EFFECT OF IMPREGNATION WITH TRANSITION METAL SALTS ON THE STRUCTURE AND PROPERTIES OF ACTIVATED CARBONS OBTAINED FROM PLUM STONES

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Introduction

The interest towards Activated Carbons (AC) obtained from various vegetal raw material remains constant due to their high adsorption properties, thus allowing to use them not only in matters concerned with environment protection, but also in medicine. Besides that, it is known that oxidized ACs are sorbents with selective properties [1], and the processes of their impregnation with metals change their properties. For example, the processes of regeneration of such carbons can be carried on at relatively low temperatures [2]. Activated carbons can be used as catalyst supports [3]. Earlier, we investigated the thermal regeneration of non oxidized and non-impregnated activated carbons from nut and peach shells. [4,5]. Characteristics of some non-impregnated AC are given [6]. Hereinafter we present the results of some ACs investigations, the carbons having been obtained from vegetal raw materials (plum and peach stones shell). Their surface has been modified by oxidization and then subjected to impregnation by means of salts of some transitional metals. We have also investigated the thermal regeneration of researched AC saturated with p-nitroaniline and some commercial pesticides

Experimental

Initial Activated Carbon CA-36 (in) prepared from plum stones (Moldova) as previously described [7} was used.
The oxidation was performed using 50% nitric (V) acid under heating on water bath for 8 hours taking the ratio AC : HNO_3 = 50 g : 150 ml. Impregnated samples were obtained from oxidized AC using as support the aqueous solution of the following salts:$TiOSO_4$. $2H_2O$, $CuSO_4$.5H2O, $FeCl_3$.$6H_2O$ in the appropriate concentration (0.1 gml $^{-1}$). After that the solutions were heated and constantly stirred until total elimination of the liquid. The sample with Ti salt was treated with HNO_3 or HCl so as to stop the hydrolysis. For saturation of the samples of investigated carbons, use was made of aqueous solutions of p-nitroaniline for which the ratio – the solution volume to the carbons mass- was maintained constant. . The temperature was of 25^{o}C. To preserve this temperature, a thermostatic automatic shaker was used during 3 days. The adsorbent particles were separated from the liquid phase by filtration through a paper filter. The carbon samples were later dried in the open air at 25^o C for constant weight. P-nitroaniline was used without additional purification . For TG,DTG,DTA researches, use was made of the thermoanalyser of the type Derivatograph Q-1000D (MOM, Hungary). Activated Carbons structure characterization was performed using a Quantichrome equipment.

Results and Discussion

Table 1 shows the general characteristics of investigated ACs. One can notice how the structure parameters change as a result of the oxidization and impregnation processes. We have also investigated the impact of oxidization and impregnation processes on ACs thermal regeneration A typical nitrogen adsorption isotherm for the sample of CA-36(ox+Ti) is shown in Fig. 1. Fig.2 shows thermoanalytical curves CA-36-(ox+Cu) compared with CA-36-(ox+Cu+p-nitroaniline) of simulation regeneration processes, while Table 2 , contain data of corresponding estimations. Fig. 3 represents the TG curves of simulation of regeneration processes of CA-24 saturated with 2,4 – D-diclorfenoxiacide,(2,4-D), and CA-23 (from peach stones) saturated with Atrazine(At), while Fig. 4 represents the DTA curves of the same

regeneration processes. It was established that .the (2,4-D) desorption occurs in the range 155-300°C and At- in range 230-390°C (Fig. 3,4). The results obtained from analyzing curves TG/DTG/DTA of p-nitroaniline desorption from the surface of ACs are summarized in Table 2 and allow us to draw some conclusions on the thermal behavior in the system activated carbon-catalyst-aniline. The catalytic impact allows the process of aniline oxidization to occur at lower temperatures: 135-320 (Cu), 150-340 (Ti), 130-320 (Fe). The catalysts effects are stronger in the presence of p-nitroaniline. Thus, using the data of thermal analysis, the optimal conditions of thermal regeneration of investigated carbons were established: 130-360 (Ta), 320-510 (Tc).

Conclusions

Oxidization and impregnation processes have led to surface modification At the same time it has been established that impregnation allows to decrease the regeneration temperature. We have also investigated the processes of thermal regeneration of activated carbons saturated with some commercial pesticides.

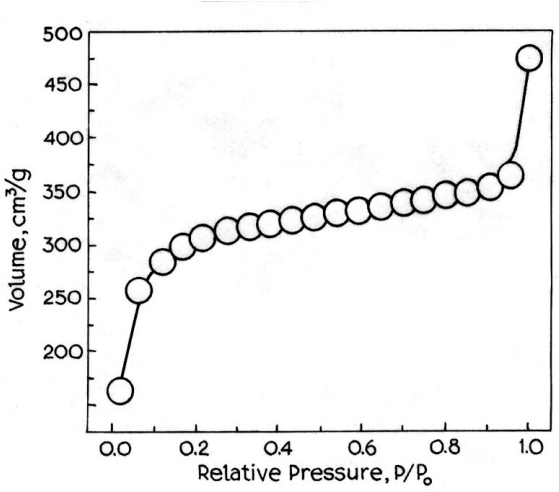

Figure 1. Typical 77k N_2 isotherm for sample CA-36(ox+Ti)

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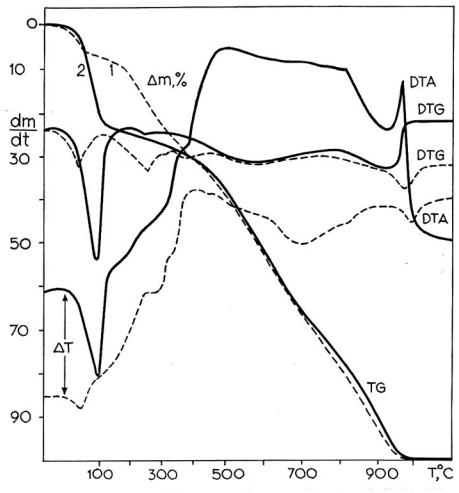

Figure 2. TG, DTG, DTA of samples: (1) CA-36 (ox+Cu); (2) CA-36 (ox+Cu+ p-nitroaniline)

Table 1. Surface area, pore volume and size, surface energy, fractal dimension

Sample	BET/Langmuir surface area (m^2/g)	Pore volume total (ml/g)	Micropore (DR) ml/g	Pore size (nm) Average(D)	Surface energy E_0[kJ/mol]	Fractal dimen-sions (NK)
CA-36 (in)	1249 / 1580	0.637	0.553	2.4	6.23	2.97
CA-36 (ox)	1260 / 1595	0.657	0.558	2.15	6.19	2.93
CA-36 (ox+Ti)	1361 / 1709	0.694	0.599	2.04	6.40	3.00
CA-36 (ox+Fe)	1239 / 1565	0.641	0.548	2.06	6.27	3.00
CA-36 (ox+Cu)	1248 / 1574	0.645	0.551	2.06	6.39	3.03

Table 2. Temperatures of water and other volatile compounds (CO) desorption T(w,v), aniline oxidation T(a), oxidation of carbon surface T(c) and carbon burn-of T(g) obtained from TG, DTG, DTA experiments, Derivatograph Q-1000D

Sample	Tw,v (^{0}C)	Ta (^{0}C)	Tc (^{0}C)	Tg (^{0}C)	100% burn off (^{0}C)
CA-36in*	35-180	-	360-480	480-830	930-980
CA-36ox+Ti*	35-200	-	300-520	520-740	790-970
CA-36ox+Ti+p-nitroaniline	35-150	150-340	340-465	465-730	740-950
CA-36ox+$CuSO_4$*	35-190	-	210-460	460-810	810-940
CA-36ox+$CuSO_4$+p-nitroaniline	35-130	135-320	320-510	510-865	865-970

*without p-nitroaniline

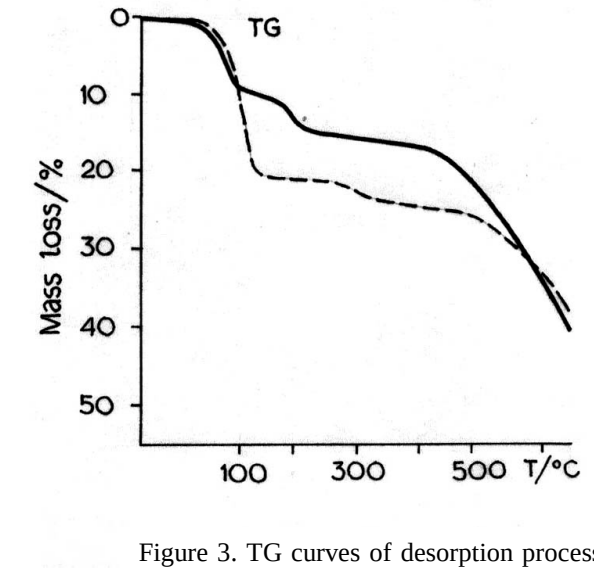

Figure 3. TG curves of desorption processes: ---- CA-23+Atrazine: ____CA-24+(2,4-D)

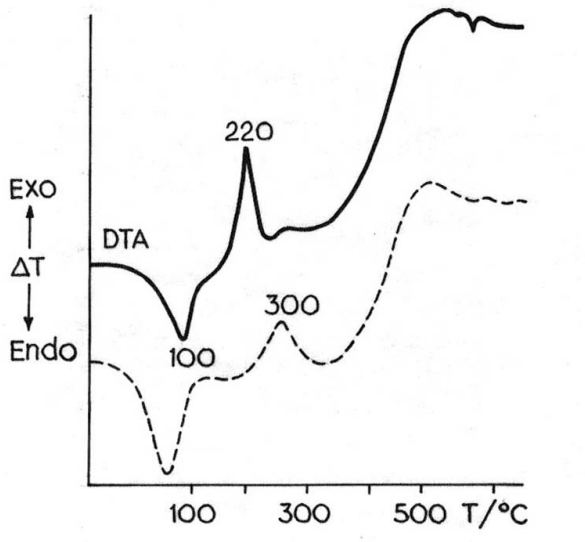

Figure 4. DTA curves of desorption processes: ----CA-23+Atrazine: ____CA-24+(2,4-D)