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PHENOL ADSORPTION ON ACTIVATED CARBONS: APPLICATION TO THE REGENERATION OF ACTIVATED CARBONS POLLUTED WITH PHENOL

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Abstract—Phenol adsorbs in two ways on activated carbons: by physisorption and chemisorption. During the course of time and by raising the temperature, chemisorption is increased and part of the physisorbed phenol becomes chemisorbed. This phenol is impossible to remove as such. Upon heating to elevated temperatures it decomposes, depositing carbon, resulting in a decrease in the adsorption capacity of activated carbons. By studying this, we have been able to find adsorption conditions which prevent phenol chemisorption and yield a method of 100% regeneration of phenol-polluted activated carbons.

Key Words— Activated carbons, phenol, chemisorption, regeneration.

1. INTRODUCTION

Activated carbons are important absorbents for the removal of organic molecules from water. But their adsorptive capacity decreases continuously with each regeneration cycle. The most often applied method to regenerate them is reactivation in oxidizing gases at elevated temperatures, which leads to high consumption of carbon.

In order to improve the regeneration yield of activated carbons polluted with organic molecules, some fundamental studies have already been conducted in this field [1–4].

Following a previous study carried out in the laboratory [5] concerned with the treatment of activated carbon for removal of phenol from water, we have tried to better understand the mechanism of phenol adsorption on activated carbons. From this study we have deduced a method for using and regenerating activated carbons polluted with phenol.

2. EXPERIMENTAL

Three activated carbons supplied by different companies and a carbon derived from a copolymer of PVC and PDVC were used. Important properties are shown in Table 1. Nitrogen and CO_2 surface areas were determined from their adsorption isotherms measured at 77 K and 298 K, respectively, in a previous study[5].

All the adsorption experiments were carried out using a 2000 ppm aqueous phenol solution. This concentration was chosen because it corresponds to a surface coverage from 90% to 100% by phenol, using 0.522 nm^2 for the surface area occupied by one phenol molecule. The thermogravimetric analysis curves (or TGA curves), on which most of the results reported in this work are based, have the same profile for a concentration range of 200 ppm to 10000 ppm of phenol in water. This means that our conclusions could have been drawn from experiments using other concentrations of phenol in the indicated range.

The principle of our experiments was as follows: 100 mg of activated carbon were mixed with 100 ml of a 2000 ppm phenol aqueous solution in 150 ml capacity stopped bottles. The suspensions were shaken mechanically for about 24 h and filtered. To investigate the phenomenon of phenol adsorption on carbons, one or several of the following operations were carried out on each sample:

—Determination of the fall in concentration of the supernatant liquid using a Beckman DU2 spectrophotometer.

—Drying of the sample generally in air at 383 K or sometimes under a flow of purified N_2 at room temperature.

—On a fraction of the sample, performing a programmed thermodesorption up to 1223 K under a flow rate at 100 ml/min of purified N_2, giving a TGA curve. For this thermodesorption, we used a Dupont 990 Analyzer, with a sensitivity of 0.2 mg/in and a heating rate of 25 K/min.

Because of the existence of some secondary phenomena, such as possible interaction between surface complexes of as-received samples and solutions of phenol, TGA curves representing the percentage of weight loss versus temperature for the same sample both unloaded and loaded with phenol will be generally given in the same figure. The correct curve is theoretically the difference between these two curves.

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Table 1. Properties of as-received activated carbons

Carbon	Mesh Size	Ash % Dry	Surface area (m^2/g) N_2	CO_2
A	12x40	7.18	975	836
B	4x10	1.60	945	540
C	8x30	0.70	835	566
D	40x70	< 50 ppm	≈ 970	1050

3. RESULTS

3.1 *Factors affecting thermal regeneration of activated carbons loaded with phenol*

On a sample of activated carbon A, we carried out our experiment of phenol adsorption and thermodesorption according to the process described above. We obtained the TGA curve 1 of Fig. 1. On this curve it can be seen that the weight loss versus temperature presents four shoulders. The foot of the first shoulder begins at 383 K, the temperature at which this sample was dried. When the samples are dried at room temperature, this foot begins to appear at about 353 K, which means that a small quantity of adsorbed phenol is lost by heating at 383 K. The three other shoulders appear between 623 K and 1223 K. These must correspond to the desorption or the decomposition of phenol molecules adsorbed in different ways or on different types of sites.

The first shoulder seems to correspond to the desorption of phenol molecules physisorbed on the surface. As expected, the diminution of the temperature of adsorption increases the magnitude of the first shoulder. Two samples of activated carbon A, pretreated at 1223 K in Ar in order to increase the total quantity of adsorbed phenol [5], were placed in contact with the usual phenol solution for 24 h at two different temperatures, 298 K and 285 K. One portion of these two samples was immediately dried at room temperature in N_2 until reaching a constant weight. It had been determined previously that all the water physisorbed on the surface was removed by such a treatment. Then, a thermodesorption was performed on this portion, giving the TGA curves 1 and 2 of Fig. 2. The shoulder of the curve corresponding to the adsorption temperature of 285 K is higher than the shoulder corresponding to the adsorption temperature of 298 K. As the surface areas, the solutions used, and the duration of contact of the samples with these solutions were the same, this difference can be explained by the nature of adsorption which could be a physisorption.

This hypothesis is confirmed by the fact that many current solvents of phenol can desorb the phenol corresponding to this first part of the TGA curves almost completely, the remaining part being unchanged. Samples of activated carbons loaded with phenol using the

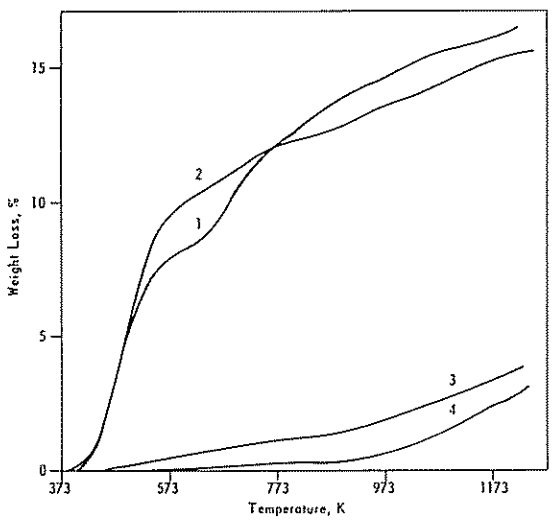

Fig. 1. 1: TGA curve for as-received activated carbon A placed in contact with 2000 ppm phenol solution for 24 h and dried at 383 K. 2: TGA curve for as-received activated carbon C, placed in contact with 2000 ppm phenol solution for 24 h and dried at 383 K. 3: TGA curve for as-received activated carbon A. 4: TGA curve for as-received activated carbon C.

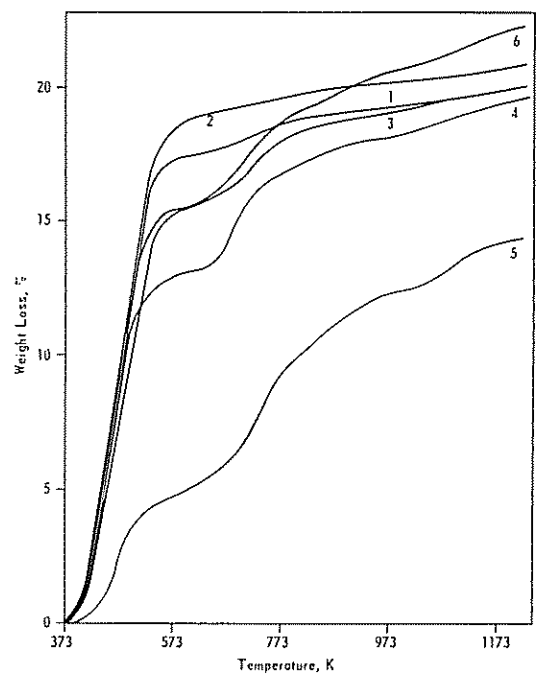

Fig. 2. 1: TGA curve for activated carbon A heat-treated at 1223 K in Ar, in contact with 2000 ppm phenol solution for 24 h at 298 K and immediately dried at room temperature. 2: The same as 1 but in contact with phenol solution at 285 K. 3: The same as 1 but dried 6 h after the end of the adsorption experiment. 4: The same as 1 but dried 24 h. 5: The same as 2 but dried at 383 K. 6: The same as 1 but in contact with the phenol solution for 48 h.

usual conditions and dried at 383 K were then washed with different solvents at their boiling temperature for 15 h. Programmed thermodesorptions were performed on samples not treated and treated by solvents. Absolute ethanol, absolute methanol, ether, acetone, benzene and water were used. Except for the sample treated with water, all the TGA curves corresponding to samples treated with solvents do not have the first shoulder. Only the results obtained with absolute alcohol (Fig. 3, curve 2) and with acetone (Fig. 4, curve 2) are presented here. The experiments with absolute alcohol were carried out with activated carbon A heat-treated at 1223 K in Ar. The experiments with acetone were carried out with as-received activated carbon A. Curves 3 (Figs. 3 and 4) represent the TGA curves corresponding to samples not placed in contact with phenol before the treatment with a solvent. Comparison of curves 3 and curves 4, corresponding to samples not loaded with solvent, shows that these two solvents are slightly adsorbed on activated carbons. This phenomenon also exists with the other solvents and is particularly marked with ether and benzene.

The fact that the phenol solvents can remove the phenol responsible for the first shoulder of the TGA curves 1 can be explained by the nature of bonding existing between phenol and activated carbons. This bonding must be weak and of the type characterizing physisorption.

The three other shoulders (curve 1, Fig. 1) seem to correspond to the decomposition of phenol molecules chemisorbed on the surface of activated carbons. We have already noted that these three shoulders remain unchanged by treating the polluted samples of activated carbons with solvents (curves 2, Figs. 3 and 4). In addition, when samples loaded with phenol are heat-treated up to 1223 K, they do not return to their initial weight; there is a weight increase. On a sample of activated carbon A pretreated up to 1223 K in N_2, we successively carried out several times the different operations described in the experimental section: adsorption of phenol at 298 K, measurement of the phenol up-take by spectrophotometry, drying at 383 K, programmed thermodesorption up to 1223 K and weighing. The results are given in Table 2. After each run the final weight increases. This increase cannot be due to phenol molecules remaining on the surface, for at 1223 K these molecules are decomposed; thus, it is certainly due to carbon atoms coming from this decomposition. This means that phenol molecules had to be strongly bonded to the surface, certainly with a bonding of the chemisorption type.

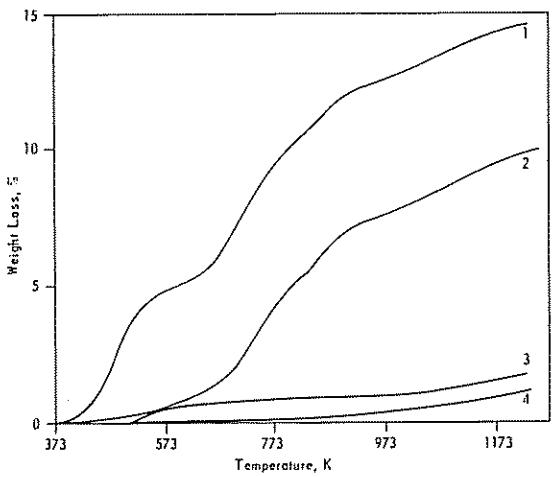

Fig. 3. 1: TGA curve for activated carbon A heat-treated at 1223 K in Ar, placed in contact with 2000 ppm phenol solution for 24 h, dried at 383 K. 2: The same as 1, but washed with boiling absolute ethanol for 15 h after drying at 383 K. 3: TGA curve for activated carbon A heat-treated at 1223 K in Ar and washed with absolute ethanol. 4: TGA curve for activated carbon A heat-treated at 1223 K.

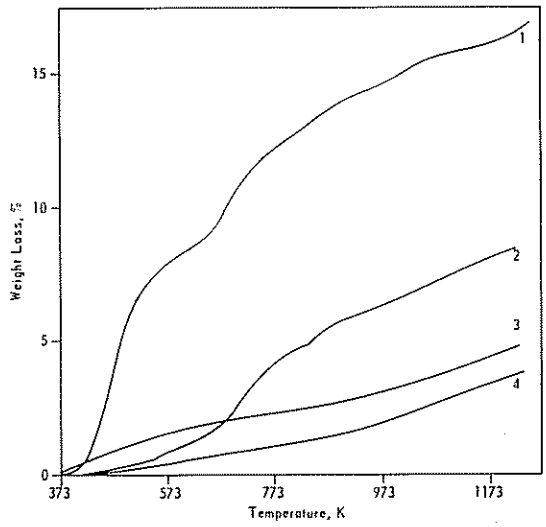

Fig. 4. 1: TGA curve for as-received activated carbon A, placed in contact with 2000 ppm phenol solution for 24 h, dried at 383 K. 2: The same as 1, but washed with boiling acetone for 15 h after drying at 383 K. 3: TGA curve for as-received activated carbon A, washed in acetone. 4: TGA curve for as-received activated carbon A.

This weight increase is accompanied by a decrease in subsequent phenol uptake. The decrease of phenol uptake could be explained either by a change in the nature of the surface or by a diminution of the surface area. But a TGA curve carried out on the sample after the last run (curve 5, Fig. 5) presents nearly the same general shape as the corresponding curve for our initial sample (curve 1, Fig. 5). This suggests that the nature of the surface is not changed by cycling, at least not the part of the surface within reach of phenol molecules.

On this sample and after the third run,† N_2 and CO_2 surface areas were determined from their adsorption isotherms measured at 77 K and 298 K, respectively. The results were 376 m^2/g with N_2 and 524 m^2/g with CO_2; the corresponding values for the initial sample being 975 m^2/g and 836 m^2/g. Not only did the surface areas decrease following cycling, but also the N_2 surface is lower than the CO_2 surface area following cycling. Before cycling the as-received carbon had a higher N_2 surface area. This means that the smallest pores have been closed, which explains the general diminution of surface area.

†All these experiments were done simultaneously on two identical samples.

Table 2. Cyclical adsorption of phenol on carbon A followed by regeneration

Initial Weight mg	Phenol up-take mg of Phenol/100 mg of carbon	Final Weight mg
100.0	25.2	103.6
103.6	22.1	112.0
112.0	20.0	118.5
118.5	18.2	-

Furthermore, some of the other pores now have their apertures diminished so that N_2 can no longer enter because of the low adsorption temperature. However, CO_2 can enter the corresponding pores because of the higher adsorption temperature and smaller minimum dimension of CO_2. The quantities of phenol adsorbed always remained nearly proportional to the CO_2 surface areas.

To summarize, we can say that the phenol responsible for the last three shoulders of the curve 1 (Fig. 1) seems to be chemisorbed. This phenol instead of being evolved by increasing the temperature is decomposed on the surface, closing some pores and diminishing the apertures of others with carbon atoms, the product of this decomposition. Thus the total surface area and, therefore, the surface area accessible to phenol decreases.†

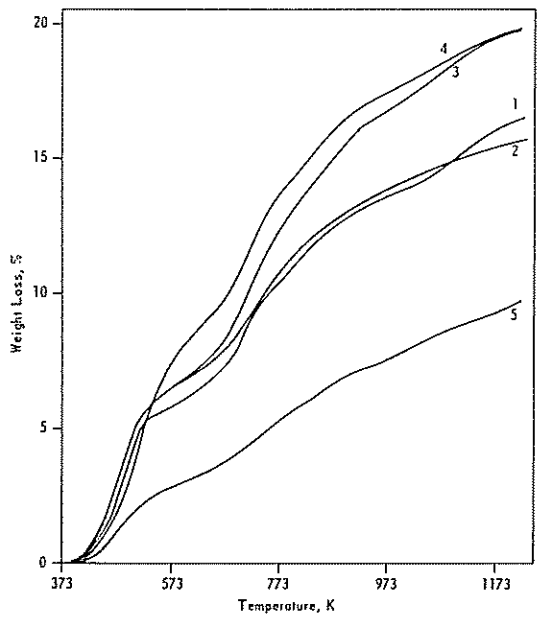

Fig. 5. 1: TGA curve for activated carbon A heat-treated in N_2 at 1223 K, placed in contact with 2000 ppm phenol solution for 24 h, dried at 383 K. 2: The same for activated carbon C. 3: The same for activated carbon B. 4: The same for activated carbon D. 5: TGA curve for activated carbon B heat-treated in N_2 and three times subjected to adsorption of phenol and heat-treatment at 1223 K in N_2, subjected to adsorption of phenol and dried at 383 K.

†If the method used to regenerate is not strong enough to decompose the chemisorbed phenol, then the decrease of surface area and of phenol capacity must be greater due to the larger size of the phenol molecule.

These phenomena can certainly explain the difficulty in regenerating activated carbons used to purify drinking water polluted with phenol. They must be avoided as far as possible; and in order to find out some ways of avoiding them, phenol chemisorption was particularly studied. As-received activated carbon A was heated in N_2 up to 1223 K and subjected to the usual adsorption operations. This sample was then divided in four parts. The first part was dried at room temperature until reaching a constant weight and then a thermodesorption was carried out giving the TGA curve 1 (Fig. 2). After 6 h the same experiment was carried out on the second part of the sample, this second part having been left at room temperature in air. The result is the TGA curve 3 (Fig. 2). After 24 h, once again the same experiment on the third part gives the curve 4 (Fig. 2). Comparing the curves 1, 3 and 4 (Fig. 2), we can see that the total weight loss is nearly the same within the precision limits for the three experiments. But the distribution of phenol between the four "types of sites" has changed: comparing curves 3 and 4 with curve 1 (Fig. 2) we can see that some phenol fixed at first, on the first "type of sites" (first shoulder) is now fixed on the other "types of sites" (last part of the curves). This is to say some phenol which was physisorbed is now chemisorbed.

The fourth part of the sample was then dried at 383 K. Curve 5 (Fig. 2) is the corresponding TGA curve. The right-hand part of the curve (the last 3 shoulders) has definitely changed. Because of the higher drying temperature, 383 K, a large part of the physisorbed phenol has become chemisorbed. The total weight loss has been reduced over that found for runs 1, 3 and 4 since significant physisorbed phenol has also been desorbed at 383 K, prior to commencing the TGA run.

On the same initial sample of carbon A, adsorption of phenol was performed for 48 h instead of 24 h, in order to see whether the same increase of chemisorption to the detriment of physisorption also occurs in aqueous solution. The TGA curve obtained, curve 6 (Fig. 2) is very similar to curve 4, with, of course, an increase of total weight loss due to an increase in total phenol uptake caused by a difference in duration of adsorption. These results show that, as expected for chemisorption, the quantity of phenol taken up increases slowly with the time of contact of the phenol solution with the adsorbent. Comparing curves 1 and 2 (Fig. 2), presented to study the physisorption of phenol, we can also see that the part corresponding to chemisorption is more developed for curve 1 obtained after adsorption at 298 K than for curve 2 obtained after adsorption at 285 K; that is, chemisorp-

tion increases with adsorption temperature. However, it is noteworthy to find that when the sample is no longer in contact with the phenol solution, some of the phenol physisorbed can become chemisorbed. This transformation increases with both increasing time and temperature.

3.2 *Sites for phenol chemisorption on activated carbon*

Considering the fact that physisorbed phenol can become chemisorbed in the course of time or by increasing the temperature, it is possible that physisorption and chemisorption occur on the same types of sites—those sites which represent nearly all the surface area, since for our experiments the surface coverage is about 90% to 100%. But comparing the TGA curve corresponding to an as-received sample (curve 1, Fig. 1) with the one corresponding to a sample of the same activated carbon heated up to 1223 K (curve 5, Fig. 2), we can see that, in spite of very little change in the surface area, chemisorption is higher for the latter sample. We therefore conclude that chemisorption occurs on particular sites which are modified by heating at 1223 K.

Three possible types of sites can be distinguished on activated carbon, to a first approximation: sites constituted by impurities, sites constituted by carbon atoms of the basal planes of graphite-like microcrystallites, and sites constituted by carbon atoms of the edges at the basal planes, also called active surface area, ASA. The hypothesis of chemisorption on impurities can be supported by the difference observed in the TGA curves obtained with activated carbon A (curve 1, Fig. 1) and activated carbon C (curve 2, Fig. 1). Carbon A is more impure (7.1% ash) than C (0.70% ash) and also has a TGA curve which presents the most developed part corresponding to chemisorption.

To try to establish the validity of this hypothesis, four samples different in origin and particularly in purity (see Table 1) were heated to 1223 K and subjected to the usual adsorption and thermodesorption operations after drying at 383 K. The general shape of the corresponding TGA curves (curves 1–4, Fig. 5) is nearly the same; therefore chemisorption does not take place primarily on impurity sites. Furthermore, the shoulders always appear at the same temperatures for the four samples, in spite of widely different origin and porosity. This shows that the shoulders manifest a desorption or decomposition effect and not a secondary effect such as, for example, phenol diffusion through the porosity.

Among the other two possible types of sites, the ASA is the most likely to chemisorb organic molecules. Thus, occupying this surface by oxygen, for example, before exposure to phenol should be a means of determining its possible role in the chemisorption of phenol. Three samples of each of the activated carbons A, C and D were chosen for the study. The first samples were heated from room temperature to 1223 K in N_2 and subjected to the usual operations of phenol adsorption and thermodesorption (TGA curves 1, 1′ and 1″, Fig. 6). The second samples were heated to 1223 K in N_2, heated at 573 K in 0.1 MPa O_2 for 15 h, and subjected to the usual operations of phenol adsorption and thermodesorption (TGA curves, 2, 2′, and 2″, Fig. 6). The third samples were heated from room temperature to 1223 K in N_2, heated at 573 K in 0.1 MPa O_2 for 15 h, and subjected only to the operation of thermodesorption (TGA curves, 3, 3′, and 3″, Fig. 6).

Comparing curves 2 with curves 3, we can see that the high temperature parts are very similar: they bend upwards. This is due to the outgassing of oxygen surface complexes. In fact the weight loss corresponding to the curves 2 is less than the weight loss corresponding to the curves 3 for the highest temperatures. The difference between the two types of curves gives curves looking like curve 4 (Fig. 6) which bends downward; but this unexpected behavior must be a secondary phenomenon due to interaction between phenol or water with oxygen surface complexes.

If we compare curves 2 with curves 1, we can ascertain that, although the two types of samples were heated at 383 K after adsorption, the part of the curves corresponding to physisorbed phenol is more developed for curves 2 than for curves 1. But, on the other hand, the parts of the curves corresponding to chemisorbed phenol are much more developed for curves 1 than for curves 2. This means that the phenol physisorbed on oxidized samples is not converted from the physisorbed state to a chemisorbed state at 383 K, presumably because of the presence

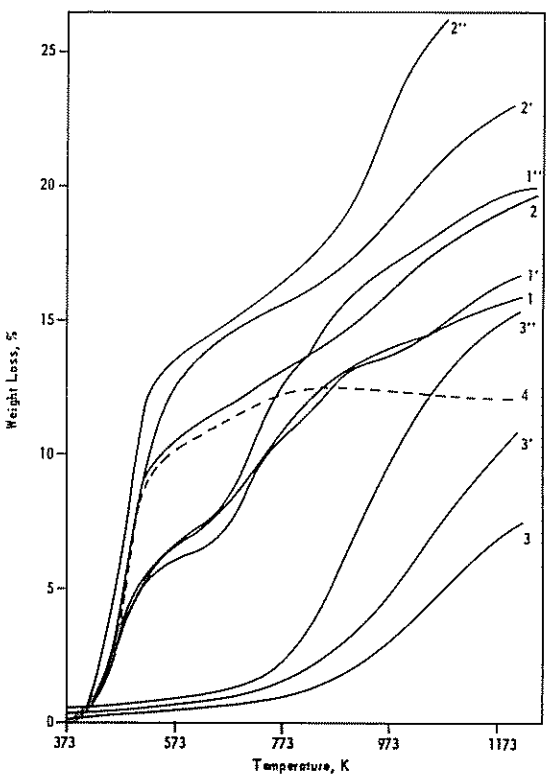

Fig. 6. 1, 1′ and 1″: TGA curves for activated carbons A, C and D, heat-treated in N_2 at 1223 K, in contact with 2,000 ppm phenol solution for 24 h, dried at 383 K. 2, 2′ and 2″: The same as 1 but on samples oxidized in O_2 for 15 h at 573 K after heat treatment in N_2. 3, 3′ and 3″: The same as for curves 2 but samples not in contact with phenol solution. 4: Difference between curves 2 and 3.

of oxygen on the sites on which phenol usually chemisorbed.

Therefore, since chemisorption of phenol takes place on each activated carbon regardless of purity and is inhibited by the presence of oxygen surface complexes, it is concluded that the sites responsible for phenol chemisorption are carbon sites of the active surface area.

In conclusion, it appears that two types of phenol adsorption are possible on activated carbons. The first type seems to be physisorption which occurs on all the surface. The phenol adsorbed in this way is removed by most of the solvents for phenol. The second type of adsorption is chemisorption, which occurs on the ASA. The phenol adsorbed in this way cannot be removed by solvents. By increasing the temperature, chemisorbed phenol is expected to decompose, leaving carbon atoms on the surface. This process must be responsible for the decreasing uptake of phenol on activated carbons after use. In the course of time and by increasing temperature, a part of the physisorbed phenol becomes chemisorbed. Mild oxidation of activated carbons by oxygen at 573 K reduces the chemisorption of phenol.

3.3 *An approach to make activated carbons more easily regenerable*

The above fundamental study allows us to foresee that to be able to regenerate activated carbons polluted with phenol chemisorption of phenol must be avoided as far as possible by fulfilling the following conditions.

—Mild oxidation of activated carbons by oxygen.
—Time reduced between the first contact of activated carbon with phenol and the process of regeneration.
—Temperature of activated carbon preferably low during its contact with phenol.

These conditions being met the best way to regenerate seems to be the utilization of a solvent of phenol. Four different samples were chosen for this study: Activated carbons A and C heated to 1223 K in N_2 and activated carbons A and C heated to 1223 K in N_2 and oxidized at 573 K in O_2 for 15 h. These samples were called respectively A^1, C^1, A^2 and C^2. The solvent used was absolute ethanol. The operational conditions were changed several times. The results are given in Table 3. These data show that:

(i) The phenol adsorption capacity of the samples degassed up to 1223 K decreases significantly with cycling, as expected, this decrease being due to chemisorbed phenol which is not removed (samples A^1 and C^1).
(ii) Decreasing the temperature of adsorption increases the uptake of phenol. This increase is due to an increase of physisorbed phenol.

Table 3. Cyclical studies on selected activated carbons

Sample	Initial Weight mg	Adsorption Temperature K	Up-take of Phenol mg/100 mg C	Solvent (see note)	Weight After 2 h at 383 K in air	Weight After 5 min at 573 K in O_2
A^1	50.0	293	25.2	(1)	52.0	51.5
	51.5	285	25.2	(1)	53.5	53.5
	53.5	293	21.9	(2)	-	-
	-	293	19.4	(3)	54.0	54.0
C^1	50.0	293	21.9	(1)	51.5	51.5
	51.5	285	19.7	(1)	53.0	52.8
	52.8	293	16.5	(2)	-	-
	-	293	15.2	(3)	53.5	53.5
A^2	50.0	293	22.6	(1)	49.5	49.0
	49.0	285	24.2	(1)	49.5	-
	49.5	293	22.3	(2)	-	-
	-	293	20.6	(3)	50.5	50.2
	50.2	293	22.3	(4)	52.5	52.5
C^2	50.0	293	20.0	(1)	50.0	50.0
	50.0	285	21.6	(1)	50.5	-
	50.5	293	20.6	(2)	-	-
	-	293	19.0	(3)	51.0	51.0
	51.0	293	20.3	(4)	54.0	54.0

(1) Absolute ethanol at 293K.
(2) Absolute ethanol at 293 K but sample not dried before reuse.
(3) Absolute ethanol already used once.
(4) Absolute ethanol containing an amount of phenol corresponding to 100 regenerations using the here described conditions.

(iii) If ethanol on the sample after regeneration is not removed by drying, the subsequent phenol capacity of the sample decreases. That is to say, although water is very miscible with alcohol, ethanol seems to be too strongly adsorbed on activated carbon to be removed by the water of the aqueous solution of phenol.

(iv) But if ethanol is removed by drying in the following run, the sample returns to its initial capacity.

(v) Heating the sample to 383 K seems to be sufficient to remove adsorbed ethanol from the surface of activated carbons.

(vi) Regeneration obtained by alcohol used once, seems to be complete, in spite of a slight increase of the final weight.

(vii) Regeneration obtained by alcohol used 100 times is not complete.

(viii) Chemisorption of oxygen on activated carbons at 573 K prior to phenol adsorption reduces the initial capacity of the carbon for phenol but makes it more regenerable. The result is that after several cycles the oxidized carbon has a greater capacity for phenol.

In spite of the good regeneration obtained by absolute ethanol, when all the conditions described above are satisfied, it is possible that after much use, activated carbons lose their phenol adsorption capacity, due to the presence of chemisorbed phenol. They then need to be regenerated in another way. A 50 mg sample of the A^2 type (heated at 1223 K in N_2 and oxidized at 573 K in O_2) was placed in contact with phenol solutions and regenerated by heating at 623 K in O_2 for 5 min, three times, thus allowing some physisorbed phenol to be chemisorbed. This temperature was also chosen because it corresponds to the end of the first shoulder of the TGA curves where all the physisorbed phenol must be removed but where the chemisorbed phenol is not yet decomposed. When the phenol uptake had decreased to 13 mg/100 mg of initial activated carbon and the weight has increased to 56 mg, we tried to regenerate the sample by heating it in O_2 at 573 K until reaching nearly the initial weight, 49.8 mg. It seems that by such treatment the chemisorbed phenol molecules are burnt preferably with respect to the C atoms of the activated carbons, the new phenol uptake was 19.0 mg/100 mg of activated carbon. Two other adsorption experiments followed by the same regeneration on this sample give successively an uptake of 18.4 mg and 16.8 mg. Thus we can see that heating activated carbons, partially deactivated by chemisorbed phenol, in O_2 at 573 K until reaching the initial weight does not give a complete regeneration but allows these carbons to be reused.

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