run was carried out, at the fixed operating conditions, by mixing 10 g of resin in a thermostated jacketed vessel with 200 mL of single or bi-component phenol/tyrosol solutions of different concentrations (200 to 600 mg/L). The vessel was placed over an orbital incubator rotating at a speed of 150 rpm. In order to determine the exact concentration of each solute and to establish the evolution of the adsorption process, water samples from the supernatant, were collected at fixed time intervals, till equilibrium was reached. The samples were stored in a plastic air tight box until HPLC analysis was undertaken. The maximum contact time of 150 or 210 minutes was used. The influence of adsorbent dosage was studied by varying the fresh mass from 2.5- 10 g. Each desorption run was done by separating the resin from the solution, after the attainment of the equilibrium conditions, and mixing that with an appropriate volume of aqueous solution 50 % in EtOH or NaOH 0.6 N. The run was performed shaking the solution at the same values of speed and temperature for 90 min. To evaluate the residual concentrations of phenol/tyrosol after each adsorption/desorption experiment, the slurry was filtered through 0.45 μm polytetrafluoroethylene (PTFE) filters and the permeate was analyzed by HPLC system composed of a Spectra-Physics liquid chromatography Model Agilent 1200 Series equipped

with SUPELCOSIL LC-18 column (length 250 mm, diameter 4.6 mm, packaging size 5 mm). The mobile phases were acetonitrile (solvent A) and 0.5% (v/v) and acetic acid in water (solvent B) at a flow rate of 1mL/min. For each compound the adsorption capacity q , mg/g and the removal efficiencies (E , %) were calculated using Eq.(1) and (2), respectively (Mbosso T. et al., 2012; Njimou J. R. et al., 2016; Özacar et al., 2008).

$$q = \frac{(C_0 - C_e) \times V}{m} \quad (1)$$

$$E(\%) = \frac{C_0 - C_e}{C_0} \times 100 \quad (2)$$

The desorption ratio of the resin, D (%) was calculated according to Eq.(3):

$$D(\%) = \frac{C_d V_d}{(C_0 - C_e) V} \cdot 100(\%) \quad (3)$$

D (%) is the desorption ratio, C_0 and C_e (mg/L) are the initial and equilibrium concentrations of analyte in the solutions, respectively, while C_d (mg/L) is the concentration in the desorption solution; V and V_d (L) are the volume of the initial adsorption and desorption solutions, respectively.

3. Results

3.1. Structure and surface chemistry of the adsorbent

Spectra of both materials treated with EtOH and after adsorption in contact with mixture of phenol/tyrosol are presented in Figure 1. The spectra have the same shape before and after adsorption, thus the structures of the used materials are not modified by the adsorption process.

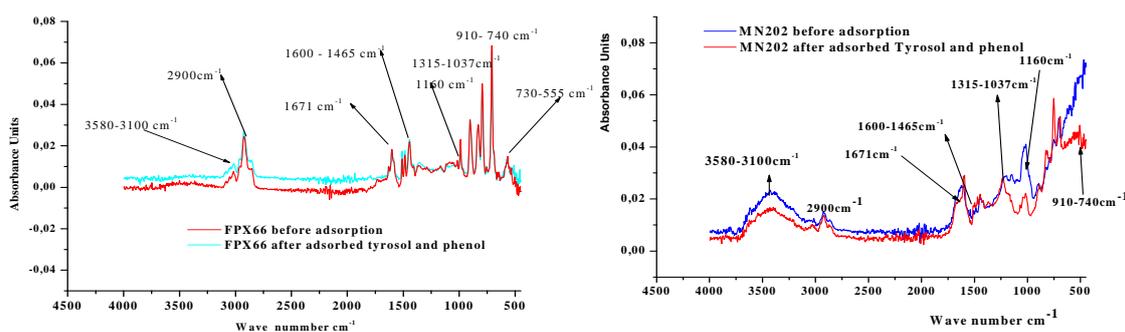


Figure 1 Infrared spectra of the FPX66 and MN202 swollen resin with EtOH 50 % before and after adsorption.

It appears that the ethanol treatment helps to keep the pores of the material active. It is possible to observe that the two fundamental vibrations in the spectra are stretched, due to the atoms which vibrate and lead to molecular deformation although they remain stable in the same bound axis (Njimou J. R. et al., 2016; Özacar et al., 2008). In general, ion exchange resins are nonpolar adsorbents generally used for adsorption of organic substances (hydrophobic compounds up to MW 20000) from aqueous systems (Croué et al., 1999). A band at 3000-2800 cm^{-1} appears to be a strong and sharp band that can be attributed to the stretching of aromatic molecules and their aliphatic C-H groups. The adsorption bands between 1604 and 1392 cm^{-1} are related to aromatic C=C-bonds. The peaks at 1315 and 1037 cm^{-1} in the spectrum belong to the phenol groups. The peak at 1160 cm^{-1} is due to aromatic C-H deformation of CH₃ (Njimou J. R. et al., 2016; Özacar et al., 2008). The absorption bands at 1600 - 1465 cm^{-1} attributed to C=C stretching in aromatic rings were also observed. It also shows the presence of a broad band attributed to O-H stretching at 3580-3100 cm^{-1} due to the presence of phenolic and alcoholic functions. The vibrations of deformation of C-H bonds in the benzene cm^{-1} are reduced and 1732 cm^{-1} peak slightly decrease to 1676 cm^{-1} in the spectrum of the FPX66 resin. The situation may be attributed to the -CO stretching of benzene ring and that one of the phenolic -OH groups (Özacar et al., 2008).

3.2. Factors affecting the efficiency of phenol/tyrosol onto FPX66 and MN202 resins

The effect of contact time onto FPX66 and MN202 resins, respectively, on the adsorption of phenol/tyrosol at $C_0 = 500$ mg/L is shown in Figure 2. The results indicate that the uptake of both solutes is rapid during the initial period of time, less than 50 min, and thereafter, becomes slower near the equilibrium. This is clearly due to the fact that a large number of vacant surface sites are available for the adsorption during the initial stage, whereas close to equilibrium the residual vacant sites are difficult to be occupied due to repulsive forces

between the solute molecules on the solid and bulk phases (Barkakati et al., 2010). No significant change in phenol/tyrosol removal was observed after a contact time of 1 hour. The higher uptake of tyrosol in binary systems adsorption on MN202 and inversely the higher phenol uptake in binary systems on FPX66 resin could be explained by the hydrophobic difference related to water solubility between both solutes, which are 25.3 and 67 g/L for tyrosol and phenol at 298 K, respectively (Valderrama et al., 2010).

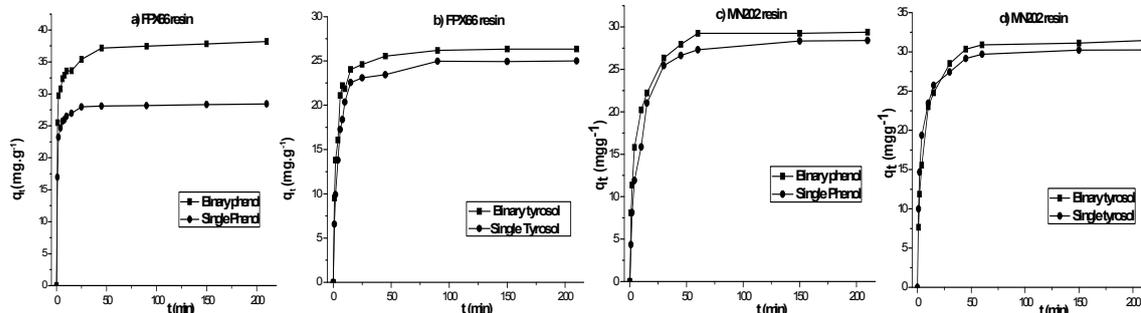


Figure 2 Comparison of single and binary systems for phenol/tyrosol adsorption onto FPX66 and MN202 resins. Experimental conditions: 10 g of swollen resin in 200 mL of phenol/tyrosol at 500 mg/L, pH not adjusted and stirred at 150 rpm, $T = 25\text{ }^{\circ}\text{C}$.

Furthermore, the greater electron density in the ring of tyrosol molecule, which supplies more p-electrons to interact with the adsorbent, is effective only with respect to MN202 resulting in a larger adsorption capacity with respect to phenol (Valderrama et al., 2007, 2010)

During the binary adsorption on MN202 resin, about 96 % of tyrosol and 85 % of phenol extraction were reached in 120 min, while in single system each solute requires 180 min to reach the same point. It indicates that phenol and tyrosol kinetic adsorption on MN202 in binary systems is faster. Similar behavior was observed for phenol and tyrosol kinetic adsorption onto FPX66 resin, thus, about 68 % and 57 % of tyrosol, 83 % and 75 % the phenol of extraction were obtained at the same period of time for both solutes in binary and single system, respectively. This behavior was observed for both adsorbents and confirms the better kinetic performance of both solutes onto both resins in bi-components system.

The effect of pH on sorption of phenol/tyrosol was studied by using 10 g of swollen resin and varying the pH values between 3 and 9. The obtained results showed that the adsorption percentage increased when the pH was raised, and this effect was more pronounced in the pH ranges of 4–5. This result which is also in accordance with previous work on OMW adsorption (Soto et al., 2011) can be explained by the fact that for the pH values below 6.6, the adsorbent is slightly positively charged due to the protons. Electrostatic repulsions then prevent the protonated resin and phenol/tyrosol (positively charged) to interact efficiently.

Finally, we studied the influence of the initial concentration of the two solutes on their adsorption capacities on FPX66 resin in the initial concentration range 200 - 600 mg/L. It was observed that the adsorbed amount increased with initial concentration, and then decreased towards equilibrium value due to the saturation of the resin. Indeed, tyrosol saturated faster than the phenol on FPX66 resin. This could be justified by the fact that FPX66 has a good selectivity for phenol compared to tyrosol.

3.3. Adsorption isotherms

Various isotherm models provided by Langmuir, Freundlich, D-R, Temkin and R-P equations have been used to describe the equilibrium characteristics of the phenol/tyrosol adsorption onto the studied polymeric adsorbents. The values of the estimated Langmuir linear relationship between the amounts (mg) of both solutes adsorbed per unit mass (g) of FPX66 resin against the concentration of phenol/tyrosol remaining in solution (mg/L) were calculated in Table 2. The K_L , q_m , R^2 values were calculated and the values of R_L at $C_0 = 500\text{ mg/L}$ were found to be less than 1 for tyrosol and phenol in single and binary adsorption on both resins verifying the favourable processes of the adsorption according to (Barkakati et al., 2010; Mbosso T. et al., 2012; Njimou J. R. et al., 2016). The estimations of linear Freundlich values k_F and n were calculated and the n values of phenol/tyrosol in single and binary systems were between 0 and 10, indicating that the adsorption of both solutes onto FPX66 and MN202 resins was favourable (Barkakati et al., 2010) at studied conditions.

The Dubinin-Radushkevich (D-R) parameters were calculated and it was observed in Table 2 that the theoretical maximum adsorption capacity Q_D (mg/g) was lowest for both solutes onto MN202, highest for tyrosol onto FPX66, highest in single and lowest for phenol in binary onto FPX66, lowest for both solutes onto MN202 compared with experimental values. The mean free energy of adsorption, E estimated by using the Polanyi and the D-R isotherm constants was in the range of 0.025- 0.38 kJ/mol which signifies the physical

adsorption reaction due to weak Van der Waals forces (Barkakati et al., 2010). The adsorption mean free energy gives information about adsorption mechanism, physical or chemical. When the E value is between 8 and 16 kJ/mol, the adsorption process follows a chemical mechanism, while when $E < 8$ kJ/mol the process follows a physical mechanism (Barkakati et al., 2010; Njimou J. R. et al., 2016; Özacar et al., 2008). In this case, the mechanism of adsorption process can be explained by chemisorption or ion exchange.

Table 2: Constants obtained from Langmuir, Freundlich, Dubinin–Radushkevich (D-R), Temkin and Redlich–Peterson (R-P) isotherm models for phenol/tyrosol adsorption FPX66 and MN202 resins.

Parameter constants for FPX66	Langmuir isotherm				Parameter constants for MN202 resin	Langmuir isotherm			
	Single component		Binary Component			Single component		Binary Component	
	Tyrosol	Phenol	Tyrosol	Phenol	Tyrosol	Phenol	Tyrosol	Phenol	
q_m (mg/g)	41.49	39.52	39.84	44.34	q_m (mg/g)	34.36	34.36	36.10	35.97
q_{exp} (mg/g)	30.24	28.41	31.44	32.38	q_{exp} (mg/g)	25.00	28.44	26.34	38.19
K_L (L/mg). 10^{-3}	3.63	8.98	4.58	11.00	K_L (L/mg). 10^{-3}	0.209	0.478	0.152	0.051
R_L	0.355	0.182	0.304	0.4	R_L	0.009	0.004	0.013	0.182
R^2	0.993	0.998	0.994	0.997	R^2	0.953	0.844	0.996	0.949
	Freundlich isotherm					Freundlich isotherm			
K_F	0.647	1.540	0.753	2.140	K_F	20.960	3.137	18.620	5.530
n	1.63	1.90	1.66	0.79	n	9.55	2.06	7.25	2.63
R^2	0.993	0.971	0.981	0.998	R^2	0.953	0.844	0.996	0.949
	Dubinin–Radushkevich (D-R) isotherm					Dubinin–Radushkevich (D-R) isotherm			
q_D (mg/g)	21.52	24.48	22.66	28.45	q_D (mg/g)	30.83	30.56	31.22	29.03
β_D (mol ² /kJ ²)	818.09	219.36	714.35	343.12	β_D (mol ² /kJ ²)	3.414	96.670	3.810	22.568
E (KJ/mol)	0.025	0.047	0.026	0.04	E (KJ/mol)	0.382	0.072	0.362	0.150
R^2	0.901	0.881	0.950	0.912	R^2	0.966	0.996	0.930	0.982
	Temkin isotherm					Temkin isotherm			
B_1 (Kj ² /mol ²)	9.252	9.258	9.291	14.971	B_1 (Kj ² /mol ²)	3.015	10.013	3.921	7.952
b (mol/kJ)	0.267	0.267	0.266	0.165	b (mol/kJ)	0.8215	0.024	0.6318	0.311
K_T (L/mg)	0.034	0.076	0.040	0.044	K_T (L/mg)	684.825	0.178	144.60	0.481
R^2	0.960	0.900	0.998	0.982	R^2	0.960	0.997	0.998	0.987
	Redlich–Peterson isotherm					Redlich–Peterson isotherm			
a_R (L/g) ^a	1.402	10.577	1.670	6.134	a_R (L/g) ^a	63.637	25.292	52.473	165.836
β	0.932	0.521	0.897	0.631	β	0.387	0.475	0.397	0.211
R^2	0.999	0.864	1	0.980	R^2	0.983	0.965	0.958	0.983

From the Temkin isotherm constants, the values of the correlation coefficients (R^2) for FPX66 and MN202, signified satisfactory representation of the equilibrium experimental data for sorption model. Therefore, it can be presumed that the adsorption of phenol/tyrosol is characterised by uniform distribution of the binding energy and the heat of adsorption of the molecules in the layer decreases linearly with coverage of the adsorbate on the surface of the adsorbent particles (Barkakati et al., 2010; Njimou J. R. et al., 2016). The estimated values of the D-P isotherm parameters a_R , k_R , β and R^2 for both solutes onto both resins are shown in Table 2. The values of β for both adsorbents were between 0 and 1, indicating favourable adsorption with the good correlation coefficient values.

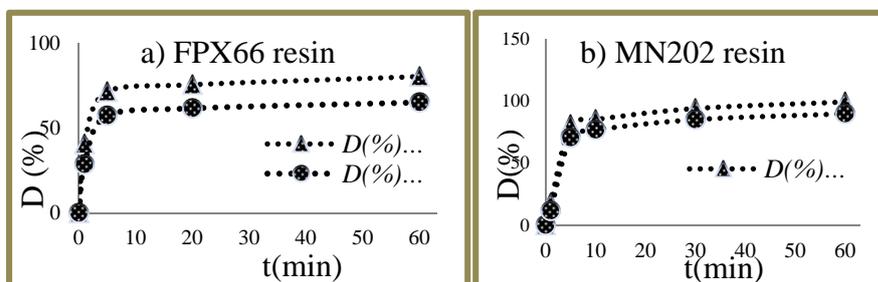


Figure 3 Evolution desorption percentage of phenol/tyrosol onto FPX66 and MN202 resins in EtOH milieu. Experimental conditions: 10 g swollen resin (containing phenol/tyrosol) in 150 mL of 50 % of EtOH solution, 150 rpm shaking speed on a shaking table during 1 hour at ambient temperature.

3.4. Desorption and reusability of adsorbents

The possibilities to reuse several times the resins were undertaken by examining the phenol/tyrosol desorption in EtOH and the desorption percentages from FPX66 and MN202 in Figure 3. The reusability of an adsorbent is an important parameter to evaluate the economic feasibility of adsorbent in an adsorption process. Desorption percentage obtained with 50 % of EtOH in aqueous solution was very fast for both adsorbents and the equilibrium was attained after 30 min. The obtained results, reported in Figure 3, show that tyrosol is adsorbed slightly and desorbed faster on FPX66 resin and inversely for the phenol on MN202 resin. Both adsorbents could be used many times without losing significant adsorption capacities for the removal of both solutes. Around 65 % of phenol is desorbed from FPX66 resin, whereas almost all the phenol is desorbed from the MN202 resin. Desorption of tyrosol is quite the same from two resins, around 85 %. So, it is clear that desorption on both resins results from the cation exchange between the protons in solution and the adsorbed solute (Soto et al., 2011). The unadsorbed fraction of analyte may be bound to the resin through a different mechanism from cation exchange.

4. Conclusions

The present study has shown that both a macro-reticular aromatic resin as FPX66 and a macro-porous polystyrene cross-linked with divinylbenzene as MN202, can be used as effective adsorbents for removal of phenol/tyrosol from aqueous solution in single and binary systems. On the first resin there was a greater adsorption of phenol compared with tyrosol and for both resins the adsorption of phenol/tyrosol involved a very fast kinetics (equilibrium was reached after about 60 min). Adsorption seems to proceed with five isotherm models namely Langmuir, Freundlich, Dubinin Radushkevich, Redlich-Peterson and Temkin as expressed by the good correlations on both resins. Desorption with ethanol permitted a good recovery of both adsorbates that is between 60 and 75 % for the FPX66 and a very good recovery that is above 80 %, for the MN202. Through the proposed procedure, the recovery of polyphenols from the nanofiltration permeate stream seems to be viable by the examined resins adsorption/desorption processes.

Acknowledgments

We wish to acknowledge the support received by the European Commission in the framework of Mundus ACP that permitted this research at the Department of Chemical Engineering of the University of Rome "La Sapienza".

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