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Phenol Adsorption in Immobilized Activated Carbon with Alginate Gels

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ABSTRACT

Calcium alginate-activated carbon composites were used for phenol adsorption from aqueous solutions. These composites were prepared by mixing different amounts of powdered activated carbon with a 3% (w/v) sodium alginate solution, and then dripping the mix into a calcium solution. Spherical beads were obtained with different amounts of powder-activated carbon immobilized inside the calcium alginate matrix. The adsorption on immobilized adsorbents modified the distribution equilibrium. A modified Langmuir equation was considered for analyzing adsorption isotherms and solid phase interactions. The kinetic of phenol adsorption on mixed gels is controlled by the diffusion of phenol in the particle over the gel phase, so the process can be described by one diffusional parameter: the effective diffusion coefficient of phenol in the gel phase.

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Key Words: Phenol adsorption; Immobilized activated carbon; Calcium alginate; Equilibrium; Solid phase interactions; Kinetic.

INTRODUCTION

Gel immobilization has been extensively used in biomedicine and the biotechnology industry to encapsulate enzymes, subcellular organelles, and living cells, with calcium alginate matrices being selected for this purpose.[1–3] Alginate is a polysaccharide extracted from brown algae and also from some bacteria, which shows the ability to form water insoluble gels by the reaction of the biopolymer with divalent metals such as calcium or copper and also a high retention capacity of some heavy metal ions.

The technique of immobilization on calcium alginate gels has also been applied to metal recovery. Alginate gels have been used to immobilize the water soluble EDTA (by providing a matrix for holding it) and a mixture of green algae Microcystis, both in order to improve the copper binding capacity of the alginate gel.[4–6] Alginate gels have also been successfully applied to agglutinating iminodiacetic-type Lewatit TP-207 ion exchange resin for the recovery of copper from synthetic solutions.[7] In the same way, the adsorption of some organics has been studied on immobilized activated carbon,[8,9] and also on immobilized Lewatit OC-1064 adsorbent resin,[9] using alginate as the immobilization medium in both cases. Adsorption onto activated carbon and the adsorbent resin Lewatit OC-1064 has proven to be an effective technique for removing organic compounds such as phenol from different media.[10,11] Alginate allows the preparation of spherical matrices with physical-chemical characteristics that can be adapted to the process requirements. The biopolymer matrices act as membranes, physically separating the adsorbent from the aqueous phase and improving mechanical and hydrodynamic parameters. Poisoning and abrasion are reduced at the same time.

This paper reports the performance of calcium alginate gels as an immobilization medium for activated carbon powder for subsequent application in equilibrium and kinetic studies of phenol adsorption. Experiments were carried out for calcium alginate gels containing different amounts of activated carbon powder. The adsorption isotherms were fitted to the conventional Langmuir equation but also to a modified Langmuir equation that considered the solid phase interactions. Kinetic results were correctly fitted to a homogeneous model for spherical geometry using only one diffusional parameter, known as the "linear adsorption model",[8] developed by Crank in 1975.[12] The results were compared with those estimated for activated carbon and calcium alginate gels separately.

EXPERIMENTAL METHODS

Alginate Bead Production

Single calcium alginate gels were prepared by dripping 3.0% (w/v) sodium alginate (pharmaceutical grade) aqueous solution into a magnetically stirred 0.05M calcium nitrate aqueous solution, using the device already described in a previous paper.[6,13] The same procedure was used to prepare spherical calcium alginate-activated carbon composite gels, but a known amount of activated carbon was first added to the sodium alginate solution and then the mixture was pumped into the calcium nitrate solution. After 24 hours of aging in calcium solution, beads shrank to approximately 3.0 mm in diameter, and assumed a spherical form. Powder-activated carbon showed a mean particle diameter of 37.2 μm. This value was determined by granulometric analysis in an optical measurement unit (MasterSizer × System), assuming a spherical geometry. Figure 1 shows a photograph of a single, spherical calcium alginate gel bead and another of a composite calcium alginate-activated carbon gel containing 25.4% (w/w) of powder-activated carbon. Both were prepared in the laboratory for phenol adsorption. In the case of the composite gel, the distribution of the activated carbon powder in the beads is apparently homogeneous, as shown in the image.

Determination of Equilibrium

Equilibrium data of phenol adsorption onto single and composite calcium alginate gels were determined. The gels came into contact with 100 ml of solutions with different initial concentrations of phenol at room temperature and pH = 5–6 for several days. For activated carbon, the isotherm was carried out in batch reactor. Table 1 shows the conditions of the experiment in equilibrium runs. At equilibrium, phenol concentration in solutions was measured by a UV spectrophotometer at 272 nm, and the phenol concentration in the solid phase was evaluated from the corresponding mass balance.

Determination of the Kinetic

Experiments to find the kinetic of phenol adsorption were carried out in batches at constant temperature of 298°K using a jacketed reactor. Table 2 shows the specific conditions of the experiment in each kinetic run. The initial phenol concentration in the solution was 1000 mg/L and the liquid/solid ratio

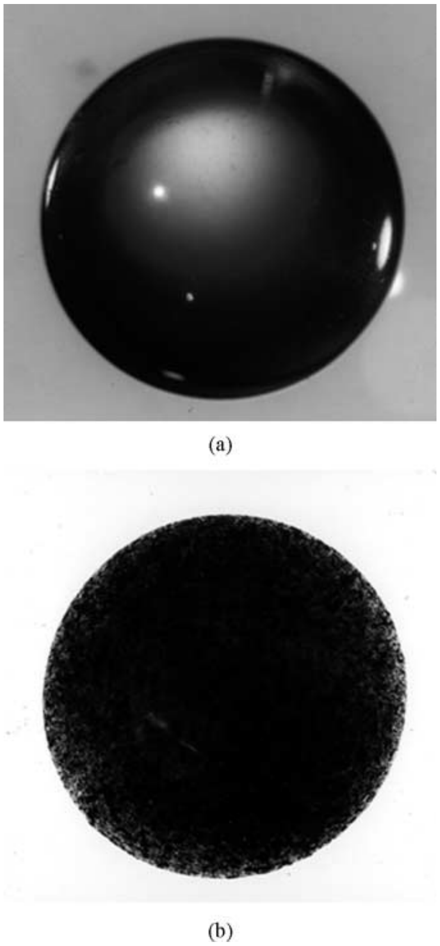

Figure 1. Photograph of a single calcium alginate gel (a) and a calcium alginate gel containing 25.3% (w/w) of powdered activated carbon (b). Both were prepared by using a 3% (w/v) sodium alginate and a 0.05M calcium nitrate solution. Magnification: 16× .

was 134–139 L/kg. Zero time was taken when adding the adsorbent to the solution. The variation of the solute concentration in the solution was monitored over time by extracting 1 mL from the solution, and concentration was measured in a UV spectrophotometer at 272 nm. The concentration of phenol in the solid phase, that is, in the adsorbent material, was evaluated by

Table 1. Summary of experiment conditions in equilibrium runs of phenol adsorption.

Parameters	Calcium alginate beads	Activated carbon powder	Calcium alginate-activated carbon composite beads (w/w) 7.0%	13.9%	25.3%
Solution volume (ml)	100	500	100	100	100
N	135	–	100	110	200
Dry sodium alginate (g)	0.0989	–	0.0984	0.0902	0.1456
Dry activated carbon (g)	–	3.51	0.0074	0.0145	0.0492
Average initial diameter (mm)	3.01	0.0744	3.68	2.88	2.86

the corresponding mass balance, taking into account the volume extracted from the solution at each period of time. In the case of phenol adsorption onto powdered activated carbon, solution samples were centrifuged prior to analytical determination. Once equilibrium was achieved (after approximately 24 hours) the solid phase was separated from the solution and its final volume was determined.

ADSORPTION ISOTHERMS: RESULTS OF THE EXPERIMENT AND DISCUSSION

Results of the Experiment

The adsorption isotherms of phenol onto single adsorbents and immobilization matrices are represented in Fig. 2. It can be noted that

Table 2. Experiment conditions in kinetic experiments of phenol adsorption at 298 K and pH = 5–6.

Parameters	Calcium alginate beads	Activated carbon powder	Calcium alginate-activated carbon composite beads (w/w) 6.2%	14.7%	24.9%
C_o (mM)	10.2	10.3	10.6	10.5	10.6
L/S (L/kg dry)	136	139	137	134	135
Average initial diameter (mm)	3.08	0.0744	2.94	2.96	2.92
N	1653	–	1658	1960	2165

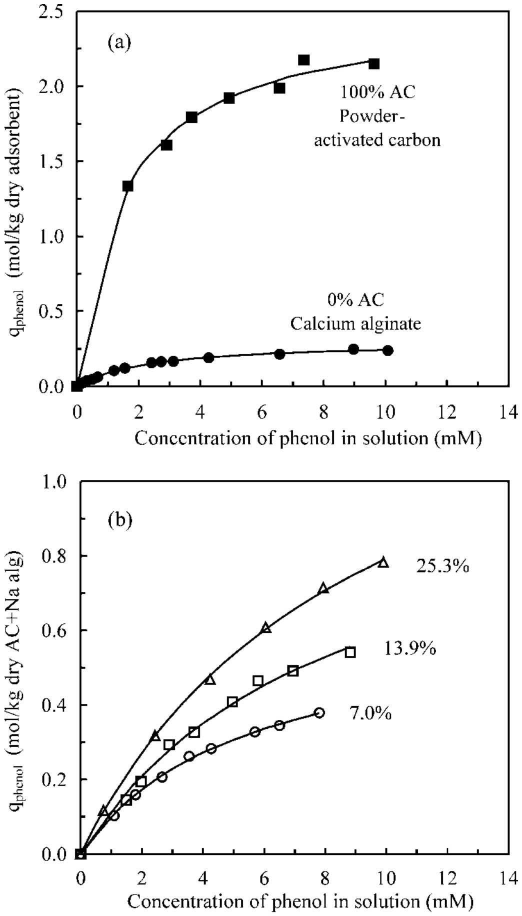

Figure 2. Adsorption isotherms of phenol at 298 K on (•) simple calcium alginate gels at pH = 5.5, (□) free powdered activated carbon at pH = 9.3 (without buffer solution), and composite calcium alginate beads with a (O) 7.0%, (□) 13.9% and (Δ) 25.3% composite calcium alginate gels containing different amounts of dry activated carbon (expressed in % w/w) at pH = 6.0. In solid lines, fit of the Langmuir equation to the experimental data on phenol adsorption with the parameters in Table 2.

the amount of phenol adsorbed increases with the amount of immobilized adsorbent in alginate beads, and with the phenol concentration in the solution. The differences increase at the highest concentrations of phenol in the solution but, in all cases, the amount of phenol adsorbed in alginate-activated carbon composite gels is smaller than the uptake of phenol onto 100% (w/w) powdered activated carbon.

Langmuir Equation

As Fig. 2 shows, the equilibrium data of phenol adsorption onto single and composite adsorbents are properly described by the conventional Langmuir Equation 1,[8−11]

$$q_{phenol} = \frac{KQC_{phenol}}{1 + KC_{phenol}} \tag{1}$$

where K is the Langmuir constant, Q is the maximum adsorption capacity, C is the concentration of phenol in solution and q is the amount of phenol adsorbed in the solid phase. The values of the fitting parameters K and Q are shown in Table 3, including the square of the correlation coefficient (r^2).

As expected, Q increases with the amount of adsorbent immobilized in alginate gels, with the relationship between the maximum adsorption capacity and the amount of adsorbent immobilized represented in Fig. 3 being linear. On the other hand, the values of K decrease as the amount of adsorbent immobilized increases until they are approximately constant, as Fig. 3 shows. The relationship of K and Q with the percentage of activated carbon inside the gels can be described by the following expressions:

$$Q = 0.319 + 4.941(X_{ads} \times 100) \tag{2}$$

$$K = \frac{0.428}{(X_{ads} \times 100)^{0.437}} \tag{3}$$

where $X_{ads} = m_{ads}/m_{tot}$ and $m_{tot} = m_{alg} + m_{ads}$, with m_{alg} and m_{ads} being

Table 3. Langmuir equation parameters for single and composite gels containing different amount of powder-activated carbon, expressed in % (w/w).

Parameters	Calcium alginate beads	Activated carbon powder	Calcium alginate-activated carbon composite beads (w/w)		
			7.0%	13.9%	25.3%
Q (mol/kg)	0.299	2.515	0.642	1.087	1.529
K (m^3/mol)	0.425	0.658	0.183	0.119	0.108
r^2	0.997	0.998	0.998	0.997	0.999

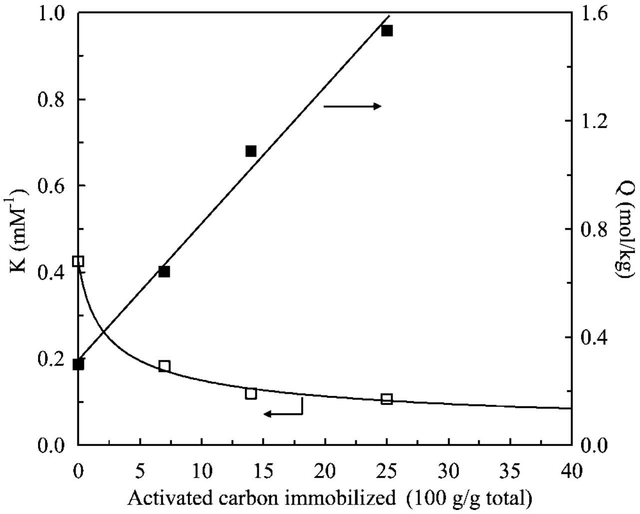

Figure 3. Relationship of the amount of powder-activated carbon immobilized in calcium alginate gels with the Langmuir constant and the maximum adsorption capacity. In solid lines, the fit to Eqs. 2 and 3.

the mass of dry sodium alginate and dry adsorbent (the activated carbon), respectively.

Interpretation of Phenol Adsorption Onto Composite Gels

In order to find a correlation between the uptake of phenol by single adsorbents that can describe adsorption onto mixed adsorbents, the following models have been considered:

Additive Adsorption Model

At first, it might be assumed that the amount of phenol adsorbed onto composite gels is the sum of that found for the biopolymer "alg" and for the adsorbent "ads," that is,

$$q_{phenol} = (q_{phenol})_{alg} X_{alg} + (q_{phenol})_{ads} X_{ads} \tag{4}$$

where $X_{alg} = m_{alg}/m_{tot}$, $X_{ads} = m_{ads}/m_{tot}$ and $m_{tot} = m_{alg} + m_{ads}$. Defining $(q_{phenol})_{alg}$ and $(q_{phenol})_{ads}$ by the Langmuir equation, Eq. (4) becomes

Eq. (5),

$$q_{phenol} = \left(\frac{K_{alg}Q_{alg}C_{phenol}}{1 + K_{alg}C_{phenol}}\right)X_{alg} + \left(\frac{K_{ads}Q_{ads}C_{phenol}}{1 + K_{ads}C_{phenol}}\right)X_{ads} \tag{5}$$

where the values of K and Q are those in Table 2. However, the representation in Fig. 4 of the experimental data set against the values estimated with Eq. (5) shows that the adsorption of phenol onto composite gels is not a single addition of the partial non-interacting adsorbent uptake. Indeed, at low concentrations of phenol in the solution, the amount of the solute adsorbed on composite gels is more than additive, and vice versa at high concentrations.[9] The values in the experiment coincided with the estimates only for a determined value of adsorption in each isotherm, as can be observed in Fig. 4: at $q_{phenol} = 0.34\,\mathrm{mol/kg}$ for gels with 7.0% (w/w) of activated carbon, at $q_{phenol} = 0.46\,\mathrm{mol/kg}$ for gels with 13.9% (w/w) of activated carbon, and at $q_{phenol} = 0.71\,\mathrm{mol/kg}$ for gels with 25.4% (w/w) of activated carbon.

The total amount of phenol adsorbed onto a composite gel of alginate-activated carbon cannot be estimated as the sum of the phenol uptake by

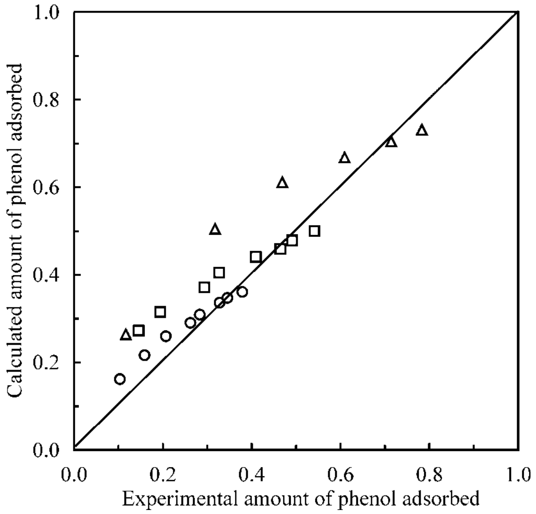

Figure 4. Comparison of experimental data of phenol adsorption onto calcium alginate-activated carbon composite gels with those estimated by Eq. (5), assuming a single addition of the partial noninteracting adsorbents. Symbols as in Fig. 2.

the materials that conform the composite gels separately, assuming that there is no interaction between the adsorbents.

Sequential Adsorption Model

Assuming that the adsorption of phenol onto activated carbon is really a function of the concentration of solute in the gel fluid, $\bar{C}_{phenol}$, the Langmuir equation for the adsorbent will be expressed as:

$$(q_{phenol})_{ads} = \frac{K_{ads} Q_{ads} \bar{C}_{phenol}}{1 + K_{ads} \bar{C}_{phenol}} \tag{6}$$

Thus, defining $\bar{C}_{phenol}$ by the Freundlich equation as $\bar{C}_{phenol} = \beta C^{n}_{phenol}$, the equation obtained is:

$$q_{phenol} = \left(\frac{\mu K_{alg} Q_{alg} C_{phenol}}{1 + \mu K_{alg} C_{phenol}} \right) X_{alg} + \left(\frac{\beta K_{ads} Q_{ads} C^{n}_{phenol}}{1 + \beta K_{ads} C^{n}_{phenol}} \right) X_{ads} \tag{7}$$

where μ and β are the interaction factors of the Langmuir parameters, and n is related to the effect of the solute concentration in the gel phase.[9] As Fig. 5

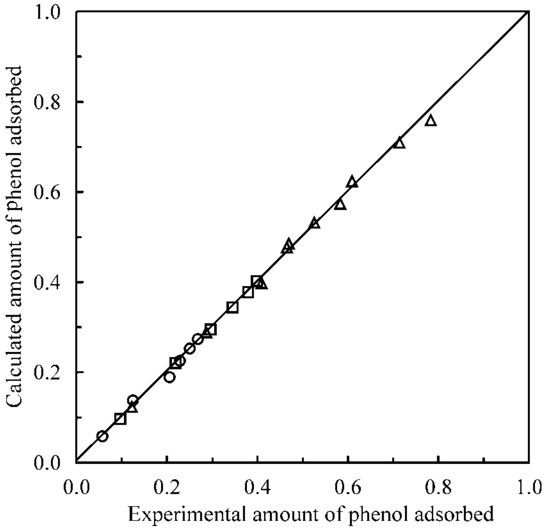

Figure 5. Comparison of experimental data on phenol adsorption on calcium alginate-activated carbon composite gels with those estimated by Eq. (7) for $\mu = 1.57$, $\beta = 0.05$, and $n = 2.49$. Symbols as in Fig. 2.

shows, this model provides a better correlation of experimental data for constant values of the equation parameters. The values are $\mu = 1.57$, $\beta = 0.05$, and $n = 2.49$, which were calculated by resolving Eq. (7) simultaneously for three isotherms of alginate-activated carbon composite gels and minimizing the sum of the square of the residuals.

KINETICS OF PHENOL ADSORPTION

Figure 6 shows the results of experiments on phenol adsorption onto powder-activated carbon, simple calcium alginate beads, and composite gels with the experiment conditions established and specified in the figure. The total amounts of phenol adsorbed at equilibrium for these assays are listed in Table 4. This parameter increases with the amount of activated carbon included in gels but, in any case, the amount involved is smaller than that obtained for free activated carbon. Although the total amount of phenol adsorbed at equilibrium in mixed adsorbents is almost proportional to the amount of activated carbon included in beads, the temporal variation of

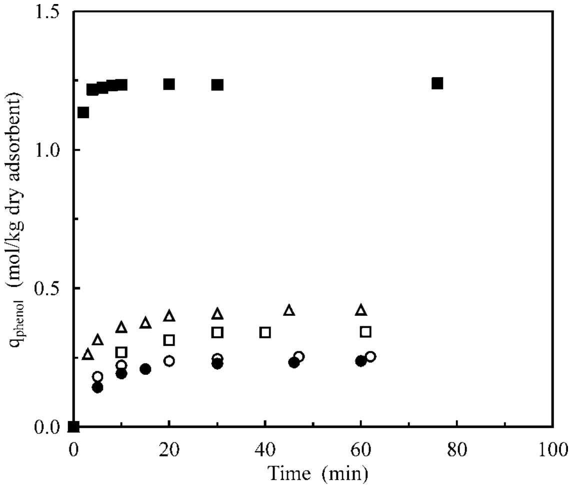

Figure 6. Phenol uptake over time onto (•) single calcium alginate beads, (□) free powder-activated carbon, and composite calcium alginate beads with a (○) 6.2%, (□) 14.7%, and (Δ) 24.9% of powder-activated carbon immobilized (expressed in % w/w) at 298 K, L/S = 134–139 L/kg, pH = 5–6, and initial concentration of phenol of 10.2–10.6 mM.

Table 4. Kinetic experimental results and estimated kinetic parameters.

Parameters	Calcium alginate beads	Activated carbon powder	Calcium alginate-activated carbon composite beads (w/w)		
			6.2%	14.7%	24.9%
q^*_{phenol} (mol/kg)	0.233	1.254	0.256	0.352	0.423
$(R_f/R_o)^3$	1,0	–	1,0	1,0	1,0
Alfa	5.0623	0.1471	4.8056	3.1591	2.4614
Average k (m^3 solution/m^3 gel)	0.331	1711	0.801	1.876	3.259
$D_{eff} \times 10^{+9}$ (m^2/s)	0.504	0.492	0.566	0.767	1.44
D_{eff}/R^2 (s^{-1})	2.12×10^{-4}	0.355	2.62×10^{-4}	3.50×10^{-4}	2.12×10^{-4}

the fractional attainment of equilibrium is independent of the gel composition in activated carbon, as Fig. 7 shows. Indeed, the evolution of the kinetics of immobilized systems was quite similar to that observed for single calcium alginate gels. Thus, the higher the amount of activated carbon immobilized is,

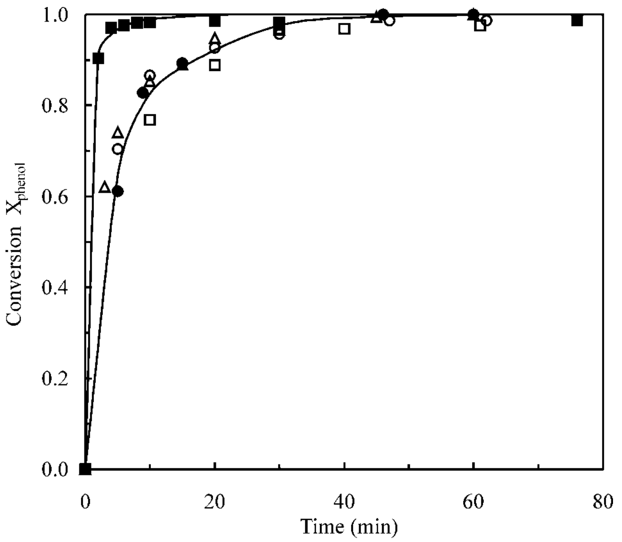

Figure 7. Variation of fractional attainment of equilibrium in time. In solid lines, fit of experimental data on kinetics to the proposed diffusion model defined by Eq. (8) for the kinetic parameters in Table 4. Symbols as in Fig. 7.

the higher the amount of phenol adsorbed is, with the adsorption process rate remaining constant.

Mainly due to the particle size, the mass transfer rate in free activated carbon is greater than for calcium alginate beads with and without activated carbon,[8] and a conversion of 90% is achieved in less than 10 minutes. However, the saturation rate of these adsorbent materials is fast, with less than 30 minutes needed to achieve a good approximation to equilibrium. On the other hand, the size of alginate beads does not apparently change during the phenol adsorption process, as shown by the data in Table 4.

During these assays no strict check on pH was kept, so as not to interfere in the kinetic of phenol adsorption. In phenol adsorption onto simple and composite alginate beads, the pH of solutions changed in the range of 5–6, so the species that is diffusing is phenol and not phenolate because the pH of solutions is always higher than the pK_a of phenol, which is nearly nine. But in the case of phenol adsorption on free activated carbon, the pH of the solution rose to nine. However, it was checked that that variation in pH did not affect phenol adsorption. Indeed, a new assay was carried out using a buffer solution of $pH = 7$ and the kinetic results were the same as those observed when the pH was nine (see curve in Figs. 6 and 7).

Pseudo-homogeneous Kinetic Model

Adsorption onto composite gels can be explained by differences in the solute concentration in the gel matrix. Phenol diffuses into the pores of alginate beads without carbon because of the concentration gradient. When carbon is immobilized, part of the phenol in the pores is adsorbed onto the activated carbon rapidly and effectively. Then, phenol concentration in the pores decreases and concentration differences increase, and consequently the mass transfer rate also increases. So, the overall kinetic rate of the process is controlled by the diffusion of the solute in the gel matrix and could be described by one diffusional parameter, the effective diffusion coefficient of phenol in the gel matrix.

For the analysis of experimental data of temporal phenol uptake a homogeneous kinetic model described by Eq. (8)[11] was adopted

$$X = 1 - \sum_{n=1}^{\infty} \left\{ 6\alpha(1+\alpha)\exp\left[-\frac{D_{eff} q_n^2 t/\left(R^2 k\right)}{\left(9 + 9\alpha + q_n^2 \alpha^2\right)} \right] \right\} \tag{8}$$

for spherical geometry with one diffusional parameter. This model was already used for a similar system.[8] The effective diffusion coefficient that best fits the experimental data was estimated by minimizing the sum of the square of the residuals between experimental and calculated values. Experimental data and model predictions are compared in Fig. 8 for the effective diffusion coefficients listed in Table 4. The homogeneous diffusion model proposed in Eq. (8) proves suitable for single adsorbents, but also for describing the kinetic of the adsorption of phenol onto immobilized activated carbon: it is possible to describe the changes in the kinetic for alginate gels with only one curve. The diffusivity of phenol on free activated carbon is higher than on simple or composite calcium alginate gels. However, the representation in Fig. 7 of the fractional attainment of the equilibrium against the dimensionless kinetic parameter $Dt(R^2K)$, derived from Eq. (8), allows for the separation of the curves, with one curve appearing for each kinetic assay. This is due to the contribution of the partition factor.

The maximum amount of phenol adsorbed on the adsorbents shows a linear relationship with the amount of activated carbon immobilized in beads, as shown in Fig. 8. The intercept at the origin is nearly 0.20 mol/kg, i.e. approximately the amount of phenol adsorbed onto simple calcium alginate gels, and the slope is 1.05×10^{-2}. On the other hand, the values of the effective

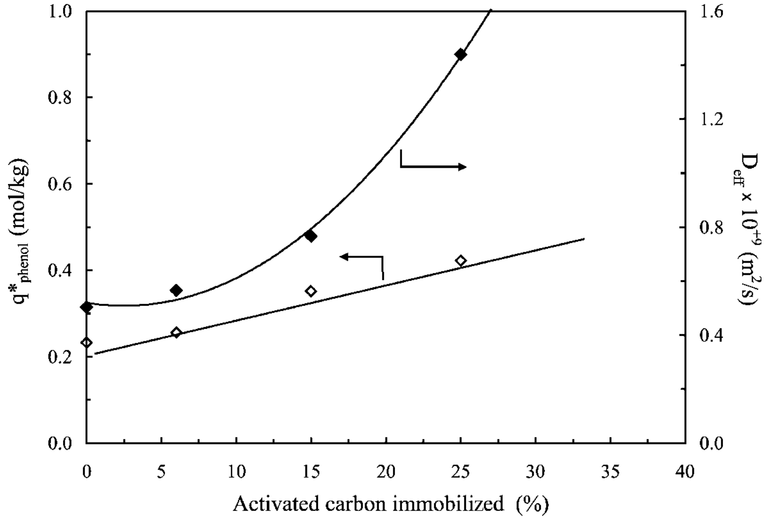

Figure 8. The effect of the amount of activated carbon immobilized in gels on the maximum adsorption capacity, the swelling of gels, and the effective diffusion coefficient of phenol in gels.

diffusion coefficients increase suddenly with the amount of activated carbon immobilized, even though the kinetic rate is constant.

In general, the estimated diffusion coefficients of phenol are smaller than the corresponding value in water $D_o = 9.43 \times 10^{-10}\,\mathrm{m}^2/\mathrm{s}$. Indeed, the diffusion of a solute in an immobilized system is affected by the alginate matrix and the solid material immobilized in that matrix, which reduces the useful volume of the gel matrix and increases the diffusion pathway of the solute.[8] But, in the case of the gels with the highest percentage of activated carbon, the effective diffusion coefficient of phenol appears higher than D_o.

CONCLUSIONS

The immobilization of powder-activated carbon in calcium alginate gels allows the adsorption of phenol from aqueous solutions. The amount of this organic compound adsorbed in composite gels increases with the amount of activated carbon immobilized inside the gels, but adsorption onto non-immobilized activated carbon is higher still.

The Langmuir equation does not lead to a good fit of experimental data on phenol adsorption either onto single adsorbents or onto composite gels of calcium alginate-powder-activated carbon. Phenol adsorption onto composite gels is not the sum of the amount of phenol uptake by each adsorbent (alginate and activated carbon) separately. The best fit of experimental data is obtained with the Sequential Adsorption Model, which considers interactions of some kinds between sorbents, assuming the interaction parameters μ and β and the empirical parameter n. The values of these parameters have been shown to be independent of the amount of activated carbon immobilized inside the gels.

In all cases, the saturation of the adsorbent material is fast, with less than 30 minutes needed to achieve a good approximation to equilibrium. The kinetic rate of phenol adsorption onto composite gels is not dependent on the amount of activated carbon immobilized and is equal to that observed for simple calcium alginate gels. However, the increasing of immobilized carbon enhances phenol adsorption, although the amount is smaller than that adsorbed by free activated carbon, with adsorption being much faster onto this material than onto alginate gels. The carbon immobilized reduces the amount of phenol in the gel matrix rapidly and effectively, increasing the concentration difference between the solid and gel phases, so the adsorption of phenol onto composite gels is controlled by the diffusion of the solute in the gel matrix. The homogenous diffusion model for spherical geometry fits experimental data of phenol adsorption onto simple nor composite adsorbents, with only one diffusional parameter: the diffusion coefficient of phenol in the gel matrix.

NOMENCLATURE

C	Concentration of solute in the liquid phase (mol/m^3)
D_{eff}	Effective diffusional coefficient (m^2/s)
k	Partition factor between the solute in equilibrium in the solid and liquid phases, calculated as $k = 3V/(4\pi R^3 N\alpha)$
K	Langmuir constant (m^3/mol)
m	Dry mass of the solid phase (kg)
n	Concentration effect of the solute in the gel phase in Eq. (7)
N	Number of spheres in the reactor
q	Amount of solutes adsorbed in the dry solid phase (mol/kg)
q^*	Equilibrium amount of solute adsorbed in the solid phase (mol/kg)
q_n	Non zero positive roots of the equation $\tan q_n = 3q_n/(3 + \alpha q_n^2)$
Q	Maximum adsorption capacity (mol/kg)
R	Radius of the spheres (m)
t	Time (s)
V	Volume of solution (m^3)
X	Fractional attainment to equilibrium
Greek Symbols	
α	Final fractional uptake of solute calculated as $\alpha = [C_o V_o/(q^*_{phenol} m_{Na\,alg})] - 1$
μ,β	Interaction factor of the Langmuir parameter in Eq. (7)
Subscripts	
AC	activated carbon
alg	alginate
ads	adsorbent
f	final (t = ∞)
o	initial (t = 0)
tot	total

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