WASTEWATER TREATMENT USING MULTIPURPOSE CARBON MATERIALS (MCM)

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Această lucrare prezintă studiile realizate pentru îndepărtarea diferiţilor poluanţi (benzen, toluen, xileni, fenol) în procesul de purificare a apelor reziduale prin adsorbţie pe diferite materiale carbonice multifuncţionale (MCM). Proprietăţile adsorptive ale diferitelor materiale carbonice multifuncţionale obţinute din diferite surse vegetale, au fost studiate prin comparaţie cu cele ale unui cărbune activ comercial. S-au determinat timpul necesar pentru atingerea echilibrului de adsorbţie în condiţii statice şi eficienţa îndepărtării poluaţilor. Toate materialele carbonice multifuncţionale studiate prezintă eficienţe bune de îndepărtare a poluanţilor studiaţi.

This paper presents the studies realized for removal of different pollutants (benzene, toluene, xylene, phenol) in the purification process of water by adsorption on various multipurpose carbon materials. The adsorptive properties of multipurpose carbon materials obtained from different vegetal sources were studied by comparison with a commercial active charcoal. The necessary time for reaching the adsorption equilibrium in static conditions as well as the removal efficiencies of the pollutants were determined. All studied multipurpose carbon materials have been shown good removal efficiencies of the corresponding pollutants.

Keywords: adsorption, active charcoal, pollutant, phenol

1. Introduction

The efficiency of various treatment processes for removing of organic pollutants has been largely documented [1]: precipitation/coagulation, chemical oxidation, sedimentation, filtration, adsorption, osmosis, ion exchange**,** ultrafiltration, electrodialysis, electrochemical degradation, flotation. New technological treatment processes are searched and developed. This research involves the following steps: chemical oxidation [2-4], solvent extraction [5],

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biological degradation [6-8], adsorption onto different adsorbents [9-12]. Now, active charcoal systems are most used in water treatment.

It is known that around 80% of the world production of active charcoal is used in liquid-phase applications [13].

The efficient use of the sustainability concept related to pollution abatement envisages management of the increasing quantity of water necessity, which determines its recirculation and reuse. Concurrently, the decline of the traditional resources used at manufacturing the active carbons and the increase of costs with raw material determine the necessity of identifying some alternative resources that do not harm the environment. The main market for liquid phase applications of the multipurpose carbon materials (MCM) like active carbons, the strongest known carbon adsorbents, is in a trend of steady development for the long and medium term, due to the implementation of the environmental legislation.

In Romania, the statistics reveal that the amounts of industrial and agricultural waste slightly grow, and mostly, the wastes are eliminated by storage.

On the other hand, after Romania has become an EU Member State, the legislation implementation becomes a stringent need, the problems of wastewater purification representing a key element.

The purpose of this paper is to study the adsorption of organic pollutants from water on multipurpose carbon materials prepared from vegetable wastes.

2. Experimental

The MCM are porous products resulted from the carbonization and activation of the following materials used in our study: xylite (the wooden part of lignite) [14, 15], peach and plum kernels, particle board PAL and soybean hulls.

Low-temperature carbonization consists in charcoal manufacture in a laboratory vertical retort. Here, the drying, preheating and conversion of the waste into charcoal were accomplished through low-temperature carbonization at 500-600°C, at a heating rate of 3-5°C/min, reaction time of maximum 60 min, in a small overpressure of nitrogen. The main advantage was the development of an important porous network in the resulted charcoal, which represents the intermediate porous structure of the MCM.

The basic principle of activation was the development of a porous network in charcoal by physical activation. This activation has been performed in a laboratory vertical retort.

The main activation parameters were: temperature between 950-1000°C; activation agent by superheated steam flow of 60 cm^3/h, nitrogen flow of 90 L/h, and activation time of 60 min.

In order to determine the adsorption efficiency and adsorption capacity the work has been done in static conditions, using as liquid effluent an aqueous solution which contained aromatic hydrocarbons (benzene, toluene, and xylene) and phenol. Basic operations for depolluting aqueous solutions of organic pollutants in static conditions are presented in Fig. 1.

The following static conditions are used:

- MCM weight (for 100 mL water): 0.1; 0.2; 0.5; 1 g;
- initial concentration of dissolved organic substances 0.12 g/L (the solubility limit for xylene was chosen);
- contact time: 0.5; 1; 2; 4 hours.

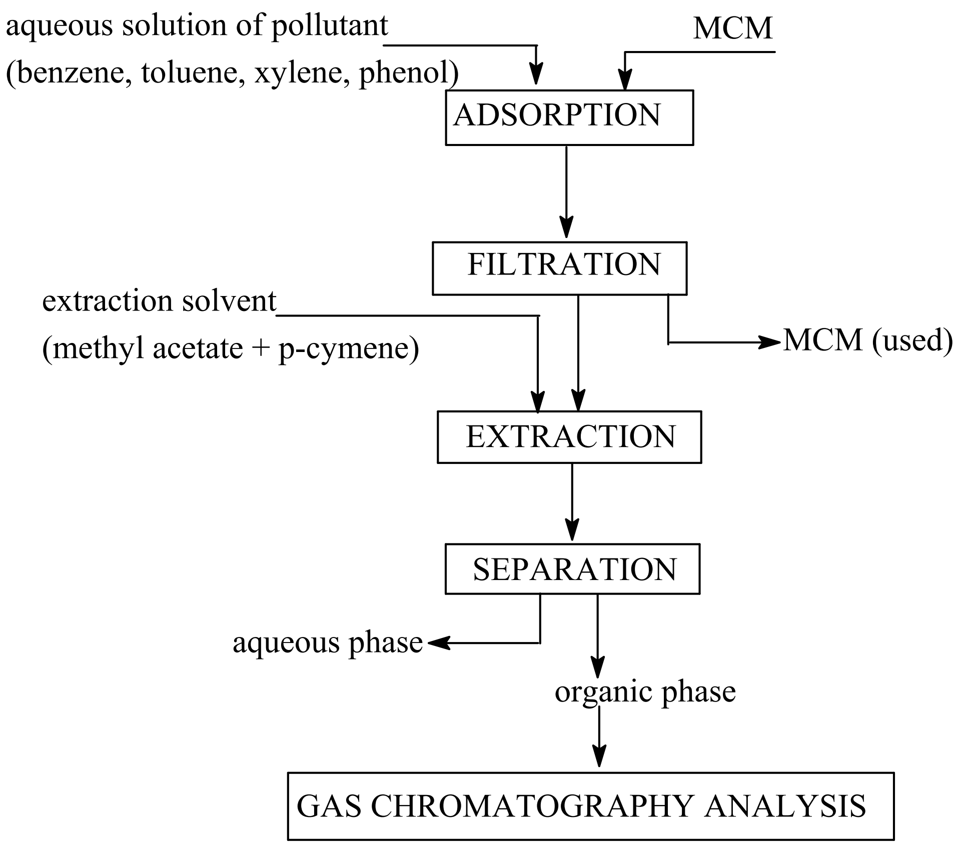

Fig. 1. Basic operation for adsorption pollutant by static conditions

The determination of the components concentration from the initial solution and after static adsorption has been performed by extraction in methyl acetate followed by gas-chromatography analysis (Chromatograph type Fissons

8330 with capillary column type WCOT CP-Sil 8CB 30 m * 0.32 mm * 0.25mm, high sensitivity FID detector coupled at a computer provided with integration and data processing soft).

3. Results and discussion

First by the time for attaining the adsorption equilibrium for static conditions was determined. Figs. 2 and 3 present the variation in time of the pollutant quantities adsorbed on two adsorbent materials (MCM – xylite and commercial charcoal). Volumes of 100 mL water with organic substances and 1 g MCM were used.

The adsorption equilibrium was reached after one hour for aromatic hydrocarbons, while for phenol was attained after about 2 hours. Similar results have been obtained for all studied MCM.

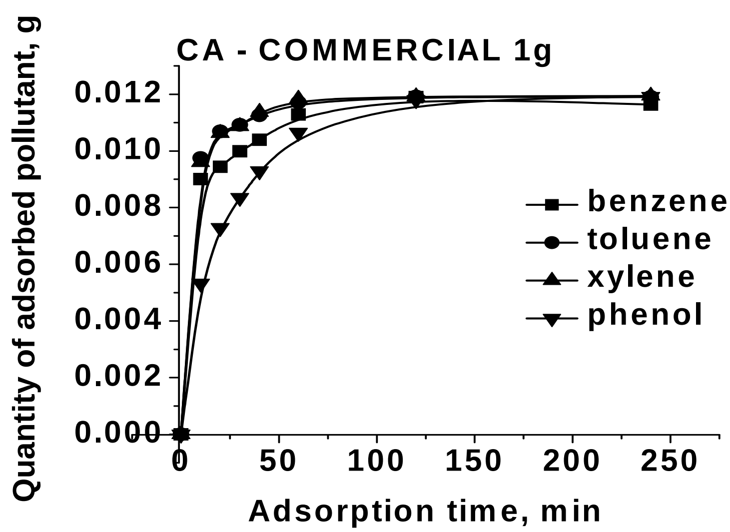

Fig 2. The variation in time of the pollutant quantities adsorbed on MCM – xylite

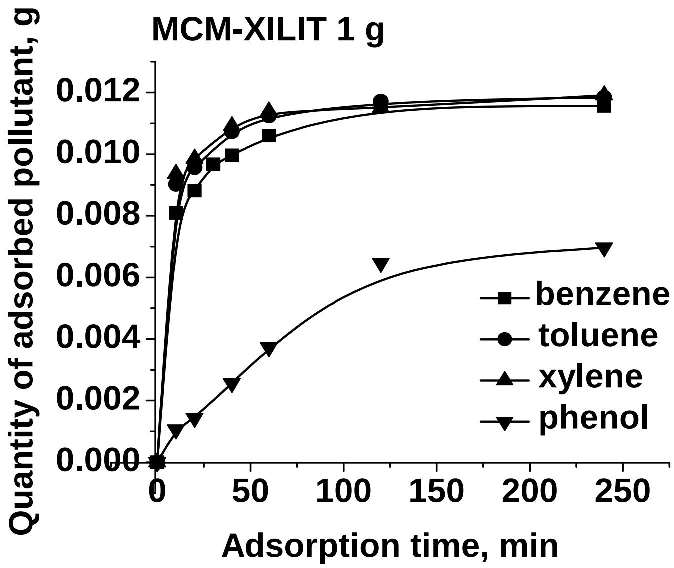

Fig. 3. The variation in time of the pollutant quantities adsorbed on commercial charcoal

The following experiments have been realized in order to determine the adsorption efficiency for benzene, toluene, xylene and phenol using 0.1 to 1 g MCM in the form of xylite, peach kernels, plum kernels, particle board PAL and soybean hulls for 100 mL aqueous solution (containing 0.012 g from each pollutant). The adsorption efficiency was calculated using the next relation:

$$E,\% = \frac{C_0 - C_f}{C_0} x100 \quad (1)$$

where: E – adsorption efficiency, C_0 – initial concentration of pollutant, C_f – final concentration of pollutant.

Fig. 4 presents the efficiency of phenol adsorption. The phenol has been selected for representation due to its lower adsorption rate from all studied compounds. The MCM obtained from peach and plum kernels exhibit the highest efficiency in phenol absorption. For 1 g adsorbent material/100 mL water, the efficiency of these materials is higher than 85 % after 30 minutes and after 4 hours of adsorption this adsorption efficiency is about 99 %.

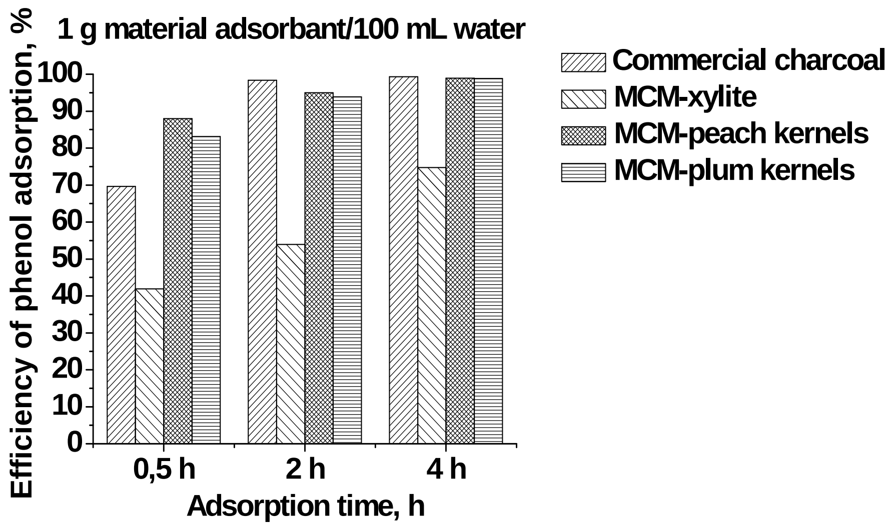

Fig. 4. The efficiency of the phenol adsorption on different MCM

In order to determine the adsorption capacity of different types of MCM, several experiments were carried out using different MCM quantities (0.1; 0.2; 0.5 and 1g MCM/100 mL in aqueous solution). The concentration of organic compounds in water was constant. After attaining the adsorption equilibrium (2h), the concentrations of organic compounds in water have been determined.

The removal of the pollutants from waste water by adsorption on active charcoal has been also evaluated by fitting Freundlich equation:

$$\frac{x}{M} = kC^{\frac{1}{n}} \quad (2)$$

where: x is the amount of adsorbed component, M the amount of sorbent, C the equilibrium concentration and k and n are Freundlich constants.
The logarithmic form of the equation becomes:

$$log\frac{x}{M} = logk + {}^{1}\!/_{n}\, logC \quad (3)$$

where k and n are indicators of the adsorption capacity and of the adsorption intensity [16].

While Freundlich equation shows equilibrium limits of waste water, the constants are sensitive especially to nature of its constituents. In order to estimate the adsorption capacity of adsorbent material, the *x/M* value corresponding to the concentration of C_0 influent was used. This value x/M_{C_0} represents the maximum quantity of pollutant adsorbed on charcoal weight unit when the charcoal is in equilibrium with the concentration of the adsorbed pollutant.

Once x/M_{C_0} is determined for a system, the theoretical necessary of charcoal can be calculated for a certain volume of liquid pollutant.

The complete elimination of the pollutant results from the equation (4):

$$y = \frac{C_0}{\left(\dfrac{x}{M_{C_0}}\right)} \tag{4}$$

where: *y* is the charcoal weight on waste water volume unit.

Figs. 5 and 6 present adsorption isotherms for xylene and phenol solutions, respectively, on different adsorbent material.

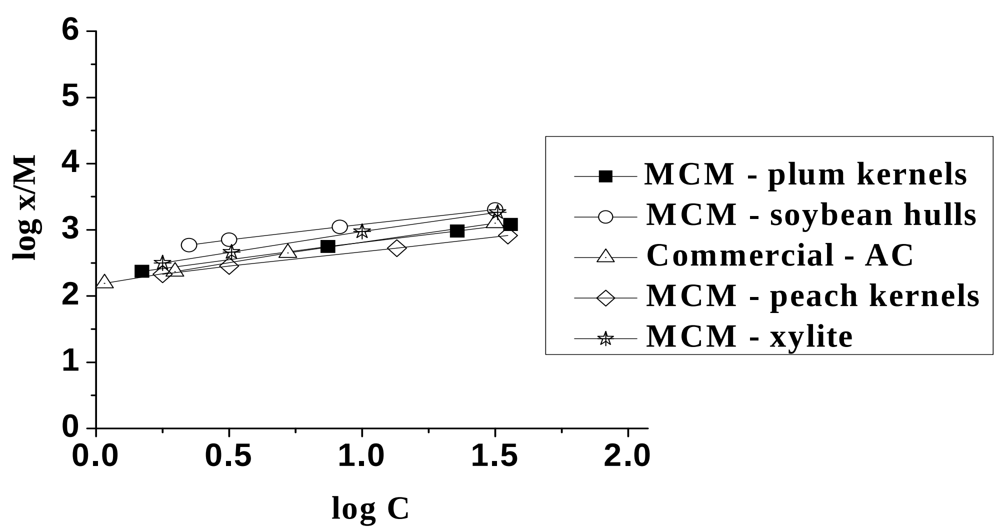

Fig. 5. Adsorption isotherms for xylene solutions

The necessary theoretical quantity of charcoal for total depolluting of a liter of solution was determined from the data obtained from adsorption isotherms.

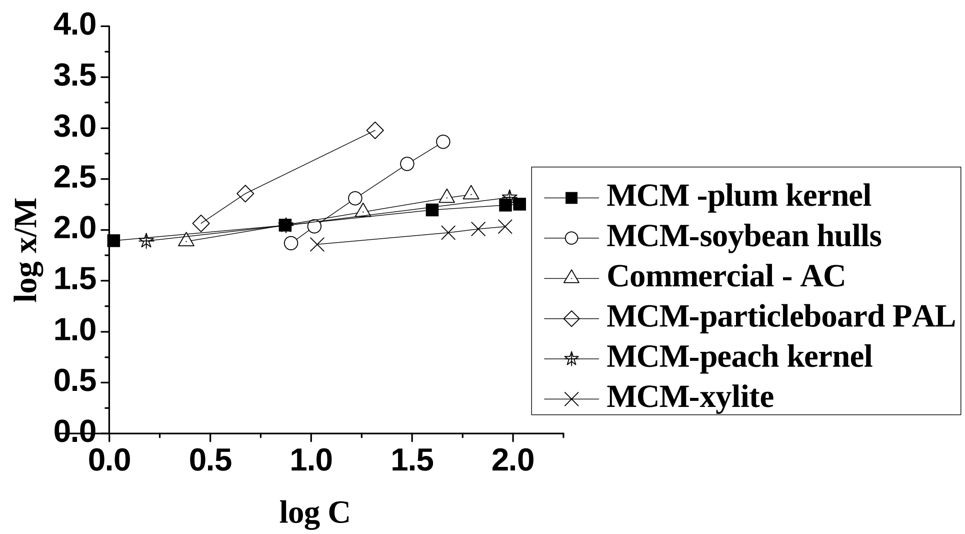

Fig. 6. Adsorption isotherms for phenol solutions

MCM quantity for depolluting a liter of solution, in static conditions is presented in table 1.

Table 1

The theoretical amount of charcoal (g) for complete depolution of 1 L of a solution with the concentration C_0 (mg/L)

Phenol (C_0 = 118.55 mg/L)	Commercial charcoal AC	MCM xylite	MCM plum kernels	MCM peach kernels	MCM soybean hulls
$log(x/M)_0$	1.74	1.67	1.89	1.85	0.74
$(x/M)_0$	54.95	46.77	77.62	70.79	5.49
$y = C_0/(x/M)_0$	2.16	2.53	1.53	1.67	21.59
Toluene (C_0 = 123.5 mg/L)	Commercial charcoal AC	MCM xylite	MCM plum kernels	MCM peach kernels	MCM soybean hulls
$log(x/M)_0$	2.38	2.40	2.31	1.99	2.56
$(x/M)_0$	239.88	251.18	204.17	97.72	263.08
$y = C_0/(x/M)_0$	0.26	0.49	0.6	1.26	0.17
Xylene (C_0 = 119.2 mg/L)	Commercial charcoal AC	MCM xylite	MCM plum kernels	MCM peach kernels	MCM soybean hulls
$log(x/M)_0$	2.17	2.42	2.33	2.23	2.58
$(x/M)_0$	147.91	263.03	213.8	169.82	380.19
$y = C_0/(x/M)_0$	0.81	0.45	0.56	0.7	0.31

The properties of the MCM were determined by measuring the specific surface area BET, the iodine value, the fixed carbon content and ash. The average values are shown in table 2.

Table 2

The physical-chemical characteristics of MCM, in case of the laboratory experiments

Type MCM	Surface area, S_{BET}, m^2/g	Micro pores volume*, cm^3/g	Iodine value, mg/g	Volatile, %	Fixed Carbon, %	Ash, %
AC commercial	871.0	0.321	920.0	1.0	96.0	3.0
MCM-xylite	547.7	0.136	758.0	1.0	91.5	7.5
MCM-soybean hulls	123	0.050	438.6	15.7	66.5	17.8
MCM-peach kernels	1257.1	0.267	912.9	1.5	96.3	2.2
MCM-plume kernels	578.22	0.156	723.6	1.8	95.5	2.7

* Micro pore average radii: 0.31-0.43 nm

In the case of aromatic hydrocarbon pollutants the adsorption capacities of all types of MCM's are comparative those of commercial active charcoal. When the phenol solutions were used the results have been different. The adsorption capacities of MCM – plum and peach kernels have similar values as commercial active charcoal. Lower values have been obtained for MCM-xylite, particleboard PAL and soybean hulls. All these results are in agreement with the physical-chemical characteristics principals of MCM (specific surface area , micro pores volume, fixed carbon), presented in table 2.

4. Conclusions

- All the investigated MCM samples have significant adsorption characteristics towards the studied organic pollutants;
- The adsorption efficiency depends on the type and characteristics of MCM, the type of dissolved organic pollutants, the contact time and the adsorbent quantity;
- For the aromatic hydrocarbons (benzene, toluene, xylene), all the studied adsorbents had good adsorption capacities;
- In case of wastewaters with various organic pollutants, the MCM from soybean hulls have higher adsorption capacities for aromatic hydrocarbons and lower adsorption capacities for phenol.

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