

Adsorption of Phenol and its Chlorinated Derivatives from Waste Waters using Hypercrosslinked Polymers

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The adsorption of phenolic derivatives from waste waters represents an important method in protecting surface water and soil from pollution [1, 2]. The adsorbents used are hypercrosslinked polymers having a high adsorption capacity, high rate of pollutant uptake, mechanical strength used recuperation facilities. The hypercrosslinked polymers have been obtained by extensive crosslinking of linear polystyrene chains. The networks so obtained are characterized by high free volume and high adsorption surface having the ability to swell in both polar and non-polar media acting as a driving force for organic compounds sorption such as phenolic derivatives [3, 4]. Experimental adsorption studies have been made for phenolic chlorinated derivatives elimination using as adsorbents MN-200 and MN-500 hypercrosslinked polymers. The adsorption capacity depends on the physical and chemical proprieties of the adsorbent the nature of the adsorbate and the adsorption conditions (adsorbate concentration, temperature, pH).

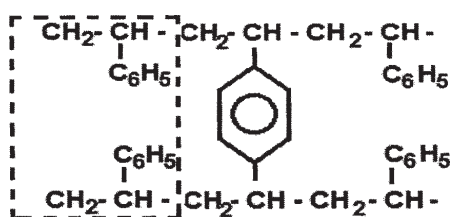
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Chlorophenols are produced when phenol-contaminated water is chlorinated in the purification process. The compounds are very distasteful even in low parts per billion, being potential health hazards.

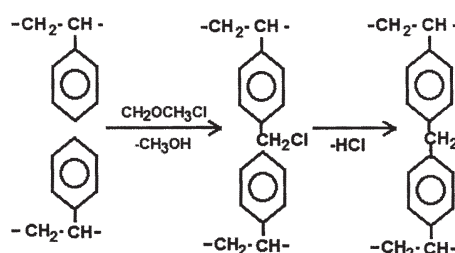
The phenols are present in many industrial wastewater streams from petrochemical, pharmaceutical, pesticide and generally from organic chemical plants [1-5]. In recent years restrictions have been placed on industry in order to prevent the discharge of phenol into receiving waterways. These measures have stimulated the development of dephenolizing processes for the treatment of waste effluents, like adsorption on solid surface-active materials, provided that adsorbents have high adsorption capacity, high rate of pollutant uptake, sufficient mechanical strength, easiness and low cost of regeneration procedures[3-4].

The above mentioned requirements are largely covered by a novel generation of polymeric sorbents represented by hypercrosslinked polystyrene materials, as developed by Davankov and Tsyurupa [6-8]. Adsorbents of this kind are quite rigid, possess large transport macropores and highly developed microporous structure, displaying both adsorption and desorption performances. They are known in literature as macronets (MN).

The hypercrosslinked polystyrene polymers are obtained by extensive crosslinking of linear polystyrene chains:



The crosslinking could be done using a bi-functional reagent as mono-chlorodimethyl ether ($\text{CH}_3\text{-O-CH}_2\text{-Cl}$) according the scheme [9]:



The monochloro-dimethyl ether is capable of forming rigid bridges, with a very restricted conformational mobility. The crosslinking of phenol groups occurs in the presence of a Friedel Crafts catalyst (SnCl_4 , TiCl_4) using as reaction media an organic solvent as ethylene dichloride ($\text{C}_2\text{H}_2\text{Cl}_2$) in order to ensure the ultimate polystyrene swelling. So, one obtain a high crosslinked network filled with organic solvent.

The hypercrosslinked polystyrene network is characterized by a very low packing density of polymer chains in space, due to the high number of rigid spacers ($-\text{CH}_2-$) holding polystyrene chain apart. That is why the free volume of the hypercrosslinked polystyrene is high. It can be considered to represent the true porosity, developing a high inner surface which makes the whole polymeric phase accessible to small sorbate molecules [10].

In spite of the high crosslink density (high number of rigid spacers) the polystyrene networks exhibit the ability to swell in contact with organic molecules, including sorbate species. The explanation consists in the fact that, after solvent ($\text{C}_2\text{H}_2\text{Cl}_2$) elimination, i.e. in the dry state, the hypercrosslinked polymer becomes strongly strained because of the rigidity of the network. When in contact with organic sorbate these inner strains relax facilitating the filling of the polymeric network. That is why the sorbate uptake could be considered as a combination of adsorption on the inner surface of polymeric chains and absorption, facilitated by relaxation of the inner strains [11]. This explains the ability of the hypercrosslinked polystyrene to

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Properties	MN-200	MN-500
Mean diameter of pores, mm	123	145
Cumulative volume, mm ³ /g	1270	605
Specific area, m ² /g	1090	415
Global porosity, %	59	51
Density, g/cm ³	1130	1570

Table 1
STRUCTURAL PROPERTIES OF MN-200
AND MN-500

Macronet type	Compound	Langmuir isotherms		
		a _m	b	R ²
MN 200	Phenol	2.75	0.345	0.991
	P-chlorphenol	3.125	0.246	0.984
	O-chlorphenol	2.387	2.18	0.942
MN 500	Phenol	2.15	0.21	0.971
	P-chlorphenol	2.00	0.24	0.982
	O-chlorphenol	2.54	0.135	0.989

Table 2
EQUILIBRIUM PARAMETERS OBTAINED
ACCORDING TO LANGMUIR EQUATION FOR
THE STUDIED COMPOUNDS ON MN-200 AND
MN-500

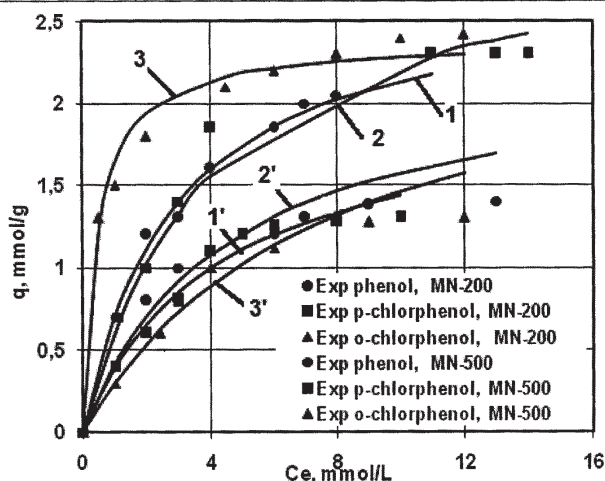


Fig 1. Adsorption isotherms of phenol and its chlorinated derivatives on MN-200 and MN-500

1,1'; 2,2', 3, 3' theoretical curves obtained from Langmuir model on MN-200 and MN-500 respectively

increase, by 3-4 times, the volume by incorporating liquid sorbates, in spite of the extremely high crosslinking of the network and, in the same time, the ability to be easy regenerated. The regeneration can be carried out by washing the sorbent by hot water or steam. In certain conditions the regeneration can be accomplished using acid or alkaline media [12].

The polystyrene matrix of macronet sorbents being hydrophobic one will readily adsorb non-polar hydrophobic impurities. In order to ensure the adsorption of polar or ionizable molecules, the addition of hydrophilic ion exchange functional groups to the matrix must be done. In the same time the hydrophilic functional groups improve the regeneration conditions of the adsorbent [13].

Hypercrosslinked polymers (macronets) exhibit adsorption activity with respect to various substances dissolved in water, such as phenols, synthetic organic dyes, pesticides, lipids, antibiotics [14-19]. They also are used as a novel type of High Performance Liquid Chromatography [20-24].

Experimental part

The adsorption of phenol and its chlorinated derivatives, m-chlorphenol and o-chlorphenol, has been performed using as sorbents the hydrophobic hypercrosslinked polymer MN-200 (Purolite Macronet) and its sulphonated derivative MN-500. The sulphonic hydrophilic functional groups have been introduced in MN-200 matrix in order to ensure the adsorption of polar or ionizable molecules and also to ensure the ion exchange properties. In the same

time the hydrophilic functional groups improve the regeneration conditions of the adsorbent [13]. Unfortunately the introduction of functional groups determines a decrease of specific area.

The main structural properties of MN-200 and MN-500 are presented in the table 1. The specific area has been determined using a porozimeter Carlo Erba Sorpty 1750.

The adsorption experiments were performed using a method based on the determination of the solute concentration before and after contact with the adsorbent. In order to ensure the uniformity the solution -adsorbent mixture was mechanically shaken. The equilibrium being attained (after 24 h) the solid phase was filtered and the concentration was measured.

A measured volume ($V=50$ mL) of phenolic solution was placed in 500 mL vessel, containing the same amounts of adsorbent ($m=0,1$ g). The initial concentration of phenolic compounds was ranged between 1 mmol/L to 25 mmol/L. The bottles were placed in a mechanical stirrer and maintained at a constant temperature ($t=25\pm 0,1^\circ\text{C}$).

A high sensitive ultraviolet method has been used, based on the fact that ionized phenol chlorinated compounds show a shift of absorption band to longer wavelengths with an increase of pH due to formation of phenolates. A SPECORD Jena spectrometer has been used. The specific wavelengths of phenol derivatives are the following: phenol, $\lambda=290\text{nm}$, o-chlorphenol, $\lambda=295\text{nm}$ and p-chlorphenol, $\lambda=300\text{nm}$.

Results and discussions

In order to evaluate the adsorption capacity of MN-200 and MN-500 for phenol and its chlorinated derivatives, the adsorption isotherms for both systems have been represented (fig. 1). The obtained data put in evidence the higher adsorption capacity of MN-200 in comparison with MN-500. The explanation consists in the fact that the functional sulphonic groups- HSO_3 introduced in Mn-200 structure diminish considerably (from 1090 to 415m²/g) the specific area, modifying also another structural properties of MN-200 (table 1). These modifications result also from the structural characterization of both solid phases using for spectral IR domain (IR 4000-400 cm⁻¹) and UV-Vis domain (250-1859 nm) the spectrometer FT-IR -620 Jasco and UV-Vis-V570 respectively.

The main spectral characterization of spectral IR domain results from spectral diagrams presented in figures 2 and 3 in coordinates Transmittance (T%) -Wave number [cm⁻¹]. One can see that the macronet MN-200 presents more simple spectral lines than the macronet MN-500 because of introduction in the structure of MN-200 of functional groups- HSO_3 . The same conclusions result from

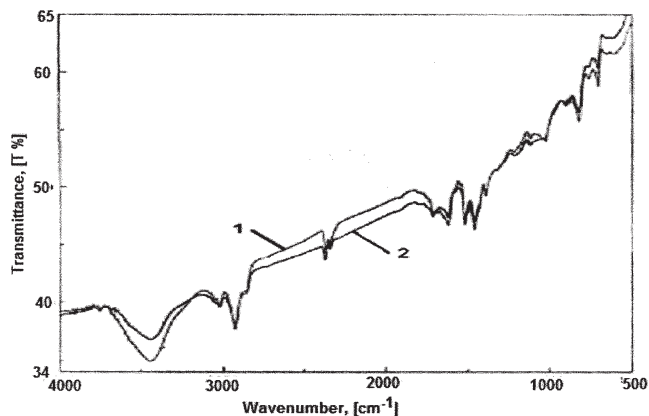


Fig. 2. Spectral diagram of macronet MN-200 in IR domain
1 temperature 25°C, 2 temperature 150°C

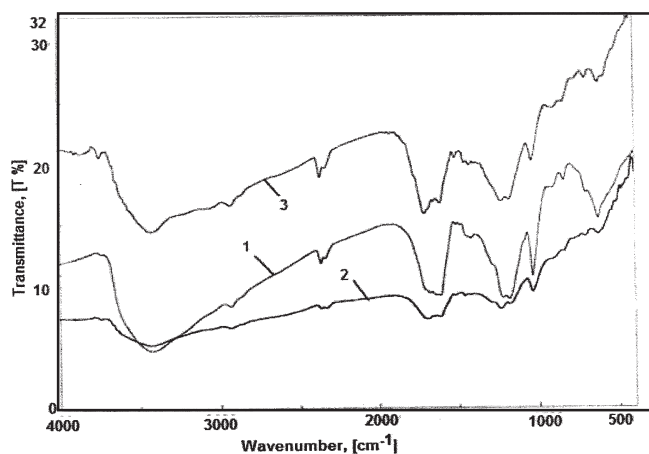


Fig. 3. Spectral diagram of macronet MN-500 in IR domain
1 Temperature 25°C, 2 temperature 120°C, 3 temperature 150°C

the diagrams presented in coordinates Reflectance (R%)-Wavelength [nm] in figures 4 and 5, in UV-Vis domain.

The values of the equilibrium parameters for the studied compounds on MN-200 and MN-500 are presented in table 2.

The adsorption processes on MN-200 and MN-500 could be theoretically characterized using an appropriate equation. The shape of two groups of isotherms suggests a monolayer adsorption being characterized by Langmuir equation:

$$q = q_M \frac{bC}{1 + bC} \quad (1)$$

or their linearized form :

$$q = q_M \frac{bC}{1 + bC} \quad (2)$$

where q represents the concentration of adsorbate in solid phase mmol/g;

q_M the concentration of adsorbate adsorbed in monolayer, mmol/g;

C-the concentration of adsorbate in liquid phase, mmol/L;

b-the equilibrium constant

As results from figure 1 the Langmuir equation fits satisfactory the experimental data.

In order to verify the thermal stability of the both macronet MN-200 and MN-500 the spectral analysis has been made at 25, 120 and 150°C. The thermal stability is

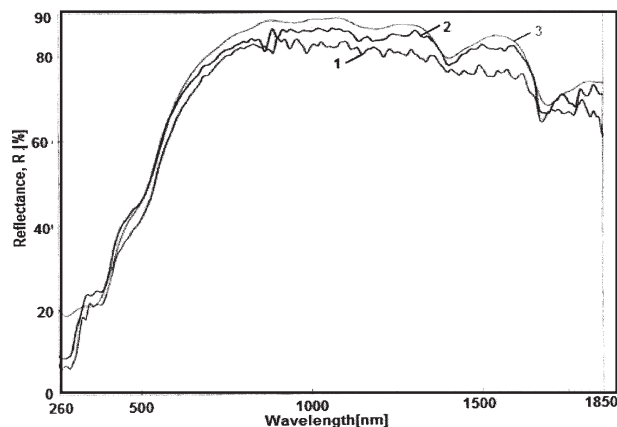


Fig. 4. Spectral diagram of macronet MN-200 in UV-Vis domain
1 temperature 25°C, 2- temperature 120°C, 3- temperature 150°C

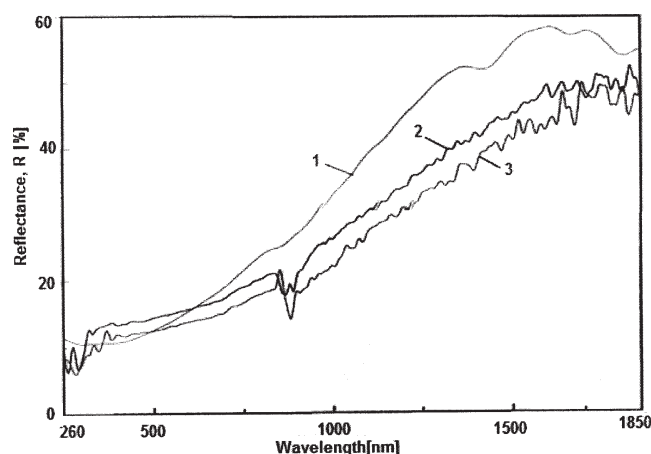


Fig. 5. Spectral diagram of macronet MN-500 in UV-Vis domain
1 temperature 25°C, 2- temperature 120°C, 3- temperature 150°C

high in both cases because of their extended conjugate structures.

Conclusions

The neutral hydrophobic sorbent macronet MN-200 exhibits the ability to swell in contact with organic molecules like phenol and its chlorinated derivatives. For this reason the sorption on MN-200 can be considered as a combination of adsorption on the inner surface of polymeric chains and absorption by the bulk polymer. The adsorption characteristics of MN-200 could be explained by the existence of large transport macropores (attaining 950 Å) which facilitate the diffusion of the sorbent molecules from the bulk fluid into the micropores, the latter ensuring the big adsorption area (about 1000m²).

The macronet MN-200 presents as advantages a high mechanical resistance and the capability to be easily regenerated using saturated or superheated stream without changing its structure and shape. So the number of the adsorption-desorption cycles becomes much more in comparison with active carbon usually used for phenolic derivative adsorption [25]. The macronet MN-500 presents a smaller adsorption capacity compared with MN-200, because the introduction of sulphonic functional groups in the structure of MN-200. This fact determines a decreasing of specific surface to about 400m²/g.

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