Silicalite-1, an adsorbent for 2-, 3-, and 4-chlorophenols


ABSTRACT

The adsorption of the three chlorophenol isomers, ortho, meta and para, by silicalite-1 has been studied at 30 °C, below the solubility (at the same temperature) in water. Large differences, up to 30 times, have been observed between the adsorption of the para- vs. the ortho-isomer. The difference of behavior observed between the isomers is assigned to the tendency to self-organization of the para-isomer. It seems probable that the adsorption sites are at the intersection channels. From a technical point of view, silicalite-1 seems a competitive adsorbent for p-chlorophenol.

Key words | dipole moment, m-chlorophenol, o-chlorophenol, p-chlorophenol, silicalite-1

INTRODUCTION

The presence of halophenols in wastewater has become a serious problem. They are considered to be priority pollutants owing to their mobility in natural water ecosystems and because of their toxicity and carcinogenic properties when present at elevated levels. According to Mexican Standards, the maximum permitted discharge limit for phenolic compounds in water is 0.001 mgL⁻¹ (NOM-127-SSA1-1994). These compounds are found in the wastewater of a number of industries, such as high temperature coal conversion and petroleum refining.

Adsorption is a well known separation process. It is widely applied to organic compound removal in wastewater treatment (Busca et al. 2008) with high removal efficiency. Activated carbon is the most widely used adsorbent because of its excellent adsorption abilities for organic pollutants. However, its high initial cost and the need for a costly regeneration system make it less economically viable as an adsorbent. So research interest into the production of alternative adsorbents to replace the costly activated carbon has intensified in recent years (Ahmaruzzaman 2008).

Silicalite-1 has an MFI (mordenite framework inverted) framework type that is almost completely aluminum depleted and, therefore, lacks a permanent lattice charge (Flanigen et al. 1978). Silicalite-1 is one of the hydrophobic forms of silica capable of adsorbing organic molecules, is characterized by high thermal and hydrothermal stabilities and a number of useful properties, such as sorption of aromatics (Talu et al. 1989), light alkanes (Zhu et al. 1998) and polyols (Mallon et al. 2010).

Figure 1 shows the pore structure of silicalite-1 which consists of a system of intersecting channels composed of zig-zag channels along X, cross-linked by straight channels along Y. Both channels are defined by 10-rings. The straight channels are approximately elliptical in shape with a 0.53 × 0.56 nm cross-section, while the zig-zag channels have a 0.51 × 0.55 nm cross-section (Krishna & Paschek 2001).

The adsorption capacities of phenol and chlorinated phenols by three different adsorbents was studied by Shu et al. (1997): pillared clays (surfactant-modified montmorillonite), silicalite (Si/Al = 126, 563 and 1,065) and zeolite beta (Si/Al = 2 and 170). High Si/Al ratio zeolites were used by those authors to adsorb organic molecules selectively from aqueous solution. They found that hydrophobic silicate with a high Si/Al ratio is an efficient adsorbent even at low organic concentration. For silicalite with a Si/Al ratio of 1,063, adsorption was 1.12 mmol/g for 3-chlorophenol.
and 0.88 mmol/g for 4-chlorophenol. Additionally (Shu et al. 1997), the smallest cross-sectional distances for phenol (4.3 Å), 2-chlorophenol (2-CP), 3-chlorophenol (3-CP) and 4-chlorophenol (4-CP) (5.0 Å), and 3,5-dichlorophenol (5.3 Å) were calculated using a semi-empirical computational chemistry program. They considered that if the smallest cross-sectional distance is larger than the pore opening, then the molecule cannot enter the pore.

Yogesh et al. (2008) examined the removal of chlorophenol compounds from water using low pressure membranes. The removal performance of the membranes was based primarily on size exclusion. Apart from size exclusion, the polarity and $pK_a$ of the compounds also influence the membrane performance. The molecular size and dipole moments of the respective molecules were calculated using a quantum chemical method. During the calculation of the dipole moment, the possibility of intramolecular hydrogen bonding between the OH group and the chlorine atom in the 2-chlorophenol was examined. The calculated results indicated that the H-bonded conformation was stable compared with the non-H-bonded.

Different studies show a strong dependence of zeolite symmetry on sorbate adsorption. Gelin et al. (1995) and Grahn et al. (2008) studied the adsorption of p-xylene on silicalite-1; they found a distinct step in the p-xylene isotherm at a loading of about half of the saturation capacity ($\sim 0.7$ mmol/g) at temperatures below 353 K. The step in the isotherm was attributed to two different adsorption sites. First, the p-xylene molecules adsorbed in the channel intersections, and then, at higher partial pressures, the p-xylene molecules adsorbed also in the sinusoidal channels. Lee Ahn (1997) carried out simulation of sorption and transport of cyclohexane in the silicalite zeolite. The results show that four cyclohexane molecules can be adsorbed in every unit cell of the zeolite and all cyclohexanes are located in channel intersections of the zeolite.

The dipole moments of chlorophenols reported in Debye units (d.u.) (Budavari et al. 1989) are shown in Table 1 together with their solubility in water, melting points (Morrison & Boyd 1960) and the molecular diameter $R$ (the largest distance between the hydrogen of the OH group and a hydrogen or chlorine in the opposite direction of the aromatic ring (Ar); H…Ar…OH for 2-CP and 3-CP, and Cl…Ar…OH for 4-CP).

This work presents the behaviors of the adsorption of the three chlorophenol isomers, 2-chlorophenol (2-CP), 3-chlorophenol (3-CP), and 4-chlorophenol (4-CP) by silicalite-1 from aqueous solutions. This silicalite-1 sample was derived from rice hull ashes (RHA) (Sánchez-Flores et al. 2008), with a Si/Al ratio of 400; they differ from those materials utilized by Shu et al. (1997).

In particular in the present paper, we will draw a comparison between hydrophobic adsorbents, exemplified by crystalline silicalite-1, obtained from an amorphous silica precursor, and the iso-structural ZSM-5.

The final objective of this work is to propose the mechanisms to explain the adsorption of different chlorophenols by silicalite-1.

### EXPERIMENTAL

#### Material

The silicalite-1 used in this work was obtained from RHA as suggested by Sánchez-Flores et al. (2008). According to the previous characterization of this material, the transmission electron microscopy image of silicalite-1 showed two types of morphology. Besides well-formed and elongated crystals, with a typical length and width of a few micrometres and a thickness of a fraction of micrometre, agglomerates of amorphous nano-particles were also detected. EDS (energy dispersive X-ray

<table>
<thead>
<tr>
<th>Isomer</th>
<th>Dipole moment (d.u.)</th>
<th>$S$ (mmol/L)</th>
<th>Melting point, $K$</th>
<th>$R$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-CP</td>
<td>1.33</td>
<td>2.18</td>
<td>282</td>
<td>0.566</td>
</tr>
<tr>
<td>3-CP</td>
<td>2.1</td>
<td>2.022</td>
<td>306</td>
<td>0.567</td>
</tr>
<tr>
<td>4-CP</td>
<td>2.22</td>
<td>2.10</td>
<td>316</td>
<td>0.632*</td>
</tr>
</tbody>
</table>

Figure 1 | Intersection sites in the structure of silicalite-1.
spectroscopy) chemical analyses showed that large crystals are composed of pure silica, while the amorphous nano-particles contain impurities such as Na, Ca, Mg and K, coming from the original plant tissues (less than 10%) giving a secondary maximum near 3.5 nm in the pore size distribution. The textural analysis, performed by measuring the N2 physical adsorption and by applying the BJH algorithm (Barret et al. 1951), yields a surface area of 232.2 m²/g, micropore volume of 0.065 cc/g calculated by the t-method (Halsey 1972) and a total pore volume of 0.191 cc/g. The surface area value reported in this paper was lower than those obtained by Sánchez et al. (2008) utilizing fume silica (338.2 m²/g) and Davisil grade 634 (377.8 m²/g) both from Aldrich.

The ²⁹Si MAS NMR (magic angle spinning nuclear magnetic resonance) spectra showed eight lines between –117 and –10 ppm corresponding to the orthorhombic phase in well-crystallized material (Sánchez-Flores et al. 2008).

Figure 2 shows the XRD (X-ray diffraction) patterns obtained in the present work, which corresponds to the crystalline structure of silicalite-1 according to the tables of the International Zeolite Association (Treacy & Higgins 2001).

Reagents

Reagent grade chemicals: 4-chlorophenol (4-CP), 3-chlorophenol (3-CP) and 2-chlorophenol (2-CP) were used as received, without further purification; all with 98.0% purity (from Sigma-Aldrich).

ZSM-5 from Zeolites International (Si/Al = 75) was used for the sake of comparison. RHA were obtained by hull calcinations of the Mexican rice grain at 500 °C for 24 h.

Adsorption techniques

Ten millilitres of solutions with different concentrations (Table 2) of chlorophenol were stirred with silicalite-1, prepared from RHA, for 72 h in a Gorbe Parmor Pỳstato model 12050-00 speed shaker equipped with a heating system adjusted to 30 °C, with a rotation speed of 120 rpm. Afterwards, the solid was separated from the liquid by centrifugation. The pH values and the concentrations were determined in the remaining solutions.

Visible–UV spectra of chlorophenols were recorded with a spectrophotometer Perkin Elmer Lambda 10. The maximum absorbance at 274 nm was chosen for quantifying 2-CP and that at 280.6 nm for 3-CP and 4-CP. For the different CP compounds the calibration curves were performed with five different concentrations between 0 and 150 mg/L (or 0 and 1.16 mmol/L). The pH determination was performed with a pH STAT Controller MeterLab PHM 290.

The amount of chlorophenol fixed by silicalite-1 was calculated by determining the difference of concentrations in the original standard and in the equilibrium solutions. The concentrations are expressed in mmol/L (10⁻³ mol/L). The fixation by silicalite-1 is obtained from the following equation:

\[ Q_e = \frac{|C_0 - C_e|V}{M} \]  

where \( Q_e \) is the retention per gram of silicalite-1 at equilibrium (mmol/g), \( V \) is the volume of the solution (L), \( M \) is the weight of silicalite-1 (g), \( C_0 \) and \( C_e \), the initial and equilibrium chlorophenol concentrations (mmol/L).

Characterization

The solid samples utilized for characterization by Fourier transform-infrared (FT-IR) spectrometry were prepared from 100 mg of adsorbent stirred with 100 mL of solution, keeping the operating conditions mentioned above. The samples were dried at room temperature (18 °C) for 3 days. FT-IR spectra were recorded with a Nicolet Nexus 670 spectrometer (Thermo Scientific, Whitman, MA), fitted with cesium iodide optics, giving a 4 cm⁻¹ resolution; 32 scans were accumulated. The samples were prepared using the KBr self-supported pellet technique in the 4,000–400 cm⁻¹ range.
RESULTS AND DISCUSSION

Adsorption

The adsorption at equilibrium increases with the dipole moment of the molecular unit (Figure 3). In the particular case of 4-CP, the concentration in solution was increased up to the onset of the precipitation. The dipole moment is not the sole factor ruling the adsorption. It also depends on the steric constraints that are behind the differences in adsorption, in the same way as for the adsorption of the similar sized xylenes on silicalite-1 (Grahn et al. 2008).

The eventual formation of internal hydrogen bonds between hydroxyl and chlorine was considered because it must be outlined that the formation of an internal H-bond occurs at the expense of the intermolecular bond. The dipole moment is a complex function of the molar charge distribution and the values given in Table 1 are generally accepted (Budavari et al. 1991). The inter- and intra-hydrogen bonds contribute to the total hydrogen bonding. The formation of the intra-species is strongly dependent on the distance OH—Cl, and thus on the geometry compatible with the isomer structure. In the para-isomer, 4-CP, an intra dipole cannot be formed, in opposition to what is observed for 2-CP, where the self-association is much weaker (Yogesh et al. 2008).

The next fundamental question that the present contribution will attempt to answer is about the adsorption sites, knowing that the internal cages are about the size of the molecules.

Keeping the same operating conditions for the isotherm measurements, the effect of the pH was investigated by adjusting the pH of solutions containing 6.69 mmol of

| Table 2 | Adsorption isotherms at 30°C of chlorophenol isomers on silicalite-1 |
|---------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| C_e (mmol/L) | Q_e (mmol/g) [2-CP] | Q_e (mmol/g) [3-CP] | Q_e (mmol/g) [4-CP] | Log C_e | Log Q_e [2-CP] | Log Q_e [3-CP] | Log Q_e [4-CP] |
| 0.0179 | 0.018 | -1.7471 | -1.7474 |
| 0.0192 | 0.037 | -1.7167 | -1.4318 |
| 0.045 | 0.11 | -1.3467 | -0.9586 |
| 0.0521 | 0.091 | -1.2831 | -1.0409 |
| 0.064 | 0.247 | -1.1938 | -0.6073 |
| 0.0646 | 0.11 | -1.1897 | -0.9586 |
| 0.1095 | 0.184 | -0.9605 | -0.7351 |
| 0.135 | 0.332 | -0.8696 | -0.4788 |
| 0.15 | 0.472 | -0.8239 | -0.3260 |
| 0.19 | 0.404 | -0.7212 | -0.3936 |
| 0.2094 | 0.29 | -0.6790 | -0.5376 |
| 0.2126 | 0.368 | -0.6724 | -0.4341 |
| 0.26 | 0.518 | -0.5850 | -0.2856 |
| 0.5 | 0.654 | -0.3010 | -0.1844 |
| 0.5636 | 0.527 | -0.2490 | -0.2781 |
| 0.79 | 0.765 | -0.1023 | -0.1163 |
| 1.37 | 0.9 | 0.13672 | -0.0457 |
| 1.898 | 0.588 | 0.2783 | -0.2306 |

Figure 3 | Correlation between the melting points of chlorophenols, adsorption capacities and their dipole moments.
4-CP per L. Approximately 2 mmol of 4-CP were constantly retained per g. Above pH 8.2, the retention starts dropping.

The experimental results to be discussed in this section are given in Table 2. This table illustrates the paramount importance of the physical properties of the chlorophenol isomers for their retention by silicalite-1. The adsorption isotherm is presented in Figure 4(a). Figure 4(b) shows that the experimental data obey reasonably well the logarithmic expression of the Freundlich adsorption isotherm (Kuleyin 2007):

\[
\log Q_e = \log k + \frac{1}{n} \log C_e
\]  
(2)

The maximum value of \(\log Q_e\) should correspond to \(\log C_e \approx \log S\), the solubility in water.

From the isotherm recorded for the para isomer at the equilibrium concentration \(\log C_e = \log S\) (Table 3) the \(Q_e\) parameter increases slightly.

The extension of the surface areas is variable, depending on the synthesis procedure. It should be pointed out that the external surface of our silicalite-1 is smaller than that reported by Song et al. (2004), but it was assumed that the molecular packing remains the same. Also, according to Song et al. (2004), the preferential adsorption sites on the internal surface are located at the intersections of the channels and the density of channel intersections in silicalite-1 is 0.68 mmol/g, somewhat lower than in ZSM-5.

Table 3 shows the values of \(Q_e\) obtained from the isotherms at \(\log C_e = \log S\), where \(S\) is the solubility given in Table 1. The equilibrium constant (K) indicative of adsorption capacity and the adsorption intensity (1/n) are higher for 3-CP than 2-CP (Table 3).

The density of structural defects, which may also be adsorption sites, has been neglected; therefore, the agreement between the orders of magnitude obtained from the experiments and from the structural predictions of Song et al. (2004) may be considered as satisfactory and as a check of the significance of the detailed isotherms.

The adsorption of chlorophenols may be summarized as follows: the ortho and meta isomer adsorption processes obey the Freundlich expression for heterogeneous surfaces; the adsorption sites are at the channel intersections, as represented in Figure 1, the retention is about 1 mmol/g, at 30 °C.

The behavior of the para isomer is different because the polarity and structural features favor the self-association. As a consequence, at the saturation of the internal adsorption, further adsorption and precipitation are initiated.

### Table 3 | Adsorption parameters, calculated from the logarithmic Equation (2)

<table>
<thead>
<tr>
<th></th>
<th>(\log K)</th>
<th>(K)</th>
<th>(1/n)</th>
<th>(R^2)</th>
<th>(Q_{\text{eq}, S})</th>
<th>(\log S)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-CP</td>
<td>0.03976</td>
<td>1.0959</td>
<td>0.61188</td>
<td>0.810</td>
<td>1.7653</td>
<td>0.3384</td>
</tr>
<tr>
<td>3-CP</td>
<td>-0.14871</td>
<td>0.7100</td>
<td>0.73647</td>
<td>0.8636</td>
<td>1.1926</td>
<td>0.3058</td>
</tr>
<tr>
<td>4-CP</td>
<td>-0.0884</td>
<td>0.8158</td>
<td>0.40983</td>
<td>0.99105</td>
<td>1.105</td>
<td>0.322</td>
</tr>
</tbody>
</table>
The structural similarity of silicalite-1 and ZSM-5 has already been outlined. It was therefore interesting to compare their performances in the adsorption of para-clorophenol. Equal weights were exposed to solutions containing the same 4-CP concentration. After equilibration, analyses reveal that they adsorbed the same amount.

The amorphous silica precursor (RHA) shows much lower adsorption capacities for the chlorophenols than silicalite-1 (Table 4), probably because RHA is an amorphous silica which contains a surface silanol group and therefore is more hydrophilic than silicalite-1 (Sánchez Flores et al. 2007).

Infrared study

Infrared spectra were explored in order to obtain additional information on the differentiation of the behaviors of 2-CP and 4-CP. FT-IR spectra of the adsorbent loaded with 4-CP or 2-CP were recorded in order to identify the functional group playing a role in the adsorption. As polar molecules permeate through the adsorbent, the whole solid, and not only the surface, must be explored. Figure 5 shows the infrared spectra between 2,800 and 3,800 cm\(^{-1}\) of 4-CP and of 2-CP adsorbed on silicalite-1. In this spectral region, there is no contribution of the inorganic framework.

Throughout the spectra, a broad phenol OH stretching vibration is observed (Socrates 2005), centered near 3,500 cm\(^{-1}\), and a doublet of weak C–H stretching bands, at 2,950 and 2,920 cm\(^{-1}\).

2-CP exhibits a strong and narrow OH stretching band at 3,550 cm\(^{-1}\) and a broad band at 3,425 cm\(^{-1}\) while 4-CP exhibits only a broad band near 3,450 cm\(^{-1}\). The interpretation is simple if we assume that the band at 3,550 cm\(^{-1}\) is due to the OH stretching of the internal dipole whereas the broad band, at 3,425 cm\(^{-1}\), witnesses the association by H-bonding with other 4-CP molecules (the spectra of 2-CP and 4-CP in aqueous solution do not show a band in this position; Coblentz Society Collection 2009). The contribution of the OH involved in the internal dipole in 2-CP is formed at the expense of the intermolecular dipole. It explains partially the weakness of the self-association of 2-CP molecules by comparison with the self-association of the 4-CP.

The suggestion by Pimentel & McClellan (1960) that the melting point is a good measurement of molecular association holds for chlorophenols as shown by the correlation between the melting point and the dipole moment in Figure 3.

CONCLUSIONS

At the saturation of the internal sites with 4-CP, the formation of aggregates starts, which promotes the precipitation. The tendency to self-association is weak for 2-CP and 3-CP and the precipitation is delayed.

The fitting of the chlorophenol molecules to the textural peculiarities of silicalite-1 and of its channels plays an important role in the adsorption selectivity.

Table 4 | Comparison between the adsorption of chlorophenols by silicalite-1 and by the silica precursor of silicalite-1, RHA

<table>
<thead>
<tr>
<th>Adsortent Adsorbate</th>
<th>Silicalite-1 C(_0) (mmol/L)</th>
<th>Q(_e) (mmol/g)</th>
<th>RHA C(_0) (mmol/L)</th>
<th>Q(_e) (mmol/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-CP</td>
<td>3.9</td>
<td>1.1</td>
<td>3.9</td>
<td>0.078</td>
</tr>
<tr>
<td>3-CP</td>
<td>15.6</td>
<td>1.2</td>
<td>3.9</td>
<td>0.120</td>
</tr>
<tr>
<td>4-CP</td>
<td>36.6</td>
<td>32.8</td>
<td>3.9</td>
<td>0.147</td>
</tr>
</tbody>
</table>

Figure 5 | FT-IR spectra of 4-CP and 2-CP adsorbed on silicalite-1.
On the surface of RHA the aggregation and the phenomenon of precipitation, as encountered with 4-CP on silicalite-1, are not observed.

ACKNOWLEDGEMENT

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REFERENCES


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