

# Combined adsorption and ion exchange equilibrium of phenol on Amberlite IRA-420

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## Abstract

Phenol can be efficiently removed from polluted wastewaters by using a strong-base anion exchanger. It was observed that its removal capacity was higher than that of other known adsorbents. This high capacity of anion exchangers for the removal of phenolic compounds has been previously observed but the reason for so high capacity has not been suitably explained yet. For that reason, isotherms of phenol removal on Amberlite IRA-420 were reproduced by both empirical and theoretical treatments. A simple empirical model was able to reproduce the measured total uptake of phenol. The pH dependent equilibrium isotherms can be explained assuming that the uptake of phenol in the resin is accomplished by two ways: ion exchange and molecular adsorption. The theoretical treatment allowed us to verify that the adsorption capacity does not depend on pH and to obtain the parameter values required for both adsorption and ion exchange isotherms. The importance of each phenomenon in the process is analyzed. Adsorption of phenol onto IRA-420 is predominant at acidic pH, whereas both adsorption and ion exchange are important at alkaline pH. The theoretical model developed herein enables the relation between phenol removal, pH and amount of resin to be determined.

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**Keywords:** Ion exchange; Adsorption; Phenol; Wastewater; Langmuir

## 1. Introduction

Phenolic compounds exist in wastewaters from olive mill, oil refineries, plastics, leather, paint, pharmaceutical and steel industries, and must be removed to satisfy the actual environmental regulations. Different techniques have been applied to remove or eliminate phenolic compounds from polluted waters, including chemical oxidation [1–4], chemical coagulation [5,6], solvent extraction [7], membrane techniques [8] and adsorption [9–13].

Adsorption by uncharged polymeric resins has been widely studied as an effective technique for removing hydrocarbons from wastewater. The use of this technique depends on various factors such as temperature, pH and sorbent characteristics such as microporosity and chemical properties [14–16]. Nevertheless, these materials have shown a lower capacity of phenol removal than that of the activated carbon F400 at alkaline pH [17]. The use of anionic resins could enable the uptake of phenol to occur by ion exchange in addition to adsorption and improve its overall removal from alkaline solutions. Ku et al. [18], studied

the phenol removal from aqueous solutions by using the resin Purolite A-510 in the chloride form and found that the phenol removal increased sharply with increasing pH. They described the isotherms by either Langmuir or Freundlich models. Nevertheless, they consider that the uptake of phenol compounds occurs only on the active sites of the resin by either adsorption or ion exchange. Thus, the same resin sites are considered to be accessible for both modes of uptake and so the ratio of the uptake of the solute via molecular adsorption and ion exchange depends on the solution pH. Nevertheless, they did not distinguish between molecular adsorption or ion exchange depending on the pH studied. Besides, the form of the functional groups of these resins depends on the prevailing solution pH [19]. According to this, the presence of OH<sup>-</sup> ions in solution would involve multicomponent exchange namely between hydroxyl, phenolate and the anion initially in the resin. Significant dissociation of phenol occurs at a pH higher than its pK<sub>a</sub> (9.83), allowing its uptake by ion exchange, which is an economic, effective and useful technique to remove pollutant ions from wastewaters and replace them by non-contaminant ions released from the ion exchanger [20]. Anasthas and Gaikar [21] have also used the ion exchange technique for the separation of alkylphenols from non-aqueous systems. They found that the separation is mainly governed by acid–base interactions

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## Nomenclature

$a_0, a_1, a_2$	parameters of $n^\infty$ expression as a function of pH
$C_B^*$	liquid phase equilibrium concentration of phenol (mol dm <sup>-3</sup> )
$K$	Langmuir equilibrium constant (dm <sup>3</sup> mol <sup>-1</sup> )
$K_{Ad}$	adsorption separation factor (dm <sup>3</sup> mol <sup>-1</sup> )
$K_{IE}$	ion exchange separation factor (dm <sup>3</sup> mol <sup>-1</sup> )
$K_{\phi^{OH}}$	phenol dissociation constant
$K_w$	water dissociation constant
$n^\infty$	total adsorption capacity as a function of pH obtained by Langmuir equation (mol kg <sup>-1</sup> dry solid)
pH	pH of the solution
$q_B^*$	solid phase equilibrium concentration of phenol in Eq. (1) (mol kg <sup>-1</sup> )
$q_{Ad}^\infty$	maximum adsorption capacity of the resin (mol kg <sup>-1</sup> dry solid)
$q_{IE}^\infty$	total ion exchange capacity of the resin (mol kg <sup>-1</sup> dry solid)
$q_{\phi^{OH}}^*$	equilibrium concentration of the undissociated phenol in the solid phase (mol kg <sup>-1</sup> )
$q_{\phi^{O^-}}^*$	equilibrium concentration of the dissociated phenol in the solid phase (mol kg <sup>-1</sup> )
$V$	volume of the solution (dm <sup>3</sup> )
$W$	weight of dry resin (kg)
<i>Greek letters</i>	
$[\phi^{OH}]$	concentration of undissociated phenol form (mol dm <sup>-3</sup> )
$[\phi^{O^-}]$	concentration of dissociated phenol form (mol dm <sup>-3</sup> )
$\phi_{measured}^{OH}$	total amount of phenol experimentally measured (mol dm <sup>-3</sup> )

between phenolic OH<sup>-</sup> groups and the basic groups of the resin structure.

In this work, a strong-base anion exchanger (Amberlite IRA-420) was used to eliminate phenol from aqueous solutions. The solid medium was considered to provide sites with fixed charges for ion exchange, as well as a high porosity on which molecular adsorption by hydrophobic interaction can take place [22]. According to this, phenol uptake by both adsorption of the undissociated form and ion exchange of the corresponding phenolate were studied. Thus, equilibrium data for phenol onto Amberlite IRA-420 in the OH<sup>-</sup> form at different pH values were obtained.

## 2. Experimental

### 2.1. Chemicals

Phenol with purity higher than 99% and 96% pure sodium hydroxide (PRS grade) were supplied by Panreac. Deminer-

alized water was used with a conductivity value lower than 5 μS cm<sup>-1</sup>. A commercial Amberlite IRA-420 ion exchange resin supplied by Rohm and Hass was used.

### 2.2. Equilibrium experiments

The experimental apparatus consisted of nine hermetically sealed 0.1-L Pyrex containers submerged in a temperature-controlled bath. The temperature was kept constant within ±0.1 K. Different known masses of resin, in the OH<sup>-</sup> form, were put in contact with phenol solution at a specific pH depending on phenol concentration (natural pH) or by means of sodium hydroxide addition. The suspension formed by the resin and the solution was vigorously agitated by means of a multipoint magnetic stirrer, until equilibrium was achieved (48 h). The accuracy of weighing was ±0.0001 g. At the end of this period, the mixtures were filtered to remove the solid phase and the phenol content was determined from the liquid phase.

The phenol concentration was analyzed by a UV detector in combination with high pressure liquid chromatography (Nucleosil C18 column: 40% water/60% acetonitrile mobile phase, 0.5 ml min<sup>-1</sup> flow rate), while the OH<sup>-</sup> concentration was obtained with a GLP 21 Crison pH meter. The standard uncertainty and reproducibility of measurements was found to be ±0.1%.

## 3. Results and discussion

### 3.1. Empirical procedure

Experimental data were fitted to the Langmuir equation [23]:

$$q_B^* = \frac{n^\infty K C_B^*}{1 + K C_B^*} \quad (1)$$

where  $n^\infty$  is the total capacity of the resin and is pH dependent;  $q_B^*$  and  $C_B^*$ , respectively, the phenol concentration at equilibrium in the resin and liquid phase; and  $K$  is the Langmuir equilibrium constant.

Different authors found that the variation of the maximum adsorption capacity of *p*-nitrophenol [10] and chlorophenol [24] onto an activated carbon with pH could be reproduced by Eq. (2). This was successfully used by Valverde et al. [25], for an ion exchange process using the resin Lewatit TP-207:

$$n^\infty = a_0 + a_1 \text{pH} + a_2 \text{pH}^2 \quad (2)$$

Experimental equilibrium isotherms, together with theoretical ones obtained with this model are plotted in Fig. 1. Fitting parameters evaluated by non-linear least-squares regression analysis and the average deviation between the experimental and theoretical data are shown in Table 1. Good agreement between experimental data and model predictions are obtained.

As can be observed in Fig. 1, the higher the pH value, the higher is the phenol removal by the solid phase. This behavior could be explained taking into account the phenol dissociation in the liquid phase (Eq. (3)). In this way, an increase of the phenolate ion concentration favors the phenol removal from the

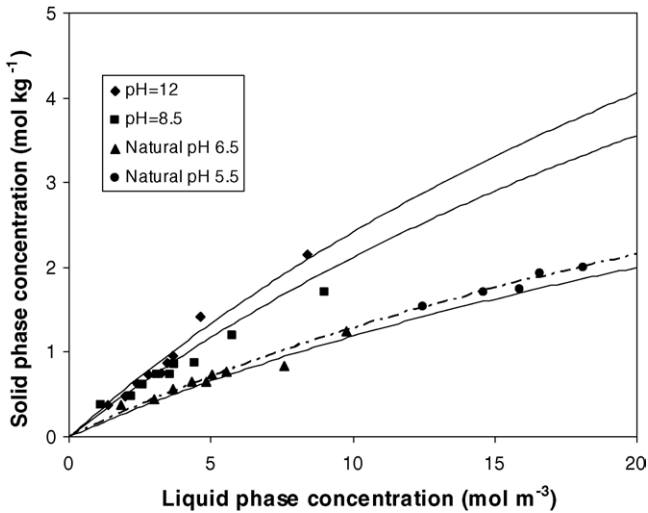


Fig. 1. Adsorption isotherms of phenol onto Amberlite IRA-420 at different pH values, experimental treatment.

liquid phase:



where  $\phi^{\text{OH}}$  and  $\phi^{\text{O}^-}$  correspond to the undissociated and dissociated phenol forms, respectively.

These results indicate that phenol removal occurs primarily by molecular adsorption at low pH; however, this empirical model does not allow us to distinguish between the mechanisms by which phenol is removed at alkaline pH, i.e. whether it occurs by the combined effect of molecular adsorption and ion exchange or by ion exchange alone.

Thus, although the empirical model satisfactorily describes the experimental data, it cannot differentiate between the mechanisms of phenol removal at alkaline pH. In order to determine the contribution of each phenomenon to phenol, removal, a new model based on both molecular adsorption and ion exchange mechanisms is developed in the following section.

### 3.2. Theoretical procedure

#### 3.2.1. Liquid phase

Additional to phenol dissociation, water dissociation takes place:

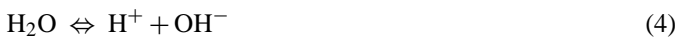


Table 1  
Equilibrium parameters in Eqs. (1) and (2) of phenol on Amberlite IRA-420

Parameters	Values
$K$ (dm <sup>3</sup> mol <sup>-1</sup> )	23.665
$a_0$	-14.977
$a_1$	4.920
$a_2$	-0.218
Average deviation (%) = $\frac{\sum_{i=1}^m \text{ABS}((q_i^{\text{exp}} - q_i^{\text{theor}})/q_i^{\text{exp}}) \times 100}{m}$	10.0

Empirical treatment;  $m$ : total number of experimental data.

If reactions (3) and (4) are combined to eliminate  $\text{H}^+$ , one obtains:



From Eq. (5):

$$\frac{K_{\phi^{\text{OH}}}}{K_w} = \frac{[\phi^{\text{O}^-}]}{[\phi^{\text{OH}}] \cdot [\text{OH}^-]} \quad (6)$$

where  $[\phi^{\text{OH}}]$  is the phenol concentration,  $[\phi^{\text{O}^-}]$  the ionic phenolate concentration  $K_{\phi^{\text{OH}}}$  and  $K_w$  are the equilibrium constants for phenol and water dissociation in the liquid phase, respectively.

When the phenol content is analyzed, the measurement detects both forms of phenol, i.e.:

$$[\phi^{\text{OH}}_{\text{measured}}] = [\phi^{\text{OH}}] + [\phi^{\text{O}^-}] \quad (7)$$

where  $[\phi^{\text{OH}}_{\text{measured}}]$  is the total amount of phenol that is experimentally measured.

Introducing the last equation in Eq. (6), one gets:

$$\frac{K_{\phi^{\text{OH}}}}{K_w} = \frac{[\phi^{\text{O}^-}]}{[\phi^{\text{OH}}_{\text{measured}} - \phi^{\text{O}^-}] \cdot [\text{OH}^-]} \quad (8)$$

The hydroxide concentration can be obtained, if the pH is known, by the well known equation:

$$\text{pOH} = 14 - \text{pH} \quad (9)$$

Then,

$$[\text{OH}^-] = 10^{-(14-\text{pH})} \quad (10)$$

Eq. (8) becomes:

$$[\phi^{\text{O}^-}] = \frac{(K_{\phi^{\text{OH}}}/K_w) \cdot [\phi^{\text{OH}}_{\text{measured}}] \cdot 10^{-(14-\text{pH})}}{1 + (K_{\phi^{\text{OH}}}/K_w) \cdot 10^{-(14-\text{pH})}} \quad (11)$$

Eq. (11) allows the concentration of phenolate in solution to be determined as a function of the total concentration of phenol and the pH of the liquid solution. The change with pH of the relative concentrations of both species, phenol and phenolate, with respect to the total concentration of phenol in solution can be observed in Fig. 2.

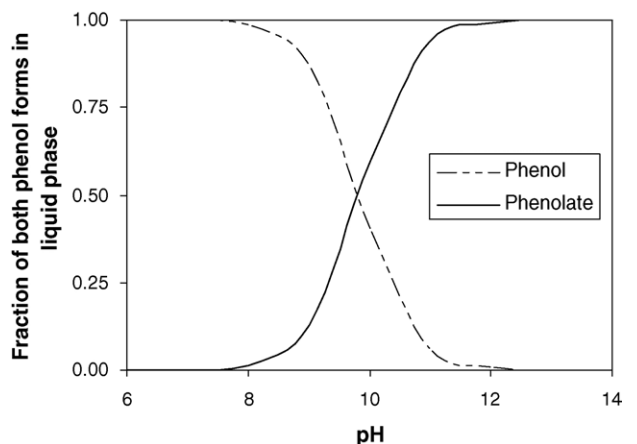


Fig. 2. Effect of the pH on phenol dissociation.

### 3.2.2. Solid phase

In this model, it has been assumed that two mechanisms for the uptake of phenol into the resin beads take place, one by ion exchange and another by adsorption. The ion exchange uptake of phenol by the resin can be described by the following equation:



Since, phenol dissociation produces  $\text{H}^+$  and the ion exchange releases  $\text{OH}^-$ , the later neutralization will decrease the initial ionic strength of the solution. Langmuir equation can be used to reproduce this phenomenon, avoiding possible uncertainties, if mass action law is used due to lower  $\text{OH}^-$  concentrations at acidic pH values.

$$q_{\phi^{\text{O}^-}}^* = \frac{q_{\text{IE}}^{\infty} K_{\text{IE}} [\phi^{\text{O}^-}]}{1 + K_{\text{IE}} [\phi^{\text{O}^-}]} \quad (13)$$

where  $q_{\text{IE}}^{\infty}$  is the maximum ion exchange capacity of the resin ( $3.8 \text{ meq g}^{-1}$  dry resin, value reported in Sigma–Aldrich catalog),  $K_{\text{IE}}$  the ion exchange separation factor and  $q_{\phi^{\text{O}^-}}^*$  is the equilibrium concentration of phenolate in the solid phase.

For the adsorption process:



where  $\text{S}^*$  and  $\text{S}\phi^{\text{OH}}$  represent active and occupied adsorption sites of the resin, respectively.

If the adsorption in the resin is assumed to be restricted to a single monolayer, the Langmuir equation can be used to represent the adsorption equilibrium:

$$q_{\phi^{\text{OH}}}^* = \frac{q_{\text{Ad}}^{\infty} \cdot K_{\text{Ad}} \cdot [\phi^{\text{OH}}]}{1 + K_{\text{Ad}} \cdot [\phi^{\text{OH}}]} \quad (15)$$

where  $q_{\text{Ad}}^*$  is the maximum adsorption capacity of the resin,  $K_{\text{Ad}}$  the adsorption separation factor and  $q_{\phi^{\text{OH}}}^*$  is the equilibrium concentration of the undissociated phenol in the solid phase. Because the ion exchange occurs between univalent ions, molar units can be used to quantify the process. This way, the following mass balance can be drawn:

$$q_{\phi^{\text{OH}}}^* + q_{\phi^{\text{O}^-}}^* = ([\phi_{\text{initial}}^{\text{OH}}] - [\phi_{\text{measured}}^{\text{OH}}]) \cdot \frac{V}{W} \quad (16)$$

where  $[\phi_{\text{initial}}^{\text{OH}}]$  is the initial phenol concentration,  $V$  the volume of the solution and  $W$  is the weight of dry resin.

Introducing Eqs. (7), (11), (13) and (15) in the Eq. (16), one obtain the following one:

$$\left( \frac{q_{\text{Ad}}^{\infty} \cdot [\phi_{\text{measured}}^{\text{OH}}] \cdot K_{\text{Ad}}}{1 + (K_{\phi^{\text{OH}}}/K_w) \cdot 10^{-(14-\text{pH})} + K_{\text{Ad}} \cdot [\phi_{\text{measured}}^{\text{OH}}]} + \frac{q_{\text{IE}}^{\infty} \cdot [\phi_{\text{measured}}^{\text{OH}}] \cdot (K_{\phi^{\text{OH}}}/K_w) \cdot 10^{-(14-\text{pH})} \cdot K_{\text{IE}}}{1 + (K_{\phi^{\text{OH}}}/K_w) \cdot 10^{-(14-\text{pH})} \cdot [1 + K_{\text{IE}} \cdot [\phi_{\text{measured}}^{\text{OH}}]]} \right) \cdot \frac{W}{V} = [\phi_{\text{initial}}^{\text{OH}}] - [\phi_{\text{measured}}^{\text{OH}}] \quad (17)$$

This equation describes the removal of phenol by the resin in terms of three unknown parameters ( $K_{\text{IE}}$ ,  $K_{\text{Ad}}$ ,  $q_{\text{Ad}}^{\infty}$ ) related to ion exchange and adsorption. Experimental data were fitted to the Eq. (17) by a non-linear least-squares regression procedure (Fig. 3). The values of the parameters obtained by fitting the experimental data to this model are shown in Table 2.

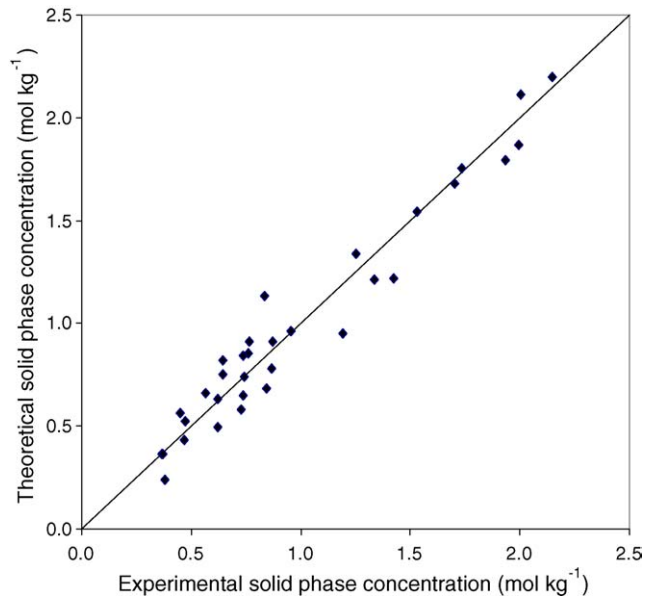


Fig. 3. Reproducibility of the experimental data by the theoretical model.

Table 2  
Equilibrium parameters in Eq. (17) of phenol on Amberlite IRA-420

Parameters	Values
$K_{\text{IE}}$ ( $\text{dm}^3 \text{ mol}^{-1}$ )	$69.6 \pm 5.6$
$K_{\text{Ad}}$ ( $\text{dm}^3 \text{ mol}^{-1}$ )	$63.5 \pm 10.0$
$q_{\text{Ad}}^*$ ( $\text{mol kg}^{-1}$ )	$3.351 \pm 0.7$
Average deviation (%) = $\frac{\sum_{i=1}^m \text{ABS}((q_i^{\text{exp}} - q_i^{\text{theor}})/q_i^{\text{exp}}) \times 100}{m}$	11.8

Theoretical treatment;  $m$ : total number of experimental data

According to these results, it is possible to conclude that both phenomena operate at alkaline pH. As can be observed in Table 2, the ion exchange capacity ( $3.8 \text{ meq g}^{-1}$  dry resin) is slightly higher than the adsorption capacity. This result indicates that an alkaline pH favors the phenol removal by this type of resin, since phenol is highly dissociated at alkaline pH. On the other hand, it is also possible to conclude that adsorption capacity does not depend on pH.

As can be seen, both modes of uptake operate under these conditions. As shown in Fig. 4, the amount of phenol removed by molecular adsorption is always less than that removed by ion exchange regardless of the liquid phase concentration.

From these isotherms one can obtain, by solving Eq. (17), the total phenol removal at a fixed pH.

Fig. 5 shows the isotherms obtained at pH lower than 8. In these conditions, the phenol dissociation is low and therefore, the molecular adsorption process is the predominant one. As expected, all the isotherms shown in Fig. 5 are coincidental.

Isotherms at alkaline pH are shown in Fig. 6. As can be seen, there is a combination of both phenomena: molecular adsorption

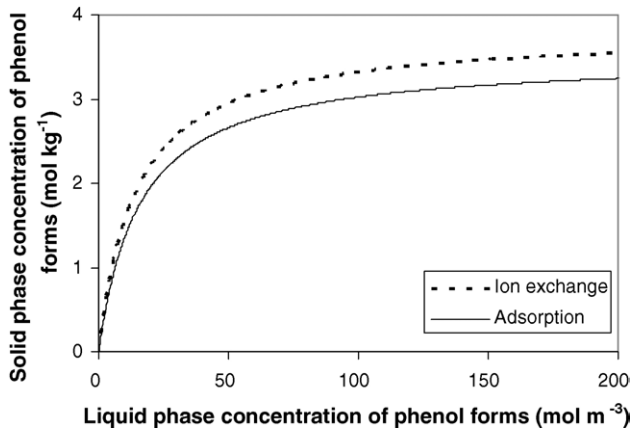


Fig. 4. Isotherms (both adsorption and ion exchange) of phenol removal by Amberlite IRA-420.

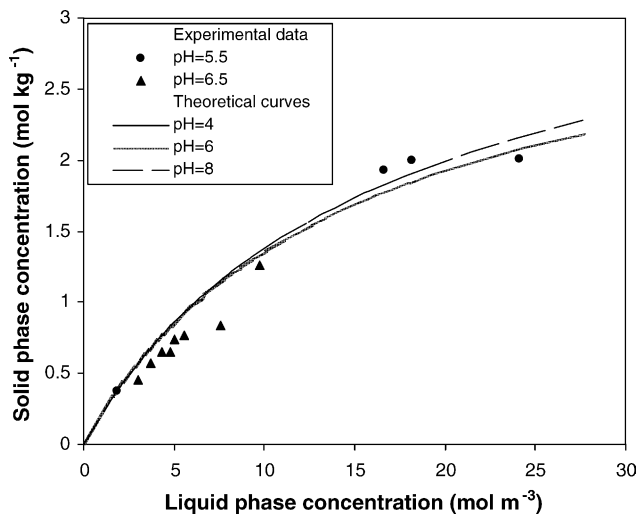


Fig. 5. Phenol removal from liquid phase by Amberlite IRA-420 for pH values lower or equal than 8.0 (phenol removal by adsorption).

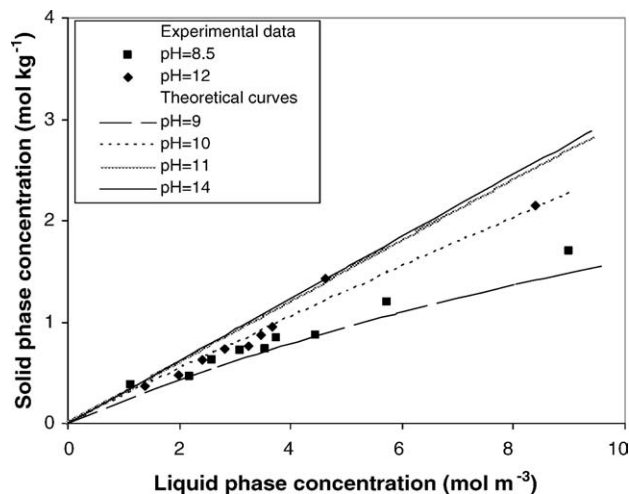


Fig. 6. Phenol removal from liquid phase by Amberlite IRA-420 for pH values higher than 8.0 (a combined elimination by both adsorption and ion exchange).

and ion exchange. As can be seen, both molecular adsorption and ion exchange contribute to phenol uptake. This can be deduced from the isotherm shapes that tend to be linear over the studied concentration range, whereas the ion exchange isotherm displays a concave shape (Fig. 4). Besides, phenol removal at high pH is higher than the amount obtained by using only the ion exchange isotherm. Finally, the ion exchange curve shape would indicate that the resin prefers ionic phenolate to hydroxide ion.

Summarizing, the resin Amberlite IRA-420 could be used to eliminate phenol from liquid phase, due to the high removal capacity observed at high pH, which is higher than the capacity shown by known adsorbents [10,12,24].

#### 4. Conclusions

Phenol can be removed by using a strong-base anion exchanger. It was observed that its removal capacity was higher than that of known adsorbents. The phenol removal was reproduced by both empirical and theoretical treatments. Based on the theoretical one, the adsorption capacity does not depend on pH, although the empirical model was able to reproduce the measured total adsorption at different pH. A theoretical model based on molecular adsorption and ion exchange was developed to fit the experimental data and to obtain the parameters related to both phenomena. Also, this analysis allowed the relative importance of the two uptake modes to be determined, to obtain the parameters that represent each isotherm (adsorption and ion exchange) and, also, the importance of each phenomenon in the process. Uptake onto Amberlite IRA-420 occurs by adsorption at acidic pH and by both adsorption and ion exchange at alkaline pH. The phenol removal increased at pH values from 9 to 14 and remained constant below 8. The developed theoretical model allowed the phenol removal to be determined depending on the value of the pH and the amount of resin.

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