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Sorption of organic pollutants onto zeolitic tuff

ABSTRACT

The isotherms of sorption of six organic pollutants (phenylmethanol (benzyl alcohol), phenol, cyclohexanol, o-xylene, toluene and cyclohexane) from water solutions onto zeolitic tuff (Si/Al ratio = 2.4) have been determined by batch experiments at 25 °C, in $1.0\cdot10^{-3}$ mol dm^{-3} Tris-HCl buffer, pH 6.0. The solutions were analyzed by gas-chromatography. The best description of the experimental data was given by the Freundlich equation, whose constants have been determined and compared with literature data.

Keywords: *organic pollutants; zeolitic tuff; sorption.*

1. INTRODUCTION

Natural zeolites are a class of microporous alumino-silicate minerals of common occurrence in volcanic ash deposits throughout the world. Because of their high ion-exchange capacity and relatively low cost, zeolites have been widely employed for water purification from ionic contaminants including heavy metals [1,2], radioactive cations [3] and ammonia [4]. The use of natural zeolite as sorbing material in permeable reactive barrier to treat heavy-metal contaminated waters has also been investigated [5]. Besides ionic solutes, zeolites also bind non-ionic organic molecules. Zeolite sorbitivity (amount of solute sorbed per unit dry mass of sorbant at the equilibrium) for these compounds depends mainly on the zeolite Si/Al ratio, with high ratios increasing the hydrophobicity of the sorption sites and hence their affinity for non-polar molecules [6].

Here we report a study on the sorption of some organic pollutants onto a zeolitic tuff rich in phillipsite and charbazide and with a low Si/Al ratio (2.4), whose sorption properties towards cations have been characterized in previous work [7-9]. The aim of this study was to explore the behavior of this tuff toward organic pollutants of common occurrence in waste water, in the perspective of developing practical applications for water purification.

2. EXPERIMENTAL

2.1. Materials

Analytical-grade phenylmethanol (benzyl alcohol), phenol, cyclohexanol, o-xylene, toluene and cyclohexane were purchased from Fluka (Germany). Methylene blue was purchased from Carlo Erba (Italy). A commercial sample of zeolitic tuff rich in phillipsite and chabazite (phillipsite-chabazite tuff, PCT), Si/Al ratio 2.4, extracted from an outcrop of the Campanian Ignimbrite formation (yellow faces) in Comiziano (Napoli, Italy), was obtained from I.Z.-Italiana Zeoliti Company (Pigneto, Modena, Italy). The mineralogical and chemical characterization of this rock has been reported elsewhere [10]. The raw material was gently crashed and sieved to obtain grains in the range 0.5–1.0 mm, and then washed several times with deionized water.

2.2. Specific surface area determination

The specific surface area (SSA) of PCT was determined with the methylene blue (MB) sorption method [11]. As MB can be sorbed by glass, polypropylene tubes were used. Fourteen mL aliquots of MB in deionized water, concentration range 1-11 mg L^{-1}, were added to 4 mg of ground PCT and kept at room temperature in a shaker at 60 rpm. At programmed times, the samples were centrifuged at 3000 rpm for 10 min and analyzed by visible spectrophotometry at 665 nm (Perkin Elmer Lambda 40), using the calibration curve $Absorbance = 0.2442\cdot Conc - 0.0049\cdot Conc^2$ as determined from the concentration–absorbance plot. MB sorption was estimated by comparing its concentration in solution before and after contact

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with PCT. The SSA of PCT was calculated with the equation $SSA = q_m N_A A$, where q_m is the monolayer capacity of PCT for MB in moles per gram; N_A the Avogadro number and A the surface area occupied per molecule of MB ($1.3 \cdot 10^{-22}$ m^2).

2.3. Sorption experiments in batch

The compounds selected were dissolved in water (10-150 mg L^{-1}) containing $1.0 \cdot 10^{-3}$ mol dm^{-3} Tris-HCl buffer, pH 6.0. For cyclohexane, because of its lower solubility in water, the higher concentration tested was 50 mg L^{-1}. Twenty mL aliquots of each solution were mixed with 50 mg of PCT in glass containers with a buthyl/PTFE cap and kept in a thermostat at 25 °C with periodical shaking. After seven days, 1.0 mL of solution was taken through the cap and analyzed by a Dani GC 1000 gas-chromatographer equipped with a spit/ splitless capillary inlet system, a FID detector and an ELITE 1 capillary column (60 m·0.32 mm, I.D. 5μm film thickness; Perkin Elmer). Measurements performed after longer times gave much the same results as after seven day incubation, so the latter was adopted as the protocol procedure.

3. RESULTS AND DISCUSSION

The specific surface area (SSA) of the PCT material determined according to the procedure described in the previous section was 31 ± 4 m^2/g, a value slightly lower than that reported (49 m^2/g) for a phillipsite-rich tuff from Jordan [7].

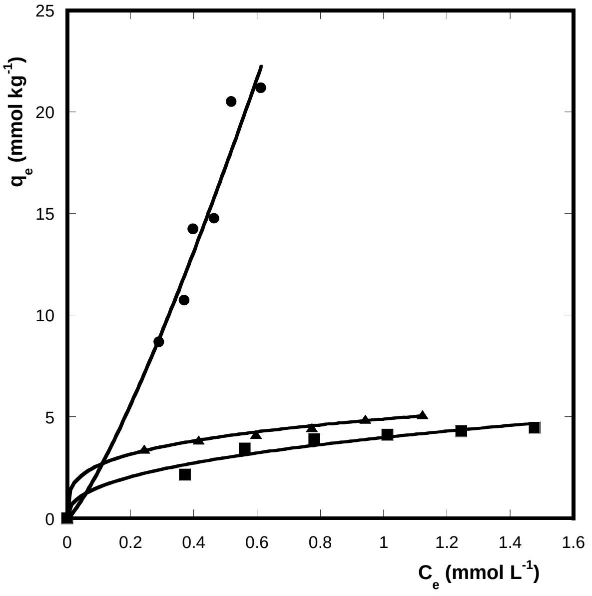

Figure 1 - Sorption isotherms of the hydrocarbon compounds toluene (■), o-xylene ((▲) and cycloexane (•), θ = 25 °C; q_e is the sorbitivity, i.e. the amount of compound sorbed per unit mass of sorbent at the equilibrium, Ce is the compound concentration in solution at the equilibrium

The sorption isotherms for hydrocarbon and hydroxyl compounds are reported in Fig. 1 and 2, respectively.

Among the hydrocarbon compounds tested, the higher sorbitivity (q_e) was observed for cyclohexane; moreover, in the concentration range analyzed, the q_e for cyclohexane showed an almost linear relationship with C_e (free sorbate concentration in solution at the equilibrium). Experiments at higher concentrations could not be performed because of low solubility in water. It is worth nothing that cycloexane has a higher octanol/water repartition coefficient (K_{OW}) than all the other compounds tested (Table 1), and this, in our opinion, might account for the behavior observed: cycloexane does not "like" water, hence it is more prone to abandon the aqueous environment and bind to the sorbent.

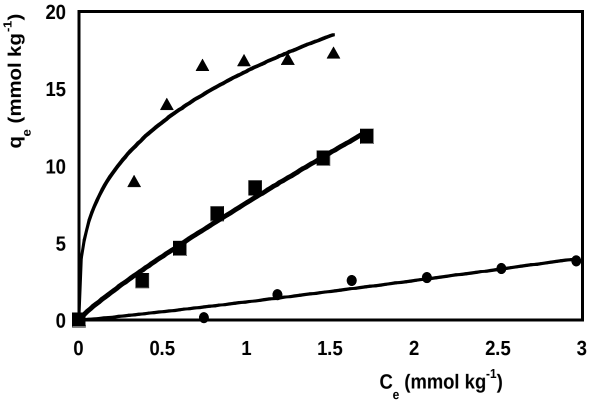

Figure 2 - Sorption isotherms of the hydroxyl compounds phenylmethanol (benzyl alcohol) (▲), phenol (■), and cyclohexanol (•), θ = 25 °C

In line with the above suggestion, the sorbitivity for hydroxyl compounds was lower than for hydrocarbon compounds and decreased with K_{OW}, with the minimum value being observed for phenylmethanol (Fig. 2 and Table 2).

The experimental sorption equilibrium data were analyzed using the equations of more common use, i.e. Langmuir, Fowler, bi-Langmuir, Freundlich and BET, [12, 13]. On the base of the relative errors of the parameters and of the statistical R^2 parameters, the best description was given by the Freundlich equation, as expected considering the mineral heterogeneity of the zeolitic tuff tested:

$$q_e = K_F (C_e)^{\frac{1}{n}} \tag{1}$$

where q_e and C_e are respectively the amount of solute bound per unit mass of sorbent and the free solute concentration in solution, at the equilibrium. K_F and n are constants (Table 1).

Table 1 - Freundlich parameters of sorption onto a zeolitic tuff and logarithm of the n-octanol/water repartition coefficients ($LogK_{OW}$) of some organic compounds. K_F and n values were obtained by least square fitting.

Compound	LogKow	KF (L mmoln-1 kg-1)	n	R2
toluene	1.5	4.0±0.1	2.4±0.5	0.968
cyclohexane	3.8	40±5	0.8±0.1	0.966
o-xylene	3.1	4.89±0.05	3.7±0.2	0.998
phenylmethanol	1.1	16.1±0.7	3.0±0.08	0.953
phenol	1.5	7.6±0.2	1.13±0.09	0.989
cyclohexanol	1.6	1.2±0.3	0.9±0.2	0.938

It is worth nothing that the K_F values reported in literature for the sorption onto activated carbon, currently the most popular sorbent for organic compounds, and for other recently introduced sorbent materials [14, 15, 16, 17] are markedly higher than those reported in Table 1 for PCT. For example, K_F values reported for the sorption of toluene and o-xylene onto activated carbon were respectively 35.8 and 54.8 $L^{1/n}$ $mg^{1-1/n}$ g^{-1}[18]; for phenol a K_F value of 54.0 $L^{1/n}$ $mg^{1-1/n}$ g^{-1} has been reported [19].

4. CONCLUSIONS

Despite its relatively low Si/Al ratio, the zeolitic tuff analyzed in this study is a good sorbent of organic pollutants, particularly so for those with a low n-octanol/water partition coefficient. The sorption occurs, however, with a relatively low, but significant efficiency, as deduced from the Freundlich constants. In designing the use of zeolitic tuffs for water depuration by toxic cations, these results should be considered.

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IZVOD

SORPCIJA ORGANSKIH ZAGAĐIVAČA NA ZEOLITSKOM TUFU

Izoterme, koje prikazuju sorpciju šest organskih zagađivača (fenil methanol – benzyl alcohol, fenol, cikloheksanol, o-ksilen, toluen i cikloheksan), iz vodenih rastvora, na zeolitskom tufu (Si/Al odnos =2.4), su određene šaržnim postupkom, na 25°C, u rastvoru pufera - 1.0·10^{-3} mol dm^{-3} Tris-HCl (pH 6.0). Rastvori su analizirani na gasnom hromatografu. Najbolje slaganje eksperimentalnih rezultata je postignuto sa Frojndlih-ovim sorpcionim modelom, čije konstante su određene i upoređene sa literaturnim podacima.

Ključne reči: *organski zagađivači, zeolitski tuff, sorpcija.*

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