Removal of Dialkylphenols from Aqueous Effluents by Selective Adsorption in a Novel, Large-pore, Silica Molecular Sieve

K. Ramesh Reddy

National Chemical Laboratory, Pune 411008, India

Dialkylphenols, like 2,3-, 2,5-, 2,6-, 3,4- and 3,5-dimethylphenols can be removed from water by selective liquid-phase adsorption in a novel, large pore, silica molecular sieve; more than 80% of the adsorbed dialkylphenols are recoverable by thermal desorption in nitrogen.

Zeolite adsorbents are conventionally used to remove polar impurities such as H_2O and H_2S from hydrocarbon streams, for example the Linde type A molecular sieve is often used to dry hydrocarbon streams in the petroleum industry. The advent of silicalite-1,[1] the medium pore, silica end-member of the ZSM-5 series provided a potential hydrophobic adsorbent for removing non-polar or less polar molecules from polar aqueous effluents. The removal of n-alkanols from water by selective adsorption on silicalite-1 has been reported.[2,3] The drawback of silicalite-1 is that owing to its pore diameter (0.56 nm) it cannot adsorb bulkier molecules, such as dialkylphenols, from aqueous effluents. At present, such effluents quite common in the organic chemical industry, are either treated with Amberlite XAD type polymeric adsorbents[4] or are incinerated. The availability of a hydrophobic, large-pore, silica molecular sieve capable of selectively adsorbing such substituted phenols is desirable.

Recently, we have synthesized and characterized a new large-pore zeolite designated as NCL-1[5] with an Si/Al ratio of $\geqslant 20$ and also its Al-free silica polymorph[5] (Si-NCL-1). The adsorption and catalytic properties of NCL-1 are characteristic of zeolites with pore openings constituted by 12-membered tetrahedra. The effective pore diameter of NCL-1 from adsorption and diffusivity measurements is close to that of mordenite (*ca.* 0.7 nm). Preliminary investigations indicate that NCL-1 possesses orthorhombic symmetry with $a = 1.195 \pm 0.003$, $b = 0.836 \pm 0.003$ and $c = 2.870 \pm 0.004$ nm. In the present communication, we report the selective adsorption of 2,3-, 2,5-, 2,6-, 3,4- and 3,5-dimethylphenols from water by the silica analogue of NCL-1 (Si-NCL-1). The sorption capacity of NCL-1 is compared with that on silicalite-1, the medium pore silica polymorph of ZSM-5 zeolite.

Samples of Si-NCL-1 and silicalite-1 were prepared according to procedures described elsewhere.[5,1] The average particle size of the samples, which were calcined overnight at 823 K, was *ca.* 50 μm. The adsorption experiments were performed in the liquid phase by equilibrating 0.5 g of Si-NCl-1 or silicalite-1 at 298 K with 5 g of an aqueous solution containing

Table 1 Amount of dimethylphenols adsorbed from aqueous solutions on Si-NCL-1 and silicalite-1[a]

Adsorbate	Kinetic dimensions of adsorbate/nm	Amount adsorbed (mg per g) on	
		Si-NCL-1	Silicalite-1
2,3-Dimethylphenol	~0.41 × 0.73 × 0.84	27	2
2,5-Dimethylphenol	~0.37 × 0.65 × 0.86	37	46
2,6-Dimethylphenol	~0.37 × 0.72 × 0.85	28	4
3,4-Dimethylphenol	~0.41 × 0.69 × 0.85	34	29
3,5-Dimethylphenol	~0.37 × 0.77 × 0.85	31	3

[a] *Conditions*: $T = 298$ K; adsorbent = 0.5 g; adsorbate = 0.5 wt% in 5 g of aqueous solution; duration = 24 h.

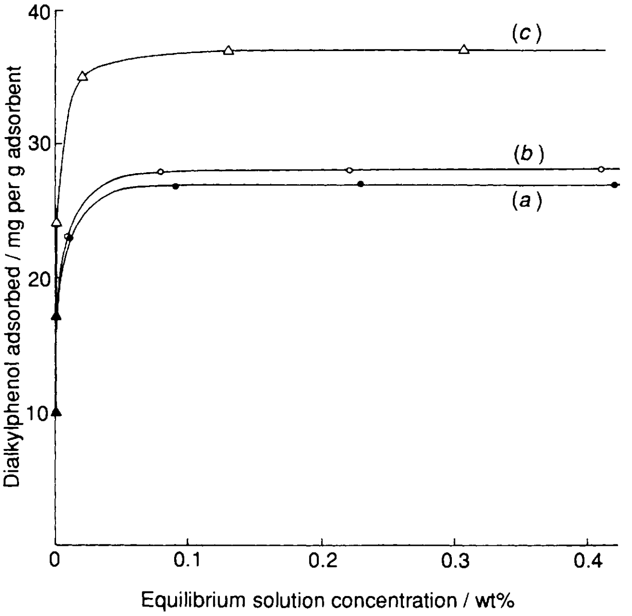

Fig. 1 The adsorption isotherms at 298 K from an aqueous solution on Si-NCL-1 sample. (*a*), (*b*) and (*c*): 2,3-, 2,6- and 2,5-dimethylphenol, respectively.

either of the five dialkylphenols in a closed conical flask for 24 h. The concentration of the dialkylphenols in the aqueous solution both before and after adsorption at equilibrium was estimated by GC (Shimadzu GC-15A) using 2 m packed column containing 20% FFAP on 60/70 mesh DMCS-AW chromosorb.

The adsorption of 2,3-, 2,5- and 2,6-dimethylphenols individually from water on Si-NCL-1 are shown in Fig. 1. The adsorption maximum is reached at the dialkylphenol equilibrium concentration of about 0.09 wt% in the aqueous solution in each case. The amount of adsorption of all the five phenols from water on Si-NCL-1 and silicalite-1 is summarized in Table 1, along with the kinetic dimensions of the adsorbates. The amount of adsorption of all the five dimethylphenols in Si-NCL-1 is fairly high ranging from 27 to 37 mg per g. On the other hand, on silicalite-1 the adsorption of 2,5-dimethylphenol is the highest (46 mg per g) followed by 3,4-dimethylphenol (29 mg per g) and to very neglible levels of 2,3-, 2,6- and 3,5-dimethylphenols (only 2 to 4 mg per g). These differences can be explained on the basis of the differences in the kinetic dimensions of the dimethylphenols and the differences in the pore dimensions of Si-NCL-1 and silicalite-1. The kinetics of adsorption of 2,3-, 2,5- and 2,6-dimethylphenols from water on Si-NCL-1 and silicalite-1 at 298 K are shown in Fig. 2. Again, the greater efficiency of the large-pore molecular sieve is evident.

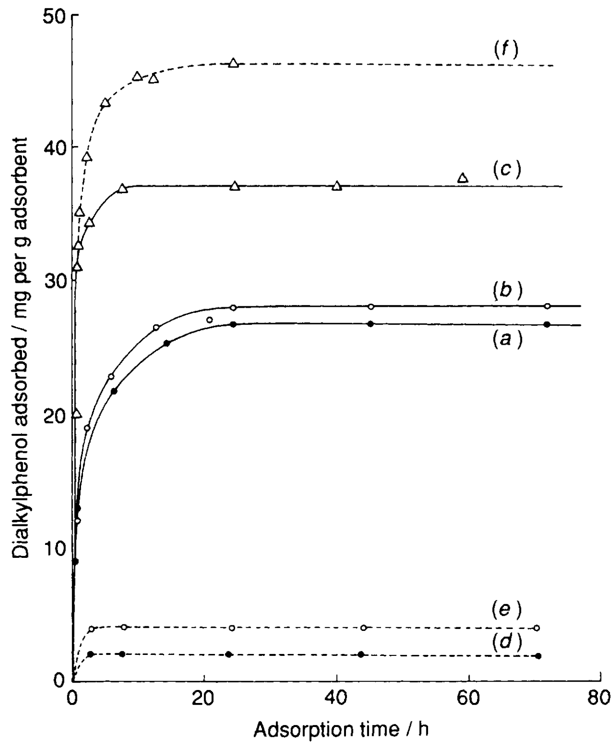

Fig. 2 Rate of adsorption of 2,3-dimethylphenol (*a*), 2,6-dimethylphenol (*b*) and 2,5-dimethylphenol (*c*) on Si-NCL-1 and 2,3-dimethylphenol (*d*), 2,6-dimethylphenol (*e*) and 2,5-dimethylphenol (*f*) on silicalite-1 from aqueous solutions containing 0.5 wt% dimethylphenol

Before carrying out the desorption experiments, 3 g of Si-NCL-1 was equilibrated with 30 g of an aqueous solution containing 0.36 wt% of 2,6-dimethylphenol at 298 K for 24 h. The 'wet' Si-NCL-1 was then filtered and dried for a few hours at 298 K. It was then loaded in a vertical glass column (1.5 cm diameter). Nitrogen was then passed through the adsorbent bed (downflow, 95 ml min^{-1}). The temperature of the column was simultaneously raised from 298 to 400 K in 2 h and held at that temperature for 2 h. The 2,6-dimethylphenol desorbed during this operation was collected in a cold trap (at 268 K) and analysed by GC. From the analysis, it is noted that *ca.* 80% of the adsorbed dimethylphenol could be recovered by thermal desorption in nitrogen. The remaining amount could be removed by purging the adsorbent in air at 823 K for 8 h and the initial adsorption capacity of Si-NCL-1 could be restored.

The author thanks Drs P. Ratnasamy and A. V. Ramaswamy for helpful discussions; and UGC, New Delhi for a research fellowship. This work was partly funded by UNDP.

Received, 28th September 1992; Com. 2/05217B

References

1 E. M. Flanigen, J. M. Bennett, J. P. Grose, R. L. Patton and R. M. Kirchner, *Nature*, 1978, **271**, 512.
2 N. B. Milestone and D. M. Bibby, *J. Chem. Tech. Biotech.*, 1981, **31**, 732.
3 N. B. Milestone and D. M. Bibby, *J. Chem. Tech. Biotech.*, 1984, **34A**, 73.
4 E. H. Crook, R. P. Mcdonnell and J. T. Mcnutty, *Ind. Eng. Chem. Prod. Res. Dev.*, 1975, **14**, 113.
5 R. Kumar, K. Ramesh Reddy, A. Raj and P. Ratnasamy, *9th Int. Zeolite Conf.*, Montreal, Canada, 1992, Paper A6; R. Kumar, K. Ramesh Reddy and P. Ratnasamy, Ind. Pat. Appl. No. 766/DEL/91; R. Kumar, K. Ramesh Reddy and P. Ratnasamy, EP Appl. No. 92300166.3.