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## ADSORPTION OF SIMAZINE AND BOSCALID ONTO ACID-ACTIVATED NATURAL CLINOPTILOLITE

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### Abstract

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/phillipsite-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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### 1. Introduction

Adsorption is one of the most effective method for water and wastewater treatment (Abdulla et al., 2013; Dabioch et al., 2013; Krishnaiah et al., 2013; Lazar et al., 2015; Ma et al., 2013; Taha et al., 2014). Among adsorbents, activated carbon is very often used for removing organic molecules as well as certain metal and inorganic molecules because of its high internal surface (between 500 - 1500 m<sup>2</sup> g<sup>-1</sup>) which makes activated carbon ideal for adsorption technique.

However, activated carbon does suffer from a number of limitations mainly related to the risk of

fouling, especially when the water stream to be treated has high suspended solids content, and to the high cost of production and regeneration (Salam et al., 2011).

For this reason, over recent years, there has been a growing interest in the development of alternative adsorbents to activated carbon.

Natural zeolites are promising materials for using in water purification technologies because of their high cation exchange capacity and microporosity. They are aluminosilicate minerals which are both environmentally acceptable and easily available all over the world. Among them, clinoptilolite is one of most abundant and frequently

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used material in adsorption studies (Günaya 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; Wilson et al., 2011), namely simazine and boscalid, were selected for the adsorption experiments.

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 ( $K_{OW} = 912$ ).

## 2. Materials and methods

### 2.1. Reagents

Simazine, boscalid, humic acids and all the other chemicals used in this study were purchased from Sigma-Aldrich. The main physicochemical properties of simazine and boscalid are reported in Table 1.

### 2.2. Adsorbent

A tuff sample rich in clinoptilolite (79%) was used for the adsorption experiments. The sample,

designated as CPL, came from the sedimentary formation of Eskişehir (Anatolia, Turkey). Non-zeolitic phases included opal (15%), quartz (1%) and feldspar (5%). A detailed description of the chemical composition of CPL is reported elsewhere (Capasso et al., 2007).

Acid activation of CPL was obtained according to the procedure optimized in a previous work (Salvestrini et al., 2010). In short, 5g CPL sample was contacted in glass flasks with 500 mL of 0.1M HCl solution and kept under continuous stirring for 2 days. Afterwards, the acid-activated solid (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 CaCl<sub>2</sub>, 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<sup>-1</sup> and 0.5-3mg L<sup>-1</sup> 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 <sup>-1</sup> )	K <sub>OW</sub>	pK <sub>a</sub>	Vapor pressure at 25°C (torr)	Water solubility at 20°C (mg L <sup>-1</sup> )	Stability in water (pH 7)
Simazine	C <sub>7</sub> H <sub>12</sub> ClN <sub>5</sub>	201.66	126 <sup>a</sup>	1.6 <sup>a</sup>	6.1×10 <sup>-9a</sup>	5.0 <sup>a</sup>	Stable <sup>a</sup>
Boscalid	C <sub>18</sub> H <sub>12</sub> Cl <sub>2</sub> N <sub>2</sub> O	343.21	912 <sup>a</sup>	12.1 <sup>b</sup>	1.5×10 <sup>-8a</sup>	4.6 <sup>a</sup>	Stable <sup>a</sup>

<sup>a</sup>Obtained from <http://www.epa.gov/pesticides/>; <sup>b</sup>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  $\lambda$  absorbance detector, equipped with a  $C_{18}$  reversed-phase column TC-18(2) Agilent ( $4.6 \times 250$  mm,  $5\mu\text{m}$  i.d.). Simazine and boscalid were eluted by a  $\text{CH}_3\text{CN}(50\%)/\text{H}_2\text{O}(50\%)$  isocratic method with a flow rate of  $1 \text{ mL min}^{-1}$  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.

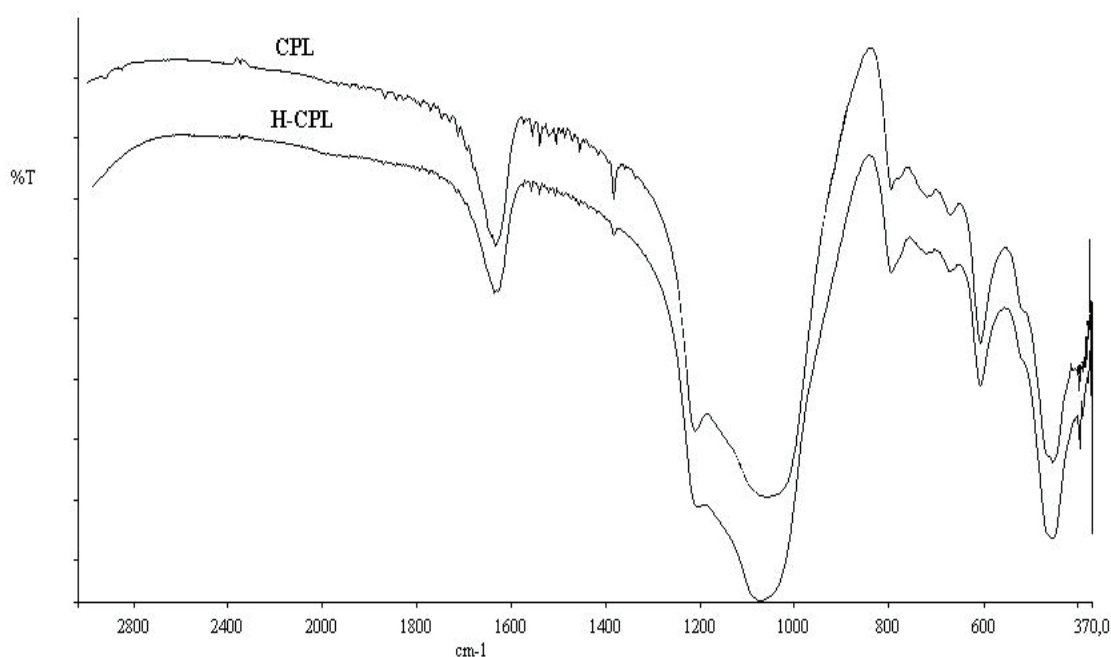
Competitive adsorption between simazine and boscalid was investigated by adding 10 mg of adsorbent to aqueous solutions containing fixed amounts of one pesticide but different amounts of the other pesticide. Samples were analyzed as described above for single-component adsorption experiments.

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  $609 \text{ cm}^{-1}$  (see Fig. 1) which reflects the dealumination and the loss of crystallinity of the sample after the acid treatment (Salvestrini et al., 2010).



**Fig. 1.** FT-IR spectra of natural (CPL) and acid-activated (H-CPL) clinoptilolite

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).

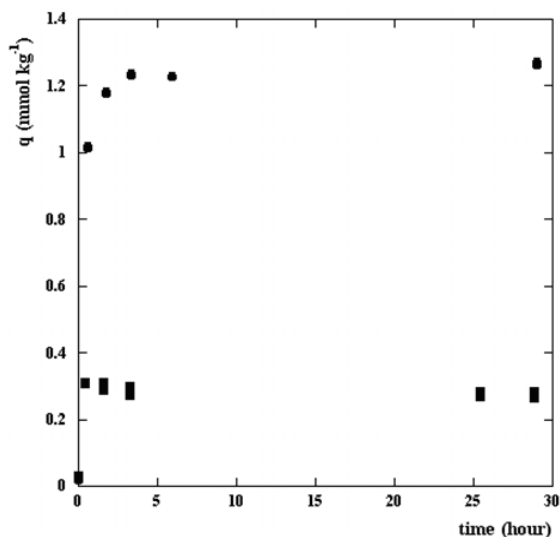
#### 3.2. Adsorption kinetics

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  $15^\circ\text{C}$  and  $45^\circ\text{C}$ , gave similar results (data not shown), suggesting that temperature has no significant effects on the adsorption process.



**Fig. 2.** Adsorption kinetics of simazine (●) and boscalid (■) onto H-CPL. Experimental conditions: T = 25°C; initial simazine concentration = 3.8 mg L<sup>-1</sup>; initial boscalid concentration = 3.0 mg L<sup>-1</sup>; mass of adsorbent = 10 mg; volume of solution = 1 mL

The curves in Fig. 3a were obtained by fitting the experimental data to the Langmuir model (Eq. 1), where  $q$  (mmol kg<sup>-1</sup>) is the adsorption amount per mass of adsorbent at equilibrium,  $q_m$  (mmol kg<sup>-1</sup>) is the maximum adsorption capacity,  $K_{sim}$  (L mmol<sup>-1</sup>) is the Langmuir equilibrium constant and  $C$  (mmol L<sup>-1</sup>) is the pesticide aqueous concentration at equilibrium.

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

The estimates of  $K_{sim}$  and  $q_m$  for the adsorption of simazine onto H-CPL are  $685 \pm 95$  L mmol<sup>-1</sup> and  $1.55 \pm 0.04$  mmol kg<sup>-1</sup>, 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.

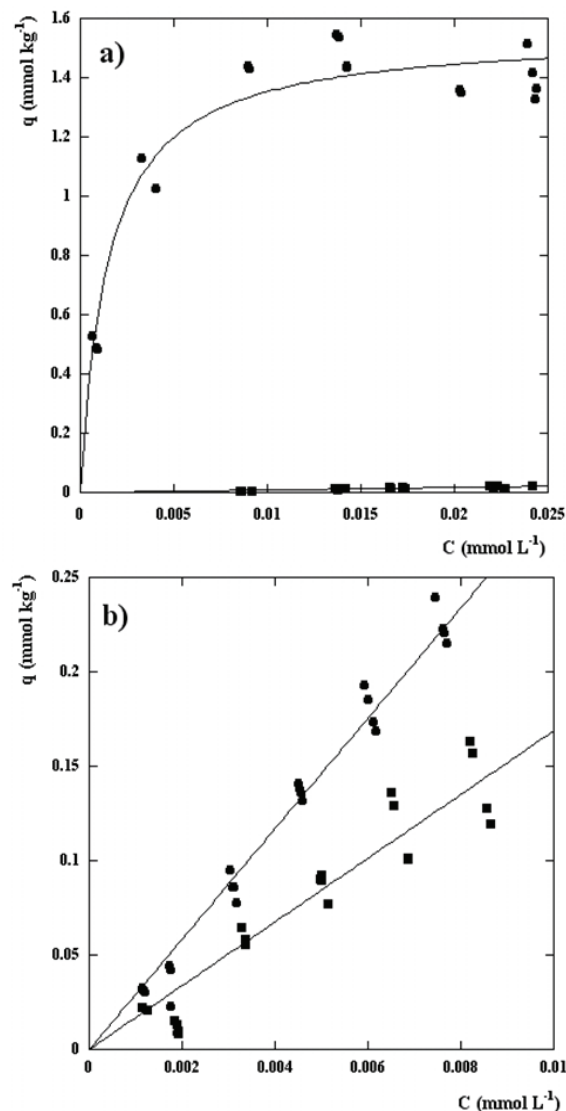
Accordingly, experimental data displayed in Figure, were modelled using a partitioning-like model (Eq. 2, linear equation), where  $K'$  (L kg<sup>-1</sup>) is the linear partitioning constant.

$$q_{bos} = K' C \quad (2)$$

The values of  $K'$  for H-CPL and CPL, determined by using Eq.(2), are  $29.2 \pm 0.7$  L kg<sup>-1</sup> and  $16.9 \pm 0.7$  L kg<sup>-1</sup>, 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.



**Fig. 3.** Adsorption isotherms of simazine (a) and boscalid (b) onto H-CPL (●) and CPL (■) at T = 25°C

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).

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

$$q_{bos} = q_{m,bos} K_{bos} C_{bos} / (1 + K_{bos} C_{bos} + K_{sim} C_{sim}) \quad (4)$$

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.

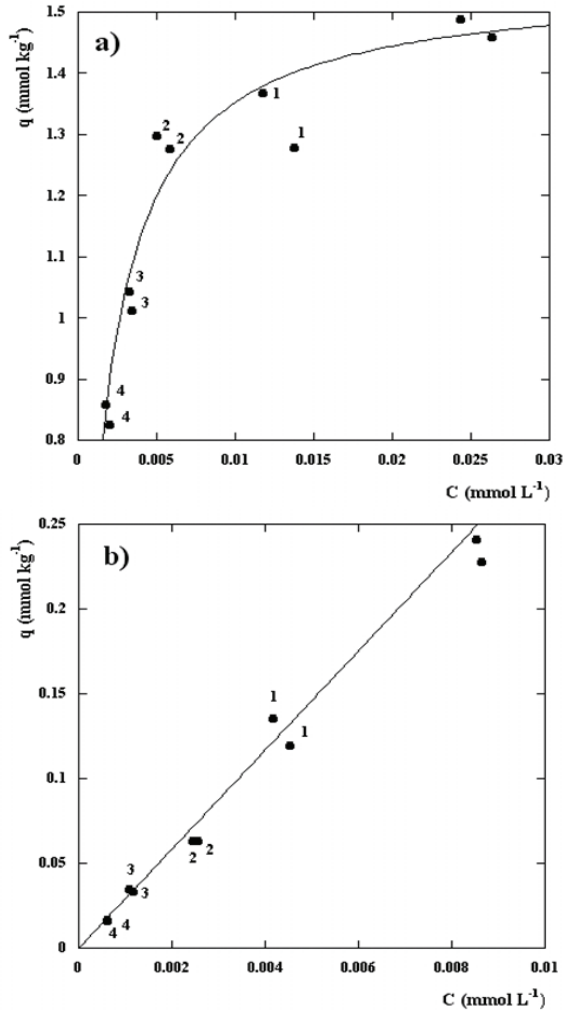


Fig. 4. Comparison between adsorption equilibrium data of simazine (a) and boscalid (b) after desorption and the calculated adsorption isotherm (numbers in Figure refer to four sequential desorption steps)

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.

$$q_{m,bos} = q_{m,sim} A_{sim} / A_{bos} \quad (5)$$

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

$$K_{bos} = K' q_{m,bos} \quad (6)$$

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

$$q_{bos} = q_{m,bos} K_{bos} C_{bos} / (1 + K_{bos} C_{bos}) \quad (7)$$

$$\approx q_{m,bos} K_{bos} C_{bos} = K' C_{bos}$$

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

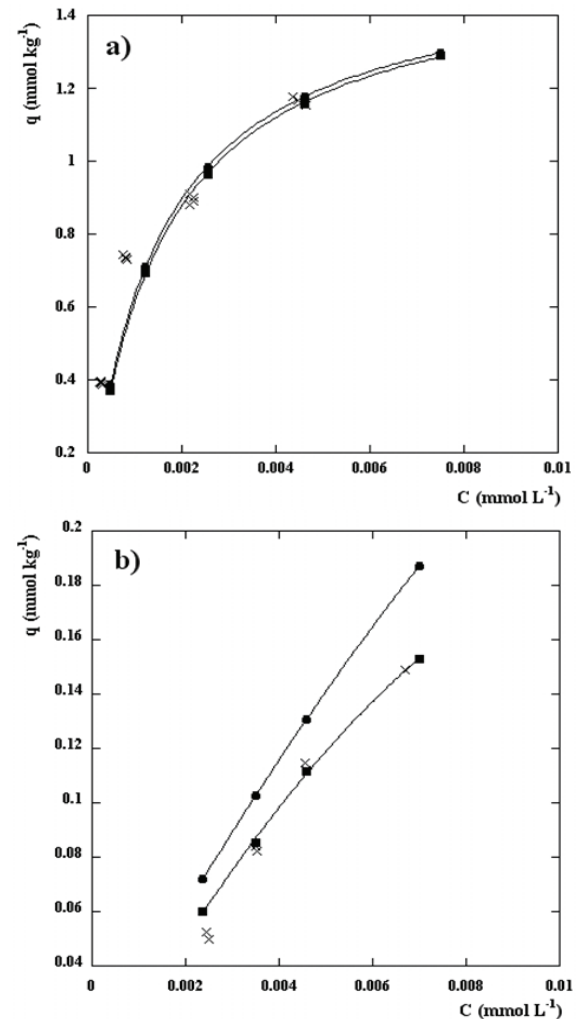


Fig. 5. Adsorption of simazine (a) and boscalid (b) onto H-CPL in binary system; (x) = experimental data; (■) = theoretical dual-component isotherm data; (●) = theoretical mono-component isotherm data

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.

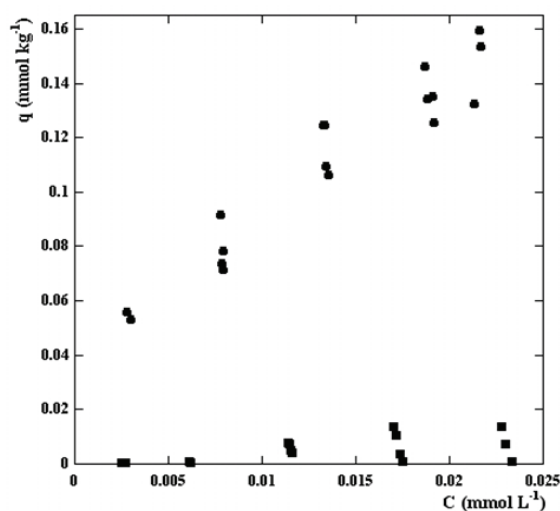


Fig. 6. Adsorption isotherms of simazine onto Na-H-CPL (●), Ca-H-CPL (■)

The effect of the presence of electrolytes was investigated on H-CPL by varying the ionic strength of the solution using NaCl or CaCl<sub>2</sub>. 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<sup>2+</sup> has a greater detrimental impact than Na<sup>+</sup> on simazine adsorption. Adsorption capacity of H-CPL decreases up to 68% in the presence of 0.48 mM CaCl<sub>2</sub>.

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<sup>-1</sup>. 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 deconstruction 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.

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

$HCO_3^-$ (mM)	NaCl (mM)	CaCl <sub>2</sub> (mM)	Humic acid (mg L <sup>-1</sup> )	Simazine uptake (%) <sup>a</sup>	Boscalid uptake (%) <sup>a</sup>
0.85	1.2	-	-	85	101
-	0.08	-	-	83	99
-	0.7	-	-	89	101
-	1.3	-	-	88	108
0.85	0.54	0.04	-	78	99
-	-	0.07	-	79	101
-	-	0.23	-	78	98
-	-	0.48	-	68	96
0.85	0.54	0.04	1	81	100
0.85	0.54	0.04	5	82	100
0.85	0.54	0.04	10	80	101

<sup>a</sup> 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

Adsorbent type	SSA (m <sup>2</sup> g <sup>-1</sup> )	pH	Zeta potential (mV)	Simazine uptake (mmol kg <sup>-1</sup> )	Boscalid uptake (mmol kg <sup>-1</sup> )
H-CPL	42	4.3	-13	1.4	0.22
Na-H-CPL	44	7.5	-32	0.4	0.17
Na-CPL	22	8.2	-38	0.023	0.14
CPL	23	8.7	-37	0.023	0.14
Ca-H-CPL	44	9.7	-41	0.019	0.13

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 ( $pK_a = 1.6$ ). 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  $pK_a$  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<sup>+</sup>-enriched) simazine, being a very weak organic base, undergoes appreciable protonation which leads to its enhanced adsorption via electrostatic interactions.

#### References

- Abdulla N.I., Al-Haidary A.M.A., Al-Jeboori M.I., Zanganah F.H.H., Al-Azawi S.R.F., Al-Dujaili A.H., (2013), Kinetics and equilibrium adsorption study of lead (II) onto low cost clays, *Environmental Engineering and Management Journal*, **12**, 483-491.
- Ahrens L., Daneshvar A., Lau A.E., Kreuger J., (2015), Characterization of five passive sampling devices for monitoring of pesticides in water, *Journal of Chromatography A*, **1405**, 1-11.
- Akgül M., (2014), Enhancement of the anionic dye adsorption capacity of clinoptilolite by Fe(3+)-grafting, *Journal of Hazardous Materials*, **267**, 1-8.
- Berner K.B., Berner R.A., (1987), *The Global Water Cycle: Geochemistry and Environment*, Prentice-Hall, New Jersey.
- Capasso S., Coppola E., Iovino P., Salvestrini S., Colella C., (2007), Sorption of humic acids on zeolitic tuffs, *Microporous and Mesoporous Materials*, **105**, 324-328.

- Dabioch M., Skorek R., Kita A., Janoska P., Pytlakowska K., Zerzucha P., Sitko R., (2013), A study on adsorption of metals by activated carbon in a large-scale (municipal) process of surface water purification, *Central European Journal of Chemistry*, **11**, 742-753.
- de Gennaro B., Catalanotti L., Bowman R.S., Mercurio M., (2014), Anion exchange selectivity of surfactant modified clinoptilolite-rich tuff for environmental remediation, *Journal of Colloids and Interface Science*, **430**, 178-83.
- Ersoy B., Çelik M.S., (2002), Electrokinetic Properties of Clinoptilolite with Monoand Multivalent Electrolytes, *Microporous and Mesoporous Materials*, **55**, 305-312.
- Günaya A., Arslankayab E., Tosunc İ., (2007), Lead removal from aqueous solution by natural and pretreated clinoptilolite: Adsorption equilibrium and kinetics, *Journal of Hazardous Materials*, **146**, 362–371.
- Huang Y., Wang W., Feng Q., Dong F., (2013), Preparation of magnetic clinoptilolite/CoFe<sub>2</sub>O<sub>4</sub> composites for removal of Sr<sup>2+</sup> from aqueous solutions: Kinetic, equilibrium, and thermodynamic studies, *Journal of Saudi Chemical Society*, doi:10.1016/j.jscs.2013.09.005, In press.
- Krishnaiah D., Anisuzzaman S.M., Bono A., Sarbatly R., (2013), Adsorption of 2,4,6-trichlorophenol (TCP) onto activated carbon, *Journal of King Saud University – Science*, **25**, 251-255.
- Lapworth D.J., Baran N., Stuart M.E., Manamsa K., Talbot J., (2015), Persistent and emerging micro-organic contaminants in Chalk groundwater of England and France, *Environmental Pollution*, **203**, 214–225.
- Lazar L., Bandrabur B., Tataru-Fărnuș R.-E., Drobotă M., Stroe S.-G., Gutt G., (2015), Equilibrium performances of Crystal-righttm CR100 zeolite used in water softening process, *Environmental Engineering and Management Journal*, **14**, 541-549.
- Leone V., Iovino P., Canzano S., Salvestrini S., Capasso S., (2013a), Water purification from humic acids by clinoptilolite-rich tuff, *Environmental Engineering and Management Journal*, **12**, No. S11, 3-6.
- Leone V., Canzano S., Iovino P., Salvestrini S., Capasso S., (2013b), A novel organo-zeolite adduct for environmental applications: sorption of phenol, *Chemosphere*, **91**, 415-20.
- Ma Y., Gao N., Chu W., Li C., (2013), Removal of phenol by powdered activated carbon adsorption, *Frontiers of Environmental Science & Engineering*, **7**, 158-165.
- Mihaly-Cozmata L., Mihaly-Cozmata A., Peter A., Nicula C., Tutu H., Silipas D., Indrea E., (2014), Adsorption of heavy metal cations by Na-clinoptilolite: Equilibrium and selectivity studies, *Journal of Environmental Management*, **137**, 69-80.
- Paul B., Yang D., Yang X., Ke X., Frost R., Zhu H., (2010), Adsorption of the herbicide simazine on moderately acid-activated beidellite, *Applied Clay Science*, **49**, 80–83.
- Qian C., Wang G., Wu J., Xu J., Qiu M., (2009), Studies on the adsorption of dyes into clinoptilolite, *Desalination*, **243**, 286-292.
- Reilly T.J., Smalling K.L., Orlando J.L., Kuivila K.M., (2012), Occurrence of boscalid and other selected fungicides in surface water and groundwater in three targeted use areas in the United States, *Chemosphere*, **89**, 228-34.
- Russo A.V., Toriggia L.F., Jacobo S.E., (2014), Natural clinoptilolite-zeolite loaded with iron for aromatic hydrocarbons removal from aqueous solutions, *Journal of Materials Science*, **49**, 614-620.
- Salam O.E.A., Reiad N.A., ElShafei M.M., (2011), A study of the removal characteristics of heavy metals from wastewater by low-cost adsorbents, *Journal of Advanced Research*, **2**, 297–303.
- Salvestrini S., (2013), Diuron herbicide degradation catalyzed by low molecular weight humic acid-like compounds, *Environmental Chemistry Letters*, **11**, 359-363.
- Salvestrini S., Capasso S., Iovino P., (2008), Catalytic effect of dissolved humic acids on the chemical degradation of phenylurea herbicides, *Pest Management Science*, **64**, 768-774.
- Salvestrini S., Sagliano P., Iovino P., Capasso S., Colella C., (2010), Atrazine adsorption by acid-activated zeolite-rich tuffs, *Applied Clay Science*, **49**, 330–335.
- Sannino F., Rocco S., Marocco A., Esposito S., Pansini M., (2012), Cyclic process of simazine removal from waters by adsorption on zeolite H-Y and its regeneration by thermal treatment, *Journal of Hazardous Materials*, **229–230**, 354–360.
- Sismanoglu T., Kismir Y., Karakus S., (2010), Single and binary adsorption of reactive dyes from aqueous solutions onto clinoptilolite, *Journal of Hazardous Materials*, **184**, 164–169.
- Taha S.M., Amer M.E., Elmarsafy A.E., Elkady M.Y., (2014), Adsorption of 15 different pesticides on untreated and phosphoric acid treated biochar and charcoal from water, *Journal of Environmental Chemical Engineering*, **2**, 2013–2025.
- Wilson P.C., Lu H., Lin Y., (2011), Norflurazon and Simazine removal from surface water using a constructed wetland, *Bulletin of Environmental Contamination and Toxicology*, **87**, 426-430.
- Zaremotlagh S., Hezarkhani A., (2014), Removal of textile dyes from aqueous solution by conducting polymer modified clinoptilolite, *Environmental Earth Sciences*, **71**, 2999-3006.