It has been recently shown that acid activation enhances the ability of zeolitic tuffs to bind weak organic bases. More specifically, tuff containing acid-resistant zeolites (i.e. clinoptilolite) exhibits higher sorption capacity than chabazite/philippite-rich tuff. Based on the above considerations, we investigated in depth the adsorption behaviour of two pesticides onto acid-activated clinoptilolitic tuff under different experimental conditions. The pesticides simazine and boscalid were chosen based on their different physico-chemical properties, simazine being a very weak organic base ($pK_a=1.6$) of low hydrophobicity ($K_{ow}=126$) whereas boscalid is uncharged in the pH range 2-10 ($pK_a=12.1$) and has a moderate hydrophobic character ($K_{ow}=912$). The acid-activated clinoptilolitic tuff adsorbent was obtained by treating a fixed amount of raw tuff with 0.1M HCl solution for two days.

The results of the experiments indicate that sorption is fast for both pesticides, reaching the equilibrium within hours. The acid treatment significantly improved the sorption capacity of the clinoptilolitic tuff for simazine, increasing the saturation level by over 70 times. In contrast, the sorption of boscalid was barely affected by the treatment. pH, cation exchange type and ionic strength appeared to play a relevant role in the sorption process, whereas the temperature and the specific surface area had no significant influence. Fast kinetics and good sorption capacity suggest that clinoptilolitic tuff, conveniently treated with acids, could be a suitable adsorbent for simazine and similar compounds.

**Key words:** acid activation, adsorption, boscalid, clinoptilolite, simazine

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used material in adsorption studies (Günay et al., 2007; Leone et al., 2013a; Mihaly-Cozmuta et al., 2014; Qian et al., 2009; Russo et al., 2014). It has been shown that the adsorption efficiency of raw clinoptilolite towards certain compounds can be enhanced by modifying its surface properties. This can be achieved, for example, by grafting (Akgül, 2014), surfactant interaction (de Gennaro et al., 2014) or association with suitable molecules (Leone et al., 2013b; Zaremotlagh et al., 2014).

Other studies have focused on the acid activation of clinoptilolite. In particular, Salvestrini et al. (2010) have found in an exploratory investigation that acid activation of clinoptilolite increases its adsorption capacity for weak organic bases. The higher adsorption efficiency of clinoptilolite with respect to other natural zeolites tested (phillipsite and chabazite) mainly depends on the higher tolerance to the acid treatment, while preserving elevated cation-exchange capacity. Although the positive effect of the acid activation on the adsorption of weak organic bases has been clearly established, some aspects of the process still remain to be elucidated. Based on the above considerations, in order to gain deeper insight into the potential applicability of acid-activated clinoptilolite for water remediation, in the present work we investigated the adsorption properties of this zeolite in different cationic-form and under different conditions of ionic strength, temperature, dissolved organic matter and pH. Two pesticides found in natural water (Ahrens et al., 2015; Lapworth et al., 2015; Reilly et al., 2012; Russo et al., 2014). It has been shown that the adsorption efficiency of raw clinoptilolite (hereafter referred to as H-CPL) was washed with Milli-Q water until no significant difference was observed in the conductance and pH of two sequential washing steps. Finally, H-CPL was collected by centrifugation and dried at 40 °C.

CPL and H-CPL were converted into their Na-exchanged (Na-CPL and Na-H-CPL, respectively) and Ca-exchanged (Ca-CPL and Ca-H-CPL, respectively) forms by contact with 3M solution of NaCl or CaCl2, respectively, for 1 day (w/w ratio 1:10). The procedure was repeated several times with fresh solutions until pH and conductivity were stabilized.

2.3. Adsorbent characterization

IR analysis of the adsorbent was performed by a Spectrum GX Perkin Elmer FT-IR spectrometer. Suitable specimens for the KBr wafer procedure were obtained by diluting 0.5 mg of sample in 95 mg of finely powdered KBr. Specific surface areas (SSA) of the adsorbents were determined according to the BET method.

The measurements were performed using a Micrometrics ASAP 2010 volumetric adsorption apparatus. Zeta potential of the materials was determined using Zetasizer 2000-Malvern Instruments.

2.4. Adsorption experiments

Adsorption measurements were carried out by batch method at different temperatures (15, 25 and 45 °C). Different amounts of each adsorbent (0.5-10 mg) were contacted with 1 mL of pesticide solution (concentration range 1.5-5 mg L⁻¹ and 0.5-3 mg L⁻¹ for simazine and boscalid, respectively) and kept under stirring on an orbital shaker at 120 rpm for 2 days. At programmed times, the samples were centrifuged for 1 min at 13000 rpm and then, a small aliquot of the supernatant was collected and analyzed by HPLC.

| Table 1. Physicochemical properties of simazine and boscalid |
|------------------------|-----------------|-----------------|-----------------|---------------------|-----------------|
| **Formula**            | **MW (g mol⁻¹)**| **Kow**         | **pKₐ**         | **Vapor pressure at 25°C (torr)** | **Water solubility at 20°C (mg L⁻¹)** | **Stability in water (pH 7)** |
| Simazine               | C₃H₄ClN₁       | 201.66          | 126*            | 1.6*                | 6.1×10⁷*           | 5.0             | Stable*          |
| Boscalid               | C₁₉H₁₂Cl₂N₂O    | 343.21          | 912*            | 12.1*               | 1.5×10⁶*           | 4.6*            | Stable*          |

* Obtained from http://www.epa.gov/pesticides; * Obtained from the chemicalize.org database by ChemAxon (http://www.chemicalize.org)
HPLC analyses were performed using a chromatographic Waters system consisting of 515 HPLC pumps and a 2487 dual λ absorbance detector, equipped with a C18 reversed-phase column TC-18(2) Agilent (4.6 × 250 mm, 5μm i.d.). Simazine and boscalid were eluted by a CH3CN(50%)/H2O(50%) isocratic method with a flow rate of 1 mL min⁻¹ and detected at wavelengths of 220 and 260 nm, respectively. Pesticide adsorption was estimated by comparing its concentration in solution before and after contact with the adsorbent.

Competitive adsorption between simazine and boscalid was investigated by adding 10 mg of adsorbent to aqueous solutions containing fixed amounts of one pesticide but different amounts of the other pesticide. Samples were analyzed as described above for single-component adsorption experiments.

Desorption experiments were carried out according to the following procedure. For a few samples, after adsorption analysis, one-half volume of solution was replaced by an equal volume of an adsorbate-free solution. Afterwards, the samples were stirred till the attainment of equilibrium (about 5 h) and then analyzed for determining the new adsorption level. The whole procedure was repeated four times.

3. Results and discussion

3.1. Adsorbent characterization

Comparison of FT-IR spectra for raw (CPL) and acid-activated (H-CPL) clinoptilolitic tuff reveals the decrease of the band intensity at 609 cm⁻¹ (see Fig. 1) which reflects the dealumination and the loss of crystallinity of the sample after the acid treatment (Salvestrini et al., 2010).

However, in agreement with the high Si/Al ratio of CPL, this decrease is small suggesting that CPL can be effectively acid-activated while preserving to a large extent its structure. Destructuration of zeolite is accompanied by the increase of its specific surface area (SSA, see Table 3).

The negative charge of the adsorbent decreases with pH (see zeta potential data in Table 3) consistently with previously published data on clinoptilolite (Ersoy and Çelik, 2002; Huang et al., 2013).

3.2. Adsorption kinetics

The rate of adsorption of simazine and boscalid onto acid-activated clinoptilolite (H-CPL) is fast for all the experimental conditions tested. The pesticides uptake occurs to a large extent in the early stages of the process and equilibrium is achieved within 5 and 2 hours for simazine and boscalid, respectively.

A typical adsorption kinetic profile for simazine and boscalid is reported in Fig. 2. The ordinate \( q \) in Figure denotes the adsorption amount of pesticide (mmol) per mass of adsorbent (kg) at any time.

3.3. Adsorption isotherms

Figs. 3a and 3b show the adsorption isotherms of simazine and boscalid at \( T = 25^\circ\text{C} \) onto H-CPL and, for comparison, onto the untreated tuff (CPL). Adsorption experiments carried out at 15°C and 45°C, gave similar results (data not shown), suggesting that temperature has no significant effects on the adsorption process.

Fig. 1. FT-IR spectra of natural (CPL) and acid-activated (H-CPL) clinoptilolite
The curves in Fig. 3a were obtained by fitting the experimental data to the Langmuir model (Eq. 1), where $q$ (mmol kg$^{-1}$) is the adsorption amount per mass of adsorbent at equilibrium, $q_m$ (mmol kg$^{-1}$) is the maximum adsorption capacity, $K_{sim}$ (L mmol$^{-1}$) is the Langmuir equilibrium constant and $C$ (mmol L$^{-1}$) is the pesticide aqueous concentration at equilibrium.

$$q_{sim} = q_m K_{sim} C_{sim} / (1 + K_{sim} C_{sim})$$  \hspace{1cm} (1)

The estimates of $K_{sim}$ and $q_m$ for the adsorption of simazine onto H-CPL are $685 \pm 95$ L mmol$^{-1}$ and $1.55 \pm 0.04$ mmol kg$^{-1}$, respectively. As it can be seen from Fig. 3a, the acid treatment significantly increases the adsorptive capacity of CPL. As a result of the acid activation, the saturation level of CPL increases by over 70 times. As regards boscalid (Fig. 3b), its adsorption onto natural CPL is higher than that of simazine. Moreover, the uptake of boscalid is barely affected by the acid treatment of the adsorbent as the adsorption onto H-CPL is only about 25% higher than that on CPL. Both the isotherms shown in Fig. 3b were found to be linear indicating that H-CPL and CPL exhibit constant affinity toward boscalid in the range of concentration investigated.

Accordingly, experimental data displayed in Figure, were modelled using a partitioning-like model (Eq. 2, linear equation), where $K'$ (L kg$^{-1}$) is the linear partitioning constant.

$$q_{bos} = K' C$$  \hspace{1cm} (2)

The values of $K'$ for H-CPL and CPL, determined by using Eq.(2), are 29.2 $\pm$ 0.7 L kg$^{-1}$ and 16.9 $\pm$ 0.7 L kg$^{-1}$, respectively.

To examine whether the adsorption process is reversible, adsorption equilibrium data of simazine and boscalid after sequential desorption steps were compared to the adsorption isotherms calculated from Fig. 3.

The results of these experiments are presented in Figs. 4a and 4b. The good agreement of the isotherms with the data suggests that the adsorption process for both simazine and boscalid is fully reversible. In order to ascertain possible competitive effects on adsorption, binary systems consisting of simazine and boscalid were also investigated. The extended Langmuir equation in the form of Eqs. (3-4) was used for this purpose, where $K_{sim}$ and $q_m,sim$ have been already calculated (Eq. 1), whereas $K_{bos}$ and $q_m,bos$ denote the boscalid Langmuir parameters (Sismanoglu et al., 2010).

$$q_{sim} = q_{m,sim} K_{sim} C_{sim} / (1 + K_{sim} C_{sim} + K_{bos} C_{bos})$$  \hspace{1cm} (3)

$$q_{bos} = q_{m,bos} K_{bos} C_{bos} / (1 + K_{bos} C_{bos} + K_{sim} C_{sim})$$  \hspace{1cm} (4)
Eqs. (3–4) are valid under the assumption that single component adsorption isotherm is described by the Langmuir model, all adsorbent sites are equivalent, each site can hold at most one molecule of simazine or boscalid and there are no interactions between adsorbate molecules.

As discussed above, the boscalid isotherm is far below the saturation level not allowing to experimentally determine $K_{bos}$ and $q_{m,bos}$. However, if simazine and boscalid compete for the same site, we can assume that they would reach at saturation the same surface coverage, thus implying that Eq. (5) can be applied, where $A_{sim}$ and $A_{bos}$ are the surface areas occupied per molecule of simazine and boscalid, respectively.

$$q_{m,bos} = q_{m,sim} A_{sim} / A_{bos}$$  \hspace{1cm} (5)

Under this hypothesis, $K_{bos}$ can be evaluated using the relationship (6).

$$K_{bos} = K' q_{m,bos}$$  \hspace{1cm} (6)

Eq. (6) can be derived considering that, at low solute concentration, the Langmuir equation reduces to Eq. (7).

$$q_{bos} = q_{m,bos} K_{bos} C_{bos} / (1 + K_{bos} C_{bos})$$

$$\approx q_{m,bos} K_{bos} C_{bos} = K' C_{bos}$$  \hspace{1cm} (7)

It follows that the values of $K_{bos}$ and $q_{m,bos}$ are $31 \pm 10$ L mmol$^{-1}$ and $1.05 \pm 0.09$ mmol kg$^{-1}$, respectively.

Figs. 5a and 5b show the experimental and the calculated adsorption isotherms of simazine and boscalid in binary systems by using Eq. (3) and (4), respectively.

In the same figures, for comparison purposes, the calculated single component isotherms are also reported. Single and simulated dual-component isotherms of simazine (Fig. 5a) are almost coincident because of the much lower adsorption affinity of
boscalid with respect to that of simazine (see $K_{sim}$ and $K_{bos}$ values).

For this reason, competitive adsorption can not be excluded a priori but in any case its possible effect is significantly small and negligible.

As regards boscalid (Fig. 5b), it can be observed that the experimental data in binary system are in good agreement with the simulated dual-component model indicating that boscalid adsorption is negatively affected by the presence of simazine.

3.4. Effect of exchangeable cations, ionic strength and dissolved organic matter

The role of the exchangeable cations in the adsorption process was investigated by using in some experiments the Na-exchanged and the Ca-exchanged form of the parent materials. Fig. 6 shows the adsorption isotherms of simazine onto H-CPL in its sodic- (Na-H-CPL) and calcic-form (Ca-H-CPL). The replacement of H$^+$ with Na$^+$ significantly decreases the adsorption performance of the adsorbent: the maximum adsorption capacity of Na-H-CPL is about 10 times lower than that of H-CPL. Nonetheless, it is interesting to note that the adsorption efficiency of Na-H-CPL is higher than that of CPL (see Fig. 3a).

In Fig. 6 is also reported the Ca-H-CPL isotherm. As a result of the calcium treatment, the adsorption capacity of Ca-H-CPL for simazine is even slightly lower than that of CPL.

The effect of the exchangeable cations on boscalid isotherms is less marked but follows a similar pattern. For the sake of brevity these results are not displayed.

Fig. 6. Adsorption isotherms of simazine onto Na-H-CPL (●), Ca-H-CPL (■)

The effect of the presence of electrolytes was investigated on H-CPL by varying the ionic strength of the solution using NaCl or CaCl$_2$. The ionic strength values selected fall in the range of values commonly found in river waters (Berner and Berner, 1987). The results of these experiments are reported in Table 2. As can be seen from the Table, the presence of salts reduces the simazine uptake for all the experimental conditions tested, while boscalid is not significantly affected. More specifically Ca$^{2+}$ has a greater detrimental impact than Na$^+$ on simazine adsorption. Adsorption capacity of H-CPL decreases up to 68% in the presence of 0.48 mM CaCl$_2$.

In some adsorption experiments, simulated natural water samples containing humic acids at concentrations normally found in river water (Salvestrini, 2013; Salvestrini et al., 2008), were used to elucidate the influence of dissolved organic matter on the process. The results (Table 2) reveal that the adsorption of both simazine and boscalid is not influenced by humic acids; the decrease of simazine adsorption with respect to the reference sample (pure water) is mainly ascribable to the presence of salts.

3.5 Effect of pH and SSA

To gain a better understanding of the role of exchangeable cations in the process, we report in Table 3 the adsorption of simazine and boscalid as a function of pH and of the specific surface area (SSA).

As can be seen from Table 3, adsorption of simazine is negligible at pH > 8 whereas it dramatically increases at lower pH up to 1.4 mmol kg$^{-1}$. It is interesting noting that the effect of pH on the adsorption of simazine onto clinoptilolite differs from that observed with other acid-activated zeolites.

For example, Sannino et al. (2012) found that the adsorption of simazine onto zeolite H-Y is low at acidic pH, increases up to pH 6.5 and then drastically decreases at higher pH. According to the authors, the uptake of simazine likely involves a typical acid-base reaction. Adsorption occurs most favourably at pH where the acid sites of zeolite Y are not neutralized thus promoting acid-base reaction with uncharged simazine.

In order to understand the mechanism by which simazine adsorbs onto clinoptilolite, we examined the SSA of the adsorbents employed in this study. It is expected that the acid treatment positively affects the adsorption properties of clinoptilolite as it leads to destructuration of the zeolite and thus enhances the available surface area for pesticides uptake (Paul et al., 2010). However, in contrast to the above cited work, we found that the increased SSA, subsequent to the acid-activation, plays a marginal role in the simazine uptake. Indeed, as can be seen from Table 3, the adsorption capacity of Ca-H-CPL is lower than that of CPL, although the former material has twice the SSA of the latter. Moreover, when acid-activated clinoptilolite is converted into its sodic- or calcic-form, it loses most of its adsorption capacity while preserving its native SSA. The replacement of H$^+$ with Na$^+$ or Ca$^{2+}$ is also accompanied by a raise of pH from 4.3 to 7.5 and 9.7, respectively, suggesting that the type of exchangeable cation is a crucial factor for the adsorption process.
Adsorption of simazine and boscalid onto acid-activated natural clinoptilolite

Table 2. Effect of the aqueous phase composition on the adsorption of simazine and boscalid

<table>
<thead>
<tr>
<th>HCO₃⁻ (mM)</th>
<th>NaCl (mM)</th>
<th>CaCl₂ (mM)</th>
<th>Humic acid (mg L⁻¹)</th>
<th>Simazine uptake (%)ᵃ</th>
<th>Boscalid uptake (%)ᵃ</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.85</td>
<td>1.2</td>
<td>-</td>
<td>-</td>
<td>85</td>
<td>101</td>
</tr>
<tr>
<td>-</td>
<td>0.08</td>
<td>-</td>
<td>-</td>
<td>83</td>
<td>99</td>
</tr>
<tr>
<td>-</td>
<td>0.7</td>
<td>-</td>
<td>-</td>
<td>89</td>
<td>101</td>
</tr>
<tr>
<td>-</td>
<td>1.3</td>
<td>-</td>
<td>-</td>
<td>88</td>
<td>108</td>
</tr>
<tr>
<td>0.85</td>
<td>0.54</td>
<td>0.04</td>
<td>-</td>
<td>78</td>
<td>99</td>
</tr>
<tr>
<td>-</td>
<td>-</td>
<td>0.07</td>
<td>-</td>
<td>79</td>
<td>101</td>
</tr>
<tr>
<td>-</td>
<td>-</td>
<td>0.23</td>
<td>-</td>
<td>78</td>
<td>98</td>
</tr>
<tr>
<td>-</td>
<td>-</td>
<td>0.48</td>
<td>-</td>
<td>68</td>
<td>96</td>
</tr>
<tr>
<td>0.85</td>
<td>0.54</td>
<td>0.04</td>
<td>1</td>
<td>81</td>
<td>100</td>
</tr>
<tr>
<td>0.85</td>
<td>0.54</td>
<td>0.04</td>
<td>5</td>
<td>82</td>
<td>100</td>
</tr>
<tr>
<td>0.85</td>
<td>0.54</td>
<td>0.04</td>
<td>10</td>
<td>80</td>
<td>101</td>
</tr>
</tbody>
</table>

ᵃ Percentage respect to the adsorbed amounts by H-CPL sample in pure water.

Table 3. Adsorption of simazine and boscalid as a function of pH

<table>
<thead>
<tr>
<th>Adsorbent type</th>
<th>SSA (m² g⁻¹)</th>
<th>pH</th>
<th>Zeta potential (mV)</th>
<th>Simazine uptake (mmol kg⁻¹)</th>
<th>Boscalid uptake (mmol kg⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H-CPL</td>
<td>42</td>
<td>4.3</td>
<td>-13</td>
<td>1.4</td>
<td>0.22</td>
</tr>
<tr>
<td>Na-H-CPL</td>
<td>44</td>
<td>7.5</td>
<td>-32</td>
<td>0.4</td>
<td>0.17</td>
</tr>
<tr>
<td>Na-CPL</td>
<td>22</td>
<td>8.2</td>
<td>-38</td>
<td>0.023</td>
<td>0.14</td>
</tr>
<tr>
<td>CPL</td>
<td>23</td>
<td>8.7</td>
<td>-37</td>
<td>0.023</td>
<td>0.14</td>
</tr>
<tr>
<td>Ca-H-CPL</td>
<td>44</td>
<td>9.7</td>
<td>-41</td>
<td>0.019</td>
<td>0.13</td>
</tr>
</tbody>
</table>

The above considerations lead us to believe that the adsorption behaviour of simazine can be related to its ionizability. The maximum adsorption capacity for simazine is achieved at low pH, where the compound is partially protonated (pKₐ = 1.6). At higher pH, uncharged simazine dominates over its protonated form leading to a marked decrement in the solute uptake.

The foregoing considerations suggest that low-energy interactions, i.e. electrostatic interactions, are the most responsible for the adsorption of simazine onto the clinoptilolitic tuff. This hypothesis is further supported by desorption experiments (Fig. 4a) which indicate that the process is fully reversible and by the absence of changes in the adsorption capacity within the range of temperature explored (15 °C - 45 °C, data not shown).

As with simazine, the adsorption of boscalid is not affected by temperature and is reversible (see Fig. 4b). As can be seen from Table 3, the adsorption of boscalid at high pH (>8) is higher than that of simazine. In such conditions, both boscalid and simazine are undissociated (see pKa values), thus suggesting that their adsorption behaviour is mainly related to their different hydrophobicity.

The small but significant increase in the boscalid adsorption at acidic pH, may reflect an increased hydrophobicity of the adsorbent with decreasing pH, as suggested by zeta potential data (see table 3) which indicate a decrease in the negative charge of the adsorbent. The increased hydrophobicity of the adsorbent enhances the hydrophobic interactions between boscalid and clinoptilolite, thus promoting the adsorption of the pesticide.

4. Conclusions

In the present work the effect of the acid-activation of clinoptilolite on the adsorption of simazine and boscalid was studied under different experimental conditions. The results indicate that the acid treatment significantly enhances the adsorption capacity of simazine whereas it has little effect on the adsorption of boscalid.

At higher pH values, boscalid is adsorbed to a greater extent than simazine in line with its higher hydrophobic character. Conversely, at lower pH (i.e. when the surface of clinoptilolite is H⁺-enriched) simazine, being a very weak organic base, undergoes appreciable protonation which leads to its enhanced adsorption via electrostatic interactions.

References


