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INTERACTION OF MONOCHLORINATED PHENOLS WITH GRANULAR ACTIVATED CARBON

G. Baldassarre

ISTITUTO DI CHIMICA APPLICATA, FACOLTÀ D'INGEGNERIA
DELL'UNIVERSITÀ, 200 VIA RE DAVID, 70125 BARI, ITALY

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The validity of an empirical model to estimate the adsorption affinity of a solute from its acidity constant (*p*Ka) was confirmed through study of the adsorption of monochlorinated phenols on granular activated carbon.

Neglecting possible adsorbate fragmentation, simplified desorption kinetic data were obtained for the massive thermal release of the investigated solutes. The resulting non-isothermal kinetic parameters confirm that thermal cleaning of the adsorbent surface is a phase-boundary controlled process involving the interruption of physical interactions according to the calculated "activation energy" values.

Adsorption on porous solids is often involved in the practical utilization of various materials.

During water and waste-water treatment, for example, the removal of certain organic pollutants is frequently accomplished through adsorption on granular activated carbon (GAC).

As concerns this subject, previous studies on batch adsorption, thermal desorption and GAC surface area measurements with selected industrial pollutants led to the inference that thermodesorption could occur under milder regeneration conditions than usually adopted (e.g. 400–500° vs. 900–1000°) [1].

Furthermore, the possibility of correlating the GAC adsorption affinity to the adsorbate acidity was envisaged [2].

This paper presents the results of further investigations on the adsorption-desorption interactions between GAC and monochlorinated phenols.

The latter are representative of by-products formed during water disinfection and are of concern for the possible contamination of aquifers and ground waters [3].

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Experimental

The solute partition was tested by adding variable amounts (5–180 mg) of dry GAC (Filtrasorb 400, Calgon Corp., Pittsburg, Pa.) to 50 ml of aqueous reagent grade *p*- and *m*-monochlorinated phenol solutions.

The initial concentrations, measured with a double beam Model 1750 spectrophotometer (Pye Unicam Ltd., Cambridge, Gt. Britain) at 276 and 264 nm, were 530 and 590 ppm for the para and the meta isomer, respectively.

All samples were shaken vigorously for 24 h at 25±1°.

About 100 mg of dry GAC, equilibrated with 100 ml of the above solutions was submitted to thermal analysis to obtain more pronounced thermal curves. Thermal measurements up to 900° were carried out at a heating rate of 10 deg/min in a dynamic N_2 atmosphere (5 l/h), using a TA1 thermoanalyzer (Mettler AG, Zürich, Switzerland).

Cylindrical Pt crucibles and Pt–Pt/Rh thermocouples were employed. The DTG and DTA sensitivities were 5 mg/min and 100 μV/s, respectively. Multiheated GAC grains were utilized as reference substance. All calculations were performed with an HP-85 personal computer.

Results and discussion

Figure 1 shows the relative solute build-up of *m*-chlorophenol (MCP) and *p*-chlorophenol (PCP), expressed as percentage removal from solution, vs. GAC dosage. Almost complete solute removal (~98%) is obtained for both solutes at a GAC dosage around 160 mg/50 ml. However, in spite of the slightly higher (10%) initial MCP concentration, its adsorption always occurs to a lower extent.

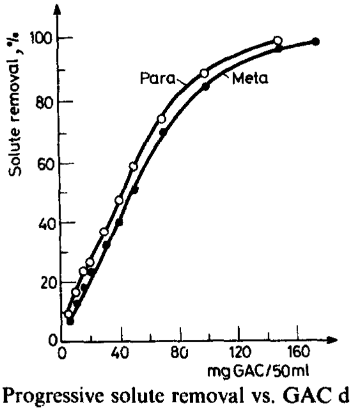

Fig. 1 Progressive solute removal vs. GAC dosage

The corresponding adsorption isotherms are reported in Fig. 2, where the reduced equilibrium concentrations ($C_{red} = C_{eq}$/solubility) are also introduced to account for different solvent affinities (S = 0.202 and 0.211 mol/l for MCP and PCP, respectively).

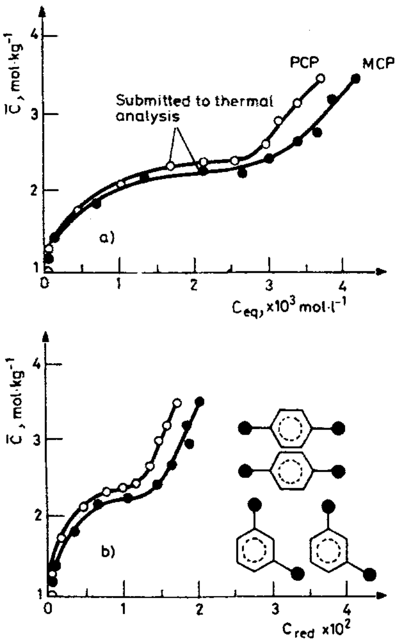

Fig. 2 Experimental adsorption isotherms (2a) and dependence on solute's solubility (2b)

Besides the initial slopes and the monolayer plateaux, a "second rise" clearly appears in the concentration range investigated.

When the isotherm slopes $\alpha(= \bar{C}/C_{eq})$ are plotted vs. C_{red} coincident straight lines appear in Fig. 3 for the investigated chloroisomers.

In the same Figure, the corresponding correlations previously obtained for phenol and its mononitro derivatives [2] are also reported (dotted lines), so that the influence of the chemical structure on the adsorption affinity is clearly evidenced by the displacement of the straight lines obtained.

In accord with their molecular electron mobilities, which play an important part in adsorption interactions, the chloro derivative traces lie between those of phenol and its more polar nitro derivatives.

From the essential parallelism of these graphical correlations, the empirical equation already proposed [2]:

$$\log \alpha = A p\mathrm{Ka} + B \qquad (1)$$

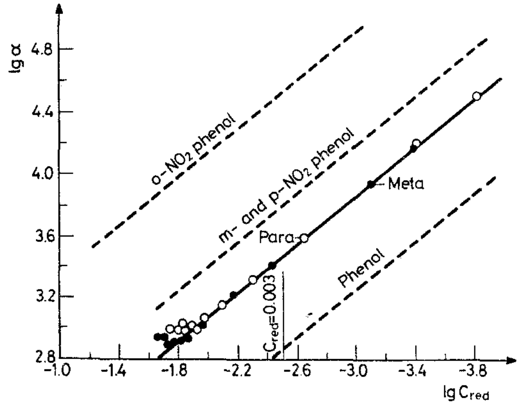

Fig. 3 Isotherm slopes $\alpha(=\bar{C}/C_{eq})$ vs. the corresponding C_{red}

was tested to examine the dependence of the solute adsorption affinity on the acidity constant (pKa), a parameter influenced by the aromatic-ring substitution.

From Fig. 3, at $C_{red} = 0.003$ a value of $\alpha = 10^{3.5}$ is obtained for both the investigated chloro derivatives.

Such a value is in good agreement with the linear correlation reported in Fig. 4, previously obtained for nitro derivatives of phenol [2].

Thus, the adsorption performance of all the phenolic derivatives investigated can be derived from that of nonsubstituted phenol, so that the earlier given physical meaning of "reference substrate" can be confirmed for the parameter B. On the other hand, considering that a coincident slope occurs with or without the chloro derivative data, the physical meaning of the "substituent parameter", A, should be related to the electronic character of the substituent rather than to its proper atomic

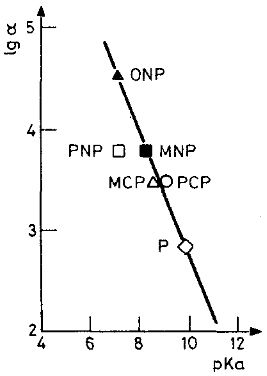

Fig. 4 Isotherm slopes α vs. pKa for a fixed C_{red} value

constitution, as previously hypothesized (2). Nitro and chloro groups share their electron-acceptor character in the phenol electron mobility.

From the partition diagrams reported in Fig. 2, useful information can also be drawn on the solute adsorption mechanism in the system examined. First, for both solutes the steep initial slope agrees with the almost complete adsorption determined experimentally, so that "high-affinity" adsorptive interactions must be assumed, following Giles' classification [4]. Furthermore, due to their bifunctional molecular structure (see Fig. 2b), a double localization of attractive forces should be attributed to the investigated solutes.

Due to the large available GAC surface allowed by the high initial GAC dosage (see the lower left area of Fig. 2), a flat adsorption of bifunctional molecules occurs until monolayer surface coverage is attained. Accordingly, the initial surface coverage rate is very high.

On the other hand, the experimental delay for the "second rise" of the meta isomer should be related to its lower adsorption affinity.

Both the irregular steric configuration and the lower electron mobility could prevent the MCP coverage regularity. As a consequence, a lower availability of still uncovered GAC surface, as well as an unfavourable ability of the already adsorbed molecules to establish adsorption forces per se, result at low GAC dosage, i.e. when a small, partly covered surface, is required to undergo additional adsorption.

The above adsorption mechanism is also evidenced by thermogravimetric investigation.

The experimenal thermodesorption patterns obtained when comparable solute amounts (~30 mg) were adsorbed to monolayer completion are reproduced in Fig. 5.

Starting from 150°, i.e. after the removal of not adsorbed liquid phase, the TG mass balances indicate adsorbed amounts almost coincident (~95%) with those determined spectrophotometrically.

Accordingly, irrespective of the probable adsorbate thermal fragmentation, about 75% of the desorption corresponds to the single DTG effect (145–470°) registered for MCP. In contrast, a smaller DTG effect (145–440°) is obtained for the less massive PCP release (50% of the adsorbed amount), together with an additional one (15% of the desorption) at higher temperature (440–680°).

Thus, at least two different energetic interactions are involved during the adsorption of this solute. A deeper penetration or a closer molecular package, which leaves more room for further adsorption, as well as stronger adsorptive interactions, must be assumed for PCP. This agrees with the two DTG effects and the higher final weight gain (~7 mg) registered for PCP thermal desorption.

In the case of the meta isomer, in contrast, the monolayer is probably due to the

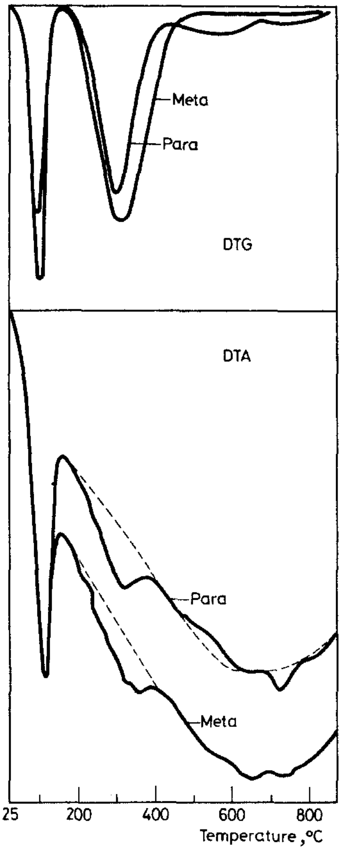

Fig. 5 Thermodesorption patterns of the investigated adsorbates

random location of the molecules, which are also less strongly adsorbed according to the larger low-temperature release associated with the unique DTG effect.

These considerations confirm the qualitative correlation between the thermodesorption effects and the adsorption mechanism examined in previous investigations [5], according to Dondur et al. [6].

From Fig. 5, a more pronounced baseline drift also appears for the DTA curves, due to the particulate samples and the high heating rate. In spite of this, besides the evaporative low-temperature effects ($T < 150^\circ$), others result which can be related to the desorption process.

First, an endothermic effect is always registered, due to the expected energetic consumption involved in solute release, thus confirming previous conclusions on exothermic release associated with the explosive character of the NO_2 group [2].

Nevertheless, it must also be noted that, from the comparable DTA peak areas corresponding to the different massive solute desorptions, a lower energetic consumption is needed to resolve the MCP adsorption interactions.

Finally, only for the PCP release, two other DTA effects appear at higher temperature on opposite sides of the baseline.

The destructive transformation of deeply entrapped solute molecules, whose by-products could result in the corresponding DTG effect, can be related to the exothermicity of the former; on the other hand, the release of the entrapped pyrolitic fragments could correspond to scarcely detectable endothermic effect of the latter.

As far as the quantitative characterization of the massive adsorbate release is concerned, kinetic computations previously performed according to the non-isothermal thermogravimetric procedure [7] indicate that $f(\alpha) = (1-\alpha)^n$ is the function of the conversion degree which best fits our TG and DTG experimental data.

According to Šesták, this function has physical significance for surface-controlled reactions [8].

Kinetic parameters obtained for PCP and MCP massive thermodesorption, using the above form of $f(\alpha)$ to solve the kinetic equation

$$d\alpha/dT = A/ae^{-E/RT}f(\alpha) \tag{2}$$

according to the Chen [9] and Zsakó [10] procedure, are listed in Table 1. The pre-exponential factors, A, obtained for both investigated samples agree well with that expected for the activated decomposition of a reactant which is in equilibrium with an adsorbed molecular layer in the bulk of the solid phase [11].

Table 1 Kinetic parameters obtained for $f(\alpha) = (1-\alpha)^n$

Adsorbate	Chen method			Zsakó method		
	$\log A$	E	n	$\log A$	E	n
Metaisomer	5	11.3	0.97	5	13	1.4
Paraisomer	6	14.3	1.0	6	14	1.2

As concerns the so-called activation energies, E, of the investigated solutes, comparable values are obtained. Although these differ from the quantities usually encountered in kinetic measurements, they could be used to confirm the easier meta isomer thermodesorption.

Finally, for the reaction order, n, figures close to unity are obtained by the Chen computation procedure, which indicates that the process occurring in the solid phase is controlled by the phase-boundary advance in the whole bulk of the sample, without the influence of the crucible employed [8]. For this parameter, higher values are obtained with Zsakó's procedure. The latter, however, derives the reaction order from the final shape of the TG curve, which is difficult to determine without well-defined thermogravimetric plateaux.

Conclusions

From the behaviour of the measured adsorption isotherms of para- and meta-chlorophenols on Filtrasorb 400 granular activated carbon, a high adsorption affinity results for both investigated solutes.

Nevertheless, from the higher massive thermal release, a weaker adsorption must be presumed for the meta isomer according to its steric and electronic features and the DTA results.

The experimentally determined partition coefficients satisfactorily fit the empirical equation previously developed to calculate the adsorption affinity of a given solute from its acidity character.

Finally, kinetic calculations confirm that the massive thermodesorption is a phase-boundary controlled process for both compounds.

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Zusammenfassung — Die Gültigkeit eines empirischen Modells zur Abschätzung der Adsorptionsaffinität eines gelösten Stoffes auf Grund der Aciditätskonstante (*p*Ka) wurde durch Untersuchung der Adsorption von monochlorierten Phenolen an granulierter Aktivkohle bestätigt. Unter Vernachlässigung einer möglichen Adsorbatfragmentierung wurden vereinfachte kinetische

Daten für die thermische Desorption der untersuchten gelösten Stoffe erhalten. Die erhaltenen, nichtisothermen kinetischen Parameter zeigen, daß die thermische Säuberung der Adsorbentoberfläche ein phasengrenzflächenkontrollierter Prozeß ist, bei dem physikalische Wechselwirkungen entsprechend den berechneten Werten der „Aktivierungsenergie“ aufgehoben werden.

Резюме — На основе изучения адсорбции монохлорфенола на гранулированном активированном угле была подтверждена справедливость эмпирической модели для установления адсорбционной способности растворенного вещества, исходя из его константы кислотности pK_a. Пренебрегая возможной фрагментацией адсорбата, получены упрощенные кинетические данные процесса полного термического освобождения исследованных растворенных веществ. Конечные неизотермические кинетические параметры подтверждают, что термическое осветление поверхности адсорбента определяется стадией фазового разрыва, включающей, согласно вычисленным значениям «энергии активации», разрыв физических взаимодействий.