**Removal of pharmaceuticals with supported ionic liquids**

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**Highlights**

* Supported Ionic Liquids are efficient adsorbents for pharmaceuticals.
* Sodium diclofenac, ketoprofen, naproxen and acetylsalicylic acid undergo different adsorption processes onto SILs.
* Different ionic structures as counter ions in SILs lead to different adsorption processes.

**1. Introduction**

The presence of organic pollutants has been shown to have potentially adverse effects on man and the environment. Mainly due to their large worldwide consumption, active pharmaceutical ingredients (APIs) were already found in a wide variety of environmental aqueous samples, in concentrations ranging from ng/L to µg/L. This is due to the inability of current technologies used in sewage treatment plant (STPs) and wastewater treatment plants (WWTPs) to remove such compounds, thus leading to serious environmental and public health concerns after long-term exposures. Therefore, the treatment of water contaminated with these compounds is extremely important.

Ionic liquids (ILs) have a great potential to remove biomolecules from aqueous solutions [1], including pharmaceuticals [2]. Despite the many advantages associated to ILs, their immobilization in materials would overcome some leaching problems. ILs can be immobilized on solid supports by the covalent bonding of the cation, resulting in functionalized materials: supported ionic liquids (SILs). Based on the high potential of SILs in separation/removal techniques and on the health and environmental concerns that we aim to overwhelm, silica based SILs will be investigated to develop an efficient approach to remove pharmaceuticals from aqueous solutions.

**2. Methods**

SILs were obtained as described in the literature [3]. Silica gel 60 was used as supported for SILs synthesis, namely SilPrMImCl, SilPrNEt3Cl, SilPrNBu3Cl SilPrN(C8)3Cl, SilPrNMe2BuCl (Figure 1). Five additional SILs were prepared from SilPrMImCl by anion exchange with the correspondent sodium salts, namely SilPrMImSCN, SilPrMImN(CN)2, SilPrMImTos, SilPrMImMale and SilPrMImNTf2.

**3. Results and discussion**

Adsorption kinetics and adsorption isotherms were performed for sodium diclofenac, ketoprofen, naproxen and acetylsalicylic acid with the synthetized SILs. The supported ionic liquid SilPrMImCl showed to be the most efficient material for the adsorption of sodium diclofenac, ketoprofen and naproxen, being the removal efficiency 91, 51 and 59%, respectively. For sodium diclofenac, the obtained adsorption equilibrium data are well described by the Langmuir or the Freundlich isotherm models, being dependent on the imidazolium supported materials counter ion. A maximum equilibrium concentration of sodium diclofenac in the solid phase of 240 mg.g-1 of adsorbent was obtained with SilPrMImCl. Regarding the ketoprofen and naproxen the obtained adsorption equilibrium data are best described by the Langmuir-Freundlich (or Sips) isotherm model and a maximum equilibrium concentration for these pharmaceuticals of 88 and 41 mgg-1 was obtained with SilPrMImCl.



**Figure 1-** Synthetic route for SilPrMImCl.

In the case of acetylsalicylic acid, the equilibrium concentration of adsorbate in the solid phase decreases in the following sequence of SILs: SilPrNMe2BuCl > SilPrNBu3Cl > SilPrN(C8)3Cl. The obtained adsorption equilibrium data are best described by the Langmuir model with a maximum equilibrium concentration of adsorbate in the solid phase of 220 mg of drug per gram of SilPrNMe2BuCl.

**4. Conclusions**

The synthetized SILs are efficient adsorbents for pharmaceuticals. However, the adsorption mechanisms and maximum equilibrium concentrations depend on the SILs chemical structure and on the drug.

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