Adsorption of Chlorinated Phenolic Derivates from Wastewater using Active Carbon

DANIELA SIMINA STEFAN[1], IRINA PINCOVSCHI[2]*

[1] Politehnica University of Bucharest Department of Analytical Chemistry and Environmental Engineering, Faculty of Applied Chemistry and Materials Science, 1-7 Polizu Str., 011061, Bucharest, Romania

[2] Politehnica University of Bucharest Department of Hydraulics, Hydraulic Machinery and Environmental Engineering, 313 Splaiul Independentei, 060042, Bucharest, Romania

The adsorption of phenol and its chlorinated derivates on active carbon has been studied considering both the characteristics of aqueous solutions of phenol at different pH values and the surface proprieties of carbon. Knowing the pH influence on protolithic equilibrium of phenolic compounds, the experimental isotherms have been fitted via Langmuir adsorption model. The effect of pH on the adsorption equilibrium has been considered due to its combined effects on the carbon surface and on the solute molecules

Keywords: adsorption, activated carbon, phenol derivates

The phenolic compounds are common water contaminants due to their widespread use in various manufacturing industries. Increasing environmental awareness in the recent times has lead to more stringent limits on the quality of water. An abundance of experimental adsorption studies on active carbon has been made in order to establish the appropriate conditions for phenolic derivatives elimination from waste water [1-20]. It has been established the physical nature of the adsorbent (pore structure, surface chemical structure, polarity) the nature of the adsorbate (surface chemical structure, polarity, *pKa*) and the adsorption conditions (*pH*, ionic strength, adsorbate concentration, temperature) [10-12, 14-22].

Active carbons are carbonaceous materials of highly developed porous structure and high specific surface area. Such proprieties made them versatile for a range of separation applications including the removal of contaminants from wastewaters [23-25].

A very important influence on adsorption efficiency has the carbon surface chemistry [1, 26, 27]. The most frequent functional groups on activated carbon surface are the phenol -hydroxyl, carboxyl, normal-lactone, anhydride and cyclic peroxide groups. Such functional groups, containing oxygen, induce on carbon surface a polar character, favouring the adsorption of polar compounds (especially organic ones). The presence of acid and basic oxides on carbon surface enhances, respectively, the negative and positive surface potential [28]. The complex carbon surface chemistry explain, also, the influence of external solution *p*H on carbon adsorption activity. Some spectrophotometric analysis put in evidence the *p*H influence on protolithic equilibrium of phenolic compounds: increasing the *p*H value till 12, the equilibrium can be practically displaced to phenolic anion form. On the contrary, at scarce *p*H values, the molecular form of phenols is quite dominating [8]. In such circumstances the presence of both molecular and ionic species must be taken into account [8, 10, 29, 30].

Theoretical approach

The phenolic compounds in aqueous medium can be considered as dissociating ones. The ratio of ionic to molecular species changes depending on the *pKa* of the solute and *pH* of the aqueous solutions. Considering the equilibrium:

$$HA \leftrightarrow H^+ + A^-$$

where HA refers to the molecular species and A^- refers to the ionized ones, one can define the equilibrium relationship:

$$Ka = \frac{[H^+][A^-]}{[HA]} = \frac{[H^+]C_i}{C_m} \quad (1)$$

where *Ka* represents the acidic constant, C_i and C_m the equilibrium concentration of ionic and molecular species, respectively.

Taking the negative logarithm of relation(1) one obtains:

$$-logKa=-log[H^+] -log\ C_i +log\ C_m$$

equivalent to the expresion:

$$pKa=pH -log\frac{C_i}{C_m} \quad (2)$$

$$\text{At } pH = pKa,\ \log\frac{C_i}{C_m} = 0 \ \ i.e.\ \frac{C_i}{C_m} = 1$$

So, the dependence of C_i and C_m on the *pKa* of solute and *pH* of aqueous medium is evident.

In order to characterize the adsorption equilibrium, both ionic and molecular species would be considered and the binary Langmuir isotherm equations will be used [8, 30, 31].

$$\theta_i = \frac{b_i C_i}{1 + b_i C_i + b_m C_m} \quad (3)$$

$$\theta_m = \frac{b_m C_m}{1 + b_i C_i + b_m C_m} \quad (4)$$

where θ_i and θ_m represent the fractional coverage of ionic and molecular species, respectively, b_i and b_m equilibrium constants.

* *email address: irinapincovschi@gmail.com*

The total functional coverage $\theta = \theta_i + \theta_m$ could be presented as follows:

$$\theta = \frac{b_i C_i + b_m C_m}{1 + b_i C_i + b_m C_m} = \frac{q}{q_M} \quad (5)$$

where q represents the equilibrium concentration of solute in solid phase (adsorbent)

q_M-the maximum concentration of solute in solid phase (corresponding to the complete surface covering in monolayer)

Considering , concomitantly, the equations:

$$C_i + C_m = C \text{ and } \frac{C_i}{C_m} = \alpha \quad (6)$$

one obtains:

$$C_i = \frac{\alpha C}{1+\alpha} \text{ and } C_m = \frac{C}{1+\alpha} \quad (7)$$

where C represents the global equilibrium concentration of two species in liquid phase.

Combining the equations (5) and (7) the Langmuir binary isotherm in its linear form can be obtained:

$$\frac{C}{q} = \frac{1+\alpha}{(b_i \alpha + b_m) q_M} + \frac{C}{1+\alpha} \quad (8)$$

Representing the equation (8) in coordinates $\frac{C}{q} - C$ one obtains a straight line having as slope $1/q_M$

Let's consider a monosolute solution. In this case the Langmuir equation has the form:

$$\theta = \frac{bC}{1+bC} = \frac{q}{q_M} \quad (9)$$

where C represents the equilibrium concentration of solute in liquid phase, b-equilibrium constant.

Considering the linear form of the equation (9) one obtains:

$$\frac{C}{q} = \frac{1}{b q_M} + \frac{C}{q_M} \quad (10)$$

Comparing the equations (8) and (10) it results:

$$b = \frac{b_i \alpha + b_m}{1+\alpha} = \frac{b_i + \frac{b_m}{\alpha}}{1 + \frac{1}{\alpha}} \quad (11)$$

The equation (11) put into evidence the correlation between the monosolute and binary system, the last containing both ionized (i) and molecular (m) species, whose concentrations, at equilibrium, are C_i and C_m, respectively.

In accordance with the equation (6) and (11) considering $C_i = 0$ it results $\alpha = 0$ and $b = b_m$. Concomitantly the equation (4) becomes:

$$\theta_m = \frac{b_m C_m}{1 + b_m C_m} \quad (12)$$

This situation appears in acid solution when dominating is the molecular form of phenolic compounds. If $C_m = 0$ one obtain $\alpha = \infty$ and $b = b_i$. Similarly the equation (3) becomes:

$$\theta_i = \frac{b_i C_i}{1 + b_i C_i} \quad (13)$$

The situation corresponds to alkaline solutions when the solute is highly ionized. Considering $C_i = C_m$ it results $\alpha = 1$ and $b = \frac{b_i + b_m}{2}$. The system being a binary one (see eq, 8) one obtains:

$$\frac{C}{q} = \frac{2}{(b_i + b_m) q_M} + \frac{C}{q_M} \quad (14)$$

The last situation occurs when *pH=pKa* (see equation 2) [1-5]. One can conclude that the adsorption of phenolic compounds on active carbon highly depends on solution *pH.* This could be supplementary explained by hydrogen bindings between the hydroxyl groups of phenolic compounds and the functional groups on carbon surface, such as carboxylic ones [32-34].

A characteristic *pH* value is pH_{PZC} (point of zero charge) corresponding to the neutral carbon surface. So, the Langmuir model parameters, q_m, b_i, and b_m, strongly depend on the *p*H of the solution-solute-adsorbent system. This dependence will be evidenced using experimental data.

Experimental part

Adsorption experiments were conducted using the method based on the determination of the solute concentration before and after contact with the adsorbent. In order to ensure uniformity the solution-adsorbent mixture was mechanically shaken. The equilibrium being attained the solid phase was filtered and the concentration was measured. A measured volume (V=50mL) of phenolic solution was placed in 500 mLbottles containing the same amounts of adsorbent (m=0.1g). The initial concentration of phenolic compounds was ranged between 1mmol/L to 20 mmol/L. The bottles were placed in a mechanical stirrer and mixed at a constant temperature (t=25±0.2°C) for ten hours. The bottles were thermostated.

A powdered active carbon has been used as adsorbent with specific surface area of about 1050 m^2/g, Before use the carbon was subject to a special washing treatment with bi-distillated water. The powdered carbon was dried at 110°C for 24 h and stored in desiccator. The particle size distribution was between 0.110-0.180mm, its density being about 0.6 g/cm^3. The phenol and its chlorinated derivatives (p-chlorphenol and o-chlorphenol) were of Merck purity.

A highly sensitive ultraviolet method has been used based on the fact that ionized phenols show a shift of absorption band to longer wavelengths with an increase of *p*H due to formation of phenolates. A SPECORD Jena Spectrometer has been used. The specific wavelengths of phenol derivates used in UV method are the following: phenol (λ=290nm) orto-chlorphenol (λ=295nm), para-chlorphenol (λ=300nm).

Results and discussions

Determination of carbon PZC (Point of Zero Charge)

The Point of Zero Charge of activated carbon was determined by placing various amounts of carbon in bottles containing 10 mL of 0.1M NaCl (prepared in distillated water) [35]. The sealed bottles were placed in a constant temperature shaker for 24 h. The equilibrium *p*H values of mixture were then measured. The limiting *p*H was taken as pH_{PZC}. In this case the obtained pH_{PZC} has the value 7.1. At *p*H value corresponding to pH_{PZC} the carbon surface is neutral. At *p*H higher than pH_{PZC} the carbon surface becomes positive, having high affinity for anions.

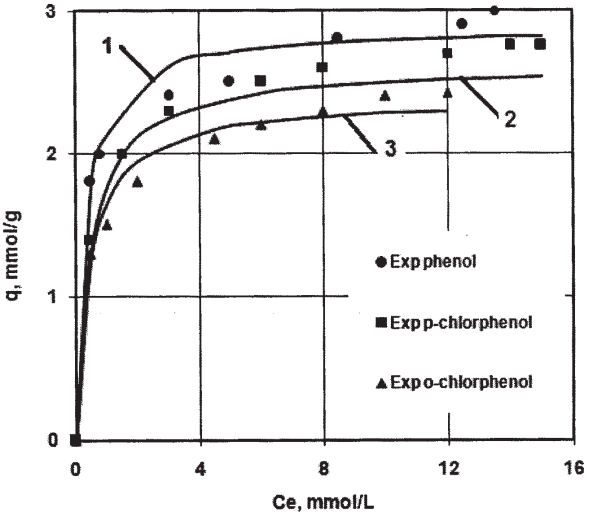

Fig 1. Adsorption isotherms of phenol and its chlorinated derivatives 1, 2, 3 - theoretical curves obtained from Langmuir model

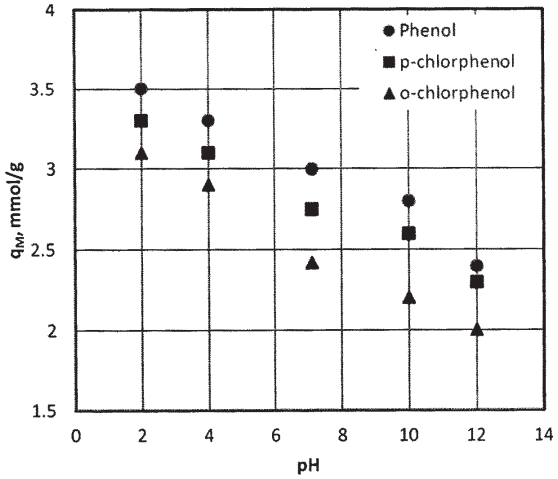

Fig. 2. The dependence of q_M on solution pH, experimental points

Compound	Langmuir isotherms		
	a_m	b	R^2
Phenol	2.882	3.126	0.928
P-chlorphenol	2.762	2.022	0.991
O-chlorphenol	2.386	2.18	0.942

Table 1
EQUILIBRIUM PARAMETERS OBTAINED FITTING LANGMUIR EQUATION

Equilibrium curves determination

In order to evaluate the adsorption capacity of carbon at equilibrium, the adsorption isotherms has been determined. Figure 1 represents the isotherms of phenol and its chlorinated derivatives at *p*H=7.1, corresponding to Point of Zero Change. The decreasing order of adsorption capacity phenol > p-chlorphenol > o-chlorphenol corresponds to a decreasing order of polarity [35, 36]. The adsorption curves are in good agreement with those fitted using Langmuir equation.

Figure 2 represents the equilibrium values of phenol and its derivatives at lower and higher *p*H values than pH_{PZC}. The decreasing form of isotherms corresponds to *p*H increasing values. The explanation is the following. At pH_{PZC} the concentration *Cm* of molecular form of phenolic compounds is equal with the concentration *Ci* of ionized form. At $pH < pH_{PZC}$ dominating is the molecular form whereas at $pH > pH_{PZC}$ the ionized form is determining. Or the phenol compounds in molecular form are stronger adsorbed than in ionized one [36, 40].

The values of the equilibrium parameters for the studied compounds on active carbon are presented in table 1.

The data presented in figure 2 confirm the big influence of *p*H on the concentration of adsorbed phenol and its chlorinated derivatives, being in good agreement with the conclusions contained in [36, 38, 39]. These data can be used in the case of phenol elimination from polluted waters having different *p*H values.

Conclusions

In the present work a study has been made concerning the adsorption of phenol and its chlorinated derivatives from wastewater. This study reveals the big influence of *p*H on the adsorption capacity of active carbon. The pH_{PZC} (Point of Zero Charge) has been determined, having the value 7,1. At the *p*H values smaller than pH_{PZC} the adsorption capacity of activated carbon considerably increases, decreasing at the *p*H values higher than pH_{PZC}. The explanation is the following. At pH_{PZC} the concentration of molecular species(*Cm*) is equal with the concentration of ionized ones (*Ci*). At *p*H values smaller than pH_{PZC} the concentration of molecular species considerably increases. At *p*H values higher than pH_{PZC}, increases the concentration of ionized species. The molecular species are stronger adsorbed than the ionized ones, the former ensuring a high adsorption capacity.

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