Elimination of isobutyl phenyl propionic acid (Ibuprofen) from wastewater by treated silica gel

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Abstract
The present study deals with the adsorption capabilities of treated silica gel to remove various pharmaceutical compounds from aqueous solutions, like the Isobutylphenylpropionic known as Ibuprofen (IBU) which is an anti-inflammatory drug widely used as antipyretics and analgesics.

In fact, this study showed that Silicagel coated was efficient for the elimination of ibuprofen. The effects of several operating parameters like contacting time, pH and temperature, were also investigated and discussed. The obtained results showed that the highest sorption of ibuprofen onto the considered sorbent took place at low pH values. Also, the addition of KCl amounts into the solutions increased the sorbent retention capacity of IBU at ambient temperature of 20°C.

Keywords: Adsorption; Ibuprofen; Kinetic; Non-steroidal anti-inflammatory; Silica gel —

I. Introduction
Many industrial wastewater effluents contain pharmaceutical pollutants which do have an environmental impact and may cause possible damages to botany and fauna present in aquatic systems (Ternes et al., 2004). One of mostly consumed medicines corresponds to the classification of the Non- Steroidal Anti-Inflammatory Drugs (NSAIDs) with more than 70 million annual prescriptions in the world. For instance, several recent reports have confirmed the presence of the NSAID Ibuprofen (IBU) in effluents of wastewater treatment plants (WTPs) at concentrations ranging between 10 and 169 mg L⁻¹ (Santos et al., 2007).

The removal of IBU from aqueous phases using different supports has been reported in the literature where it has been clearly shown that high costs and difficulties in regeneration of these supports have encouraged researchers to look for new sorbents (Gurses et al. 2004). One can cite the example of Silicagel treatment with suitably chosen polymer, showing several advantages over other commercial-grade adsorbents such as a high adsorption capacity to eliminate different kind of pollutants. However, this property may be influenced by certain operating parameters such as the solution pH which may affect the presence of surface functional groups in IBU molecule and in the sorbents, hence influencing the sorption properties of ibuprofen. Therefore the aim of this work is to investigate the efficiency of alternative Silica gel treated with polymer for the removal of ibuprofen from wastewaters.

II. Materials and methods
A commercial porous silica gel supplied by PROLABO as spherical particles with diameters ranging from 63 to 200 µm, specific area of 500 m²/g and a porous volume of 75 cm³/g. In order to eliminate any possible impurities, a washing with Hydrochloric acid was performed and followed by a rinsing with distilled water and a drying before storage in a desiccator.

The treatment of the dried Silicagel support consisted of a polyaniline coating by means of an in situ polymerization which was carried out according to the following steps:
- Introduction of Aniline (supplied 99.8% pure by ACROS ORGANICS, France) just after a distillation, into a sealed beaker containing, a priori, Ammonium persulphate (supplied by LABOSI, France);
A continuous stirring of the mixture (Aniline, Ammonium persulphate and Silicagel) for about 2h;

- Filtration and washing with Hydrochloric acid of the obtained product;
- Drying of the product at 95°C in a furnace and obtention of a fine powder of a green color confirming the surface deposition of Polyaniline as reported in the literature [Uvdal et al].

The Ibuprofen adsorbate was 99% pure and was supplied by Sigma-Aldrich. Table 1 illustrates its different physico-chemical properties are shown in Figure 1 as follows:

\[
q = \frac{(C_0 - C)}{r} V \quad (1)
\]

where \( q \) is the adsorption capacity (mg agent/g adsorbent), \( C_0 \) and \( C \) are the initial and final adsorbate concentrations, respectively in-(mg/l), \( m \) the mass of adsorbent (g), \( V \) the volume of the solution (l) and \( r \) the solid to liquid ratio (g/l).

### Table 1: Physico-chemical properties of ibuprofen

<table>
<thead>
<tr>
<th>Compound</th>
<th>Molar weight (g mol(^{-1}))</th>
<th>Water solubility (25 °C) (mg dm(^{-3}))</th>
<th>Log Kow</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ibuprofen(IBU)</td>
<td>206.28</td>
<td>21</td>
<td>4.13-4.91</td>
</tr>
</tbody>
</table>

III. Results and discussion

1. Effect of contact time

Figure 2 shows the effect of the contact time on the retention capacity of ibuprofen onto the solid support. A very rapid step was shown just at the beginning where the retention capacity increased sharply due the great availability of vacant sites at the adsorbent surface, and then practically, after 15 min, it remained constant with time, assuming that equilibrium was reached.

2. Effect of initial concentration

The results also showed that that the amount of adsorbed ibuprofen increased with an increase of the initial drug concentration. The effect of the variation of the ibuprofen concentration was important on the retention process. In order to study its effect, concentration values of 4, 8, 12, 16 and 20mg/l were considered. The results obtained are shown in Figure 2 and one can see that the retention process was really influenced by the initial concentration of the drug in the solution. In fact the elevation of the latter generated a rise in the adsorbed amount of the pollutant, while there were free sites on the surface of the adsorbent, the adsorption capacity (retention) increased up to the saturation of these sites.
3. Effect of pH on adsorption
The effect of initial pH was investigated at various values ranging between from 2 to 10 and the results are shown in figure 4. In terms of removal efficiency, 79.88% was reached at pH = 2 and decreased to 46% at pH = 10.

Changes in pH affected the dissociation of the ibuprofen molecule where, according to the dissociation constant of ibuprofen molecule, (pKa = 4.91), more than 50% of the drug compound was expected to be deprotonated. Generally, an increase in the solution pH results in partially or fully deprotonated surface functional groups and thus a loss of positive charge and/or a negative charge build up (Wang et al. 2007). When the sorption occurred above pH = 9 the anionic form of ibuprofen was dominant in solution. From practical application point of view, Silicagel treated with polyaniline, seemed to have good potential to remove higher amounts of ibuprofen from water at acidic pH.

4. Effect of ionic strength on ibuprofen sorption capacity
The effect of salt nature on the removal percentage of ibuprofen is important. Different salts, namely NaCl, KCl and CaCl2 were considered. The results are presented in figure 5 and show that the addition of KCl had a great effect on the retention of IBU. Such behavior was anticipated due to an interaction between the surface and added solutes which may block some of the adsorption active sites for ibuprofen molecules.

5. Effect of temperature on ibuprofen sorption
The effect of temperature on the removal of IBU on treated silica gel treated was investigated at different temperature as shown in figure 6. The removal percentage of IBU decreased from 65.12 to 45%, when the solution temperature increased from 20 to 50°C. Since the adsorption decreased, when the temperature increased, the system was considered to be exothermic.

6. Thermodynamic study
The calculation of thermodynamic parameters is required for the study of the nature of the retention
process and is performed by means of the following relationship:

$$\ln K_D = \frac{\ln Q_e}{C_e} - \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT}$$  \hspace{1cm} (1)$$

with \( R \) the universal gas constant \( (R \approx 8.314 \text{ J/mol K}) \), \( T \) the temperature \( (K) \), \( K_d \) the distribution coefficient, \( Q_e \) the adsorbed quantity onto the solid \( (\text{mg/g}) \), \( C_e \) the concentration at equilibrium \( (\text{mg/l}) \), \( \Delta H^0 \) the standard enthalpy \( (\text{J/mol}) \) and \( \Delta S^0 \) the standard entropy \( (\text{J/mol K}) \).

The values of \( \Delta H^0 \) and \( \Delta S^0 \) were calculated from the slope and intercept of the plot of \( \ln K_D \) versus \( 1/T \) and \( \Delta G^0 \) can be calculated using the following relationship:

$$\Delta G^0 = -RT \ln K_D$$  \hspace{1cm} (2)$$

The results are shown in the following table:

<table>
<thead>
<tr>
<th>Support</th>
<th>( \Delta H ) (kJ/mol)</th>
<th>( \Delta S ) (kJ/mol K)</th>
<th>( \Delta G ) (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Treated Silica gel</td>
<td>-0.007</td>
<td>-0.815</td>
<td>238.8</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>251.00</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>263.22</td>
</tr>
</tbody>
</table>

The positive values of \( \Delta G^0 \) indicate that the adsorption process of ibuprofen is not spontaneous and that the retention process is a chimisorption. The negative values of \( \Delta H^0 \) indicates that the nature of the reaction is exothermic and is expressed by the reduction of the amount adsorbed of ibuprofen with increasing temperature and the positive value of \( \Delta S^0 \) with the support indicates increasing randomness at the solid-solution interface.

7. Adsorption kinetics study

A kinetic study was performed by testing two kinetic models for the obtained experimental data as follows:

a. Pseudo-first-order model: it is described by the following equation:

$$\log (q_e - q_t) = \log (q_e) - k_1 t / 2.303$$  \hspace{1cm} (3)$$

where \( q_e \) and \( q_t \) refer to the amount of ibuprofen adsorbed \( (\text{mg g}^{-1}) \) at equilibrium and at any time, \( t \) \( (\text{min}) \), respectively and \( k_1 \) is the equilibrium rate constant of pseudo first-order adsorption \( (\text{min}^{-1}) \).

b. Pseudo-second-order model: it is represented as:

$$\frac{t}{q_t} = \frac{1}{k_2 Q_e^2} + \frac{t}{q_e}$$  \hspace{1cm} (4)$$

Where \( k_2 \) is the equilibrium rate constant of pseudo-second-order adsorption \( (\text{g mg}^{-1} \text{ min}^{-1}) \). Experimental kinetic data were adjusted according to the indicated models. Table 2 showed that the second order equation model provided the best correlation with experimental results. This fact indicates that the sorption of ibuprofen on adsorbent followed the pseudo-second order kinetics.

<table>
<thead>
<tr>
<th>Model</th>
<th>First order kinetic</th>
<th>Second order kinetic</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( k_1 )</td>
<td>( R^2 )</td>
</tr>
<tr>
<td></td>
<td>( k_2 )</td>
<td>( R^2 )</td>
</tr>
<tr>
<td>Silica gel</td>
<td>0.01329</td>
<td>0.93385</td>
</tr>
</tbody>
</table>

8. Adsorption isotherm

In order to optimize the design of adsorption system of the ibuprofen removal, it was important to establish the most appropriate correlation for the equilibrium curves. These equilibrium adsorption capacity curves can be obtained by measuring the adsorption isotherm of ibuprofen onto adsorbent. Different models of sorption isotherms including Langmuir, Freundlich and BET were tested in the present study, as shown in Table 4. \( Q_e \) is the equilibrium sorbate concentration on the sorbent, \( Q_{\text{max}} \) is the maximum adsorption capacity, \( K_L \) is Langmuir constant, \( K_F \) is Freundlich constant related to the sorption capacity, \( n \) is the heterogeneity factor and \( K_{\text{BET}} \) is BET constant.

A model can be considered the most suitable to satisfactorily describe the sorption process if it provides the highest \( R^2 \). Consequently the high \( R^2 \) (0.995) for the BET model indicates that the adsorption of ibuprofen onto treated Silica gel followed the BET model, confirming that the adsorption was of multilayers.
Table 4: Isotherm constants of the three models

<table>
<thead>
<tr>
<th>Model</th>
<th>Linear form</th>
<th>Constants</th>
<th>Support</th>
</tr>
</thead>
</table>
| Langmuir| \[
\frac{C_e}{q_e} = \frac{1}{K_L} + \frac{1}{Q_m K_L} \]                      | \[ K_L = -5.7943 \]         | Treated    |
|         |                                                                             |                            | Silica gel |
|         |                                                                             | \[ R^2 = 0.99114 \]         |            |
| Freundlich| \[
\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \]                                | \[ K_F = 6.84535 \]         |            |
|         |                                                                             | \[ n_F = -6.36375 \]        |            |
|         |                                                                             | \[ R^2 = 0.9793 \]          |            |
| BET     | \[
\frac{C_e}{q_e(C_0 - C_e)} = \frac{1}{q_m K_{BET} - 1} \left[ \frac{C_e}{C_0} \right] \] | \[ K_{BET} = 0.79337 \]     |            |
|         |                                                                             | \[ q_m = 1.75334 \]         |            |
|         |                                                                             | \[ R^2 = 0.99544 \]         |            |

IV. Conclusion

The removal of ibuprofen from the aqueous solutions through treated Silicagel was considered. The effect of key operating parameters such as the initial pH, the initial drug concentration, the ionic strength and the temperature, on the adsorption capacity was investigated. The adsorption kinetic study of ibuprofen onto Silicagel showed that the process followed a pseudo second order rate. The thermodynamic study confirmed that the retention process was based on chimisorption and that it was not spontaneous with the adsorption of ibuprofen following the BET model.

References

[1]. Ternes ,T.A.,Hermann ,N 2004 ,A rapid method to measure the solid water distribution coefficient (K-d ) for pharmaceutical and musk fragrances in swedge sludge water .Res 38 4075-4084


Structural characteristics of activated carbons and ibuprofen adsorption affected by Bovine serum albumin Langmuir 20(7):2837–2851


