

# Shape-Selective Adsorption of Substituted Aniline Pollutants from Wastewater

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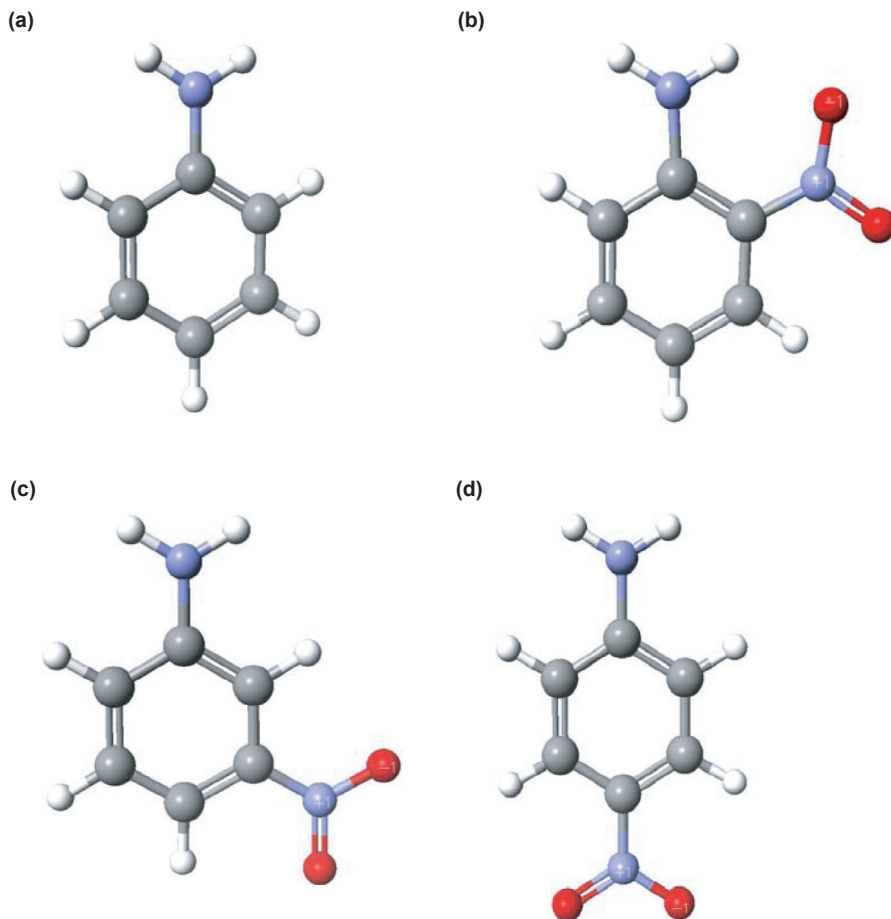
**ABSTRACT:** ZSM-5 zeolite was used to treat wastewater containing aniline, 2-nitroaniline (2-NA), 3-nitroaniline (3-NA) and 4-nitroaniline (4-NA). Each molecule was removed from aqueous solution by Type I Langmuir adsorption onto ZSM-5. The quantities adsorbed varied greatly due to their shape-selective adsorption within the pores of ZSM-5. Aniline and 4-NA had maximum adsorption amounts of 161 and 265 mg g<sup>-1</sup>, respectively, while the maximum amounts of 3-NA and 2-NA were 94.3 and 37.2 mg g<sup>-1</sup>, corresponding to reductions of 64% and 86%, respectively, relative to 4-NA. This outcome was caused by the increase in the effective diameter for adsorption when the nitro group was located at the 2- and 3- positions of the molecule. This significantly reduced their ability to enter into, and diffuse through, the pores of ZSM-5. These findings underpin the importance of choosing the correct substrate when using such materials for water purification.

## 1. INTRODUCTION

Aniline, 2-nitroaniline (2-NA), 3-nitroaniline (3-NA), and 4-nitroaniline (4-NA) are highly toxic, carcinogenic species that are widely used in azo dyes, paints, pharmaceuticals and agrochemicals (Damborsky and Wayne Schultz 1997; Bhunia *et al.* 2003; Wang *et al.* 2008). Aniline, for example, causes the transformation of haemoglobin to methaemoglobin, which has a lower affinity for oxygen than haemoglobin, and therefore reduces blood's ability to transport oxygen. All four compounds are soluble in water, and therefore their inclusion in industrial wastewater streams, and subsequent assimilation into groundwater aquifers, pose a significant threat to human health. The structures of these compounds are shown in Figure 1.

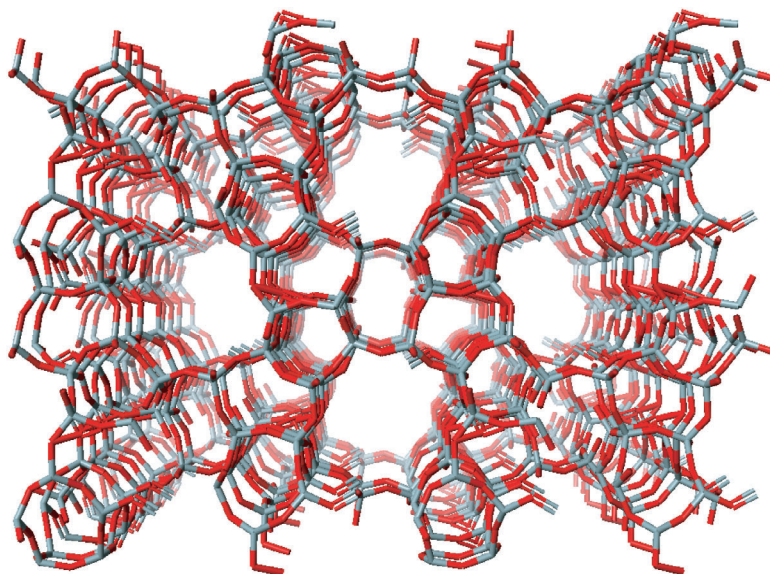
A number of techniques, including oxidation, membrane separation and biodegradation have been used to remove such harmful compounds from water (Lee *et al.* 1997; Saupe 1999; Williams *et al.* 1999; Judd and Jefferson 2003; Gautam *et al.* 2005; Qureshi *et al.* 2007; Sun *et al.* 2007). Organic pollutants may also be removed from aqueous solution by adsorbing them onto solid substrates. Such systems are particularly favourable because the pollutant is easily separated from the purified water by filtration of the pollutant-loaded solid adsorbent. Activated carbons (Derylo-Marczewska and Marczewski 2002; Li *et al.* 2009a, b), polymer resin (Zheng *et al.* 2007), clays (Ko *et al.* 2007) and mesoporous oxides (Bibby and Mercier 2003; El-Safty *et al.* 2012) have been used as adsorbents of various aniline-type compounds. Zeolites are high-surface area inorganic materials that have been used in areas such as

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**Figure 1.** Chemical structures of adsorbates used in the study: (a) aniline, (b) 2-nitroaniline, (c) 3-nitroaniline, and (d) 4-nitroaniline.

heterogeneous catalysis, separation science and microelectronics. They are built from elementary units of  $\text{SiO}_4$  and  $\text{AlO}_4$  tetrahedral chains, which are linked together by common oxygen atoms (Weitkamp 2000). Copper-exchanged zeolites have been used to remove aniline, which was then catalytically decomposed under heating (O'Brien *et al.* 2004, 2008). The 2-NA and 4-NA were found to adsorb readily onto dealuminated Faujasite zeolite (Koubaisy *et al.* 2011). The ZSM-5 zeolite (Figure 2) contains a mixture of straight and 'zig-zag' 10-membered ring pores, which intersect to form a distinct three-dimensional macromolecule (Weitkamp 2000). In this study, ZSM-5 is used to adsorb aniline, 2-NA, 3-NA and 4-NA from an aqueous solution. The study results show that the amount of adsorption is strongly dependent on the position of the nitro group on the aniline molecule; aniline and 4-NA have very similar properties, while the increased effective molecular diameter for the 2- and 3-positions of the nitro group significantly suppress adsorption. The findings are rationalized on the basis of shape-selective adsorption.



**Figure 2.** Schematic diagram of ZSM-5 zeolite viewed along [100] axis.

## 2. EXPERIMENTAL ANALYSIS

Adsorption isotherms were measured at ambient temperature (18–20 °C) by allowing ZSM-5 to reach equilibrium with each of the adsorbates over a range of initial solution concentrations. Stock solutions of aniline (99%, Fluka), 2-NA, 3-NA and 4-NA (99%, Aldrich) were first prepared by dissolving 0.2 g in 1 dm<sup>3</sup> distilled water, which were then used to prepare solutions at a concentration range of 4–60 mg dm<sup>-3</sup> for the adsorption experiments. Approximately 100 cm<sup>3</sup> of the solution was added to 0.01 g ZSM-5 (Zeolyst, Si/Al = 30) in a glass beaker, which was stirred continuously for 1 hour at ambient temperature. At the end of adsorption, the solution was extracted from the suspension by centrifuging (Hermle Z 200 A) at 3500 rpm for 5 minutes, which allows for analyzing the solution by UV-Visible spectroscopy (HP 8453) at the following wavelengths: 280, 282, 278 and 381 nm for aniline, 2-NA, 3-NA and 4-NA, respectively. The masses adsorbed were calculated from the differences between initial and final solution concentrations.

## 3. RESULTS AND DISCUSSION

### 3.1. Equilibrium Time

The initial experiments were conducted to determine the time interval required to reach equilibrium. This was done by measuring the quantity adsorbed on ZSM-5, and that remaining in solution, as a function of adsorption time. The results (data not shown) demonstrated that equilibrium was reached within 10 minutes. The actual time required to reach equilibrium may

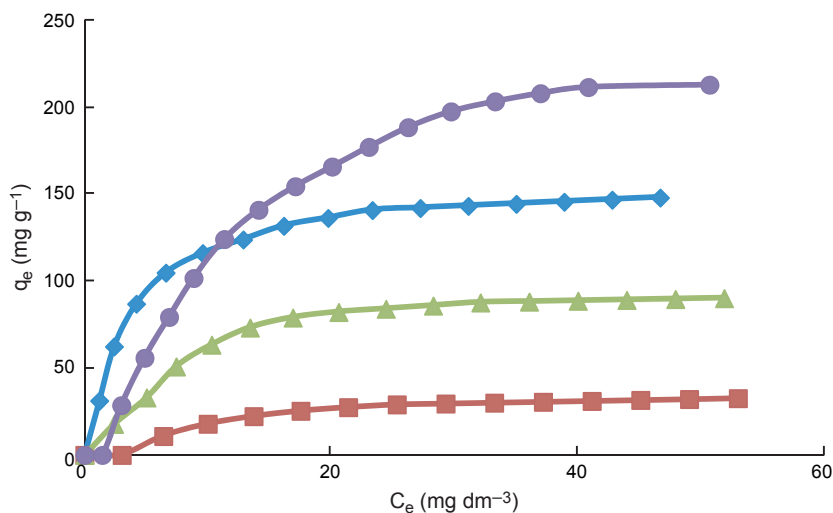
be shorter in duration but an accurate determination of this time was not achievable using the method described here due to centrifugation step (5 minutes), during which adsorption can still occur. In any case, an exact value of equilibrium time is not needed, only that the time interval is exceeded during experiments. Therefore, adsorption was allowed to proceed for 1 hour in all experiments.

### 3.2. Adsorption Isotherms

The adsorption isotherms of the four compounds are shown in Figure 3, where  $q_e$  is the amount of adsorbate adsorbed per gram of zeolite and  $C_e$  is the equilibrium concentration of adsorbate in solution at equilibrium. In general, each molecule was adsorbed over a range of concentrations showing that ZSM-5 is an effective adsorbent for removing aniline, 2-NA, 3-NA and 4-NA from aqueous solutions. In all cases, the shapes of the isotherms are consistent with Type I Langmuir adsorption, where the adsorption reaches a maximum value corresponding to monolayer coverage (Brunauer *et al.* 1940). This is not surprising, because ZSM-5 has a uniform distribution of pores with diameter in the range of 0.51–0.56 nm and does not contain any ‘large’ supercages, thereby preventing multi-layer adsorption. These results are in good agreement with those reported previously (O’Brien *et al.* 2004, 2008), which showed that adsorption of aniline onto ZSM-5 and beta zeolite also obeys Type I behaviour.

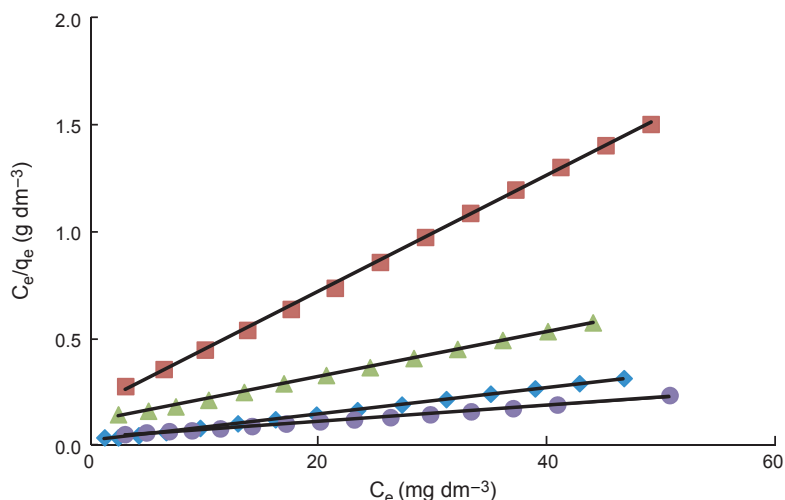
The adsorption data were next tested to assess their fit to the Langmuir model in equation (1) (Langmuir 1918)

$$q_e = \frac{K_L C_e}{1 + A_L C_e} \quad (1)$$



**Figure 3.** Adsorption isotherms on ZSM-5: aniline (closed diamonds); 2-nitroaniline (closed squares); 3-nitroaniline (closed triangles); 4-nitroaniline (closed circles).

Type 1 adsorption was confirmed by plotting the linear form of equation (1), that is,  $C_e/q_e$  versus  $C_e$ , which was used to calculate the Langmuir constants  $K_L$  (intercept),  $A_L$  from the gradient  $A_L/K_L$  and maximum uptake  $K_L/A_L$ . The Langmuir plots are all straight lines confirming Type I adsorption for each of the four compounds (Figure 4). The corresponding  $R^2$  values of 0.997–0.999 (Table 1) provide further evidence for the excellent correlation of results over the entire concentration range.



**Figure 4.** Langmuir adsorption plots on ZSM-5: aniline (closed diamonds); 2-nitroaniline (closed squares); 3-nitroaniline (closed triangles); 4-nitroaniline (closed circles).

**TABLE 1.** Properties of Aniline/Substituted Aniline and Langmuir Constants for Their Adsorption onto ZSM-5

Adsorbate	Solubility (g dm <sup>-3</sup> )	pK <sub>a</sub>	K <sub>L</sub> (dm <sup>3</sup> g <sup>-1</sup> )	A <sub>L</sub> (dm <sup>3</sup> mg <sup>-1</sup> )	K <sub>L</sub> /A <sub>L</sub> (mg g <sup>-1</sup> )	R <sup>2</sup>
Aniline	36	4.63	42.4	0.263	161	0.999
2-NA	1.2	1.0	5.46	0.147	37.2	0.999
3-NA	1.0	2.47	9.09	0.096	94.3	0.999
4-NA	0.8	-0.26	26.0	0.098	265	0.997

Although the adsorption properties of the different compounds share common features in their overall profiles, the findings illustrate a clear distinction between the amounts of each molecule adsorbed over the range of initial solution concentrations. For ease of comparison, this effect will be discussed quantitatively with respect to the maximum quantities adsorbed, that is,  $K_L/A_L$ . Table 1 shows that these values proceed in the following order: 2-NA (37.2 mg g<sup>-1</sup>), 3-NA (94.3 mg g<sup>-1</sup>), aniline (161 mg g<sup>-1</sup>) and 4-NA (265 mg g<sup>-1</sup>). We hereby attribute these findings to the shape-selective adsorption of the NA molecules, due to differences in their physical dimensions that determine their entry into, and movement through, the pores of ZSM-5. Both aniline and 4-NA

are linear-shaped molecules that are identically proportioned with respect to the porous network of ZSM-5. This is because the nitro group at the 4-position is at the opposite side of the benzene ring as the  $\text{NH}_2$  group and, being effectively 'hidden', has no effect on the adsorption of 4-NA onto the surface of ZSM-5. Therefore, 4-NA is adsorbed onto ZSM-5 unhindered by any geometric confinement, in a manner similar to that of aniline. By contrast, the effective diameter of the 3-NA particle is greater than that of either aniline or 4-NA due to the bulky nitro group at the 3-position, reducing its entry and ability to move through the ZSM-5 pore. This significantly decreases the quantity of 3-NA that is ultimately adsorbed; the maximum uptake of 3-NA is reduced by 64% relative to 4-NA. The nitro group at the 2-position has an even greater effect on adsorption; in this case, 86% less 2-NA is adsorbed than 4-NA at maximum adsorption. The nitro group at the 2-position is in close proximity to the  $\text{NH}_2$  group, which may reduce its ability to move freely due to repulsion between both electron-rich functional groups. This increases the effective diameter to an even larger extent than that observed for 3-NA, further reducing the amount adsorbed.

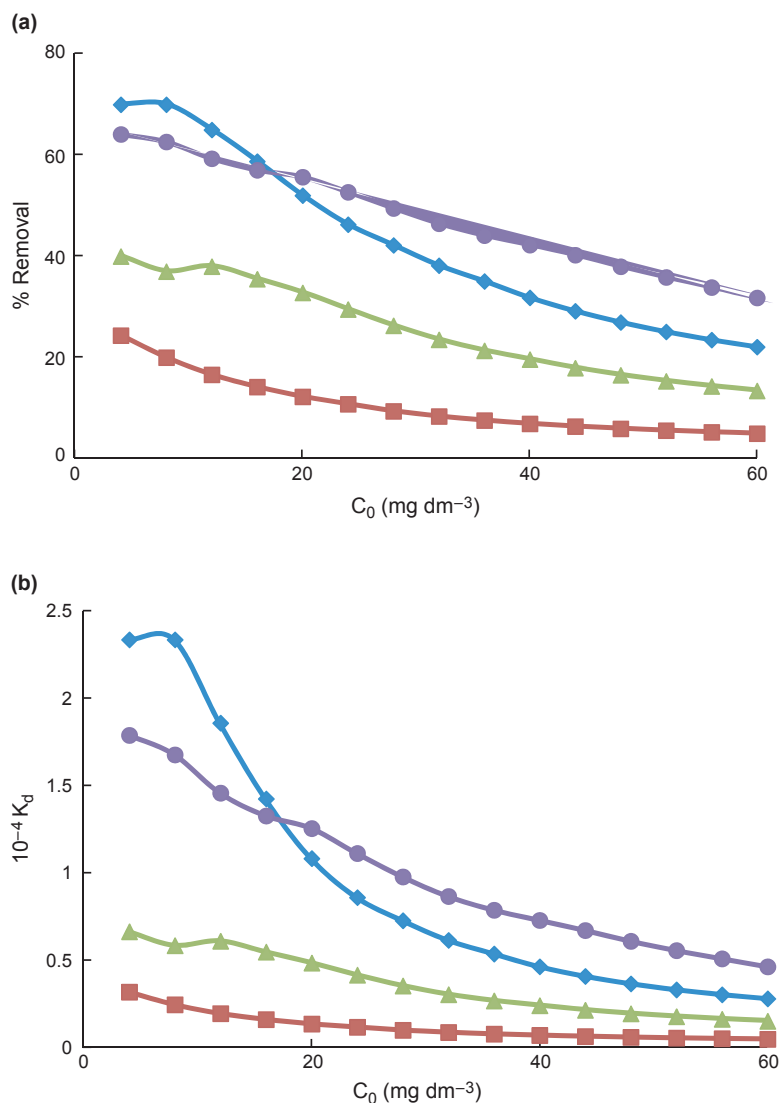
A further way to analyze the adsorption data is by calculating the %Removal, equation (2), and distribution coefficient,  $K_d$ , equation (3), which are shown as follows:

$$\% \text{Removal} = \frac{C_0 - C_e}{C_0} \times 100\% \quad (2)$$

$$K_d = \frac{100(C_0 - C_e)}{0.01C_e} \quad (3)$$

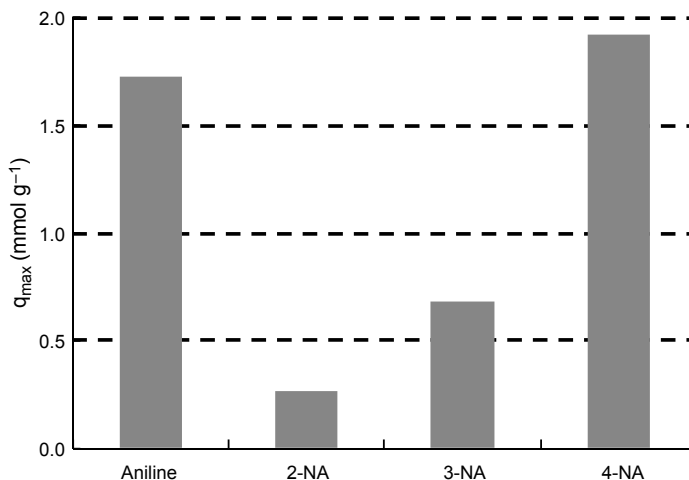
The variation of %Removal and  $K_d$  with initial concentrations are shown in Figures 5(a and b), respectively, where  $C_0$  is the initial solution, that is, before the addition of zeolite. Not surprisingly, the %Removal and  $K_d$  profiles of all the four compounds share common properties with the shape-selective adsorption results mentioned earlier. At initial concentrations below  $10 \text{ mg dm}^{-3}$ , the following approximate amounts are removed from solution by adsorption: 60–70% of aniline/4-NA, 40% of 3-NA and 20% of 2-NA. Thereafter, the results show a general decrease in both %Removal and  $K_d$  with increasing concentration but the shape-selective adsorption based on molecular dimensions remains, whereby the adsorption continues to decrease in the order 4-NA, 3-NA and 2-NA. The decrease of %Removal and  $K_d$  with increasing concentration is consistent with the use of a fixed mass of zeolite, which obviously limits the amount of material that may be adsorbed from solution as the concentration progressively increases. As the maximum uptake of the zeolite pores is approached, any further increase in concentration reduces the amount that may be adsorbed, which is recorded as a decrease in %Removal and  $K_d$ .

It seems appropriate to consider whether differences in the amounts adsorbed may be due to factors other than the molecular dimensions of the adsorbates. One possible explanation is that the effects observed here are due to differences in chemical properties between the molecules. Fortunately, it is possible to make such a comparison. As previously stated, aniline and 4-NA have identical physical dimensions with respect to their entry into the pores of ZSM-5, because of the position of the nitro group at the opposite end of the  $\text{NH}_2$  group. However, 4-NA and aniline are of course chemically distinct from each other, due to the presence of a nitro functional group with its own characteristic chemical properties and the additional consequences of the lone-pair electrons of this nitro group interfering with the electronic resonance of an otherwise aniline molecule. Some relevant examples of the resulting



**Figure 5.** (a) %Removal and (b) distribution coefficient,  $K_d$ , on ZSM-5: aniline (closed diamonds); 2-nitroaniline (closed squares); 3-nitroaniline (closed triangles); 4-nitroaniline (closed circles).

disparities between these two compounds are seen in their solubility in water,  $36 \text{ g dm}^{-3}$  for aniline and  $0.8 \text{ g dm}^{-3}$  for 4-NA, and  $\text{pK}_a$  values, 4.63 for aniline and  $-0.26$  for 4-NA. Any differences in adsorption due to chemical properties alone will be measured by the differences in the results for these two molecules. Our results show that the maximum quantities adsorbed,  $q_{\text{max}}$ , in Figure 6 are  $1.73 \text{ mmol g}^{-1}$  for aniline and  $1.92 \text{ mmol g}^{-1}$  for 4-NA. This demonstrates that there is only a 10% disparity between the number of molecules adsorbed going from 4-NA to aniline, which is significantly less than the reductions for 3-NA (64%) and 2-NA (86%). Further evidence that the differential adsorption on ZSM-5 is not due to the chemistry



**Figure 6.** Maximum uptake,  $q_{\max}$ , on ZSM-5, calculated from  $K_L/A_L$  in Langmuir adsorption plot.

of the adsorbates is supported by the near identical values of  $q_{\max}$  for the adsorption of 2-NA (1.59 mmol g<sup>-1</sup>) and 4-NA (1.53 mmol g<sup>-1</sup>) on dealuminated Faujasite (Koubaissy *et al.* 2011). This zeolite contains pore openings and cages of diameter 0.73 and 1.3 nm, respectively, both of which are larger than the pores of ZSM-5, 0.51–0.56 nm (Weitkamp 2000). The 2-NA and 4-NA may therefore enter the pores of Faujasite unhindered by any geometrical confinement. In another study, adsorption isotherms showed that 2-NA and 4-NA adsorb in very similar quantities to each other on activated carbon (Derylo-Marczewska and Marczewski 2002). Because there is no significant divergence between the maximum uptakes of both molecules on Faujasite and activated carbon, the maximum uptake value is considered to be unaffected by differences in chemical properties of the adsorbates. The changes in the amounts adsorbed on ZSM-5 are not, therefore, primarily due to differences between the chemical properties of 2-NA, 3-NA and 4-NA.

The solubility of 2-NA, 3-NA and 4-NA (Table 1) are 1.2, 1.0 and 0.8 g dm<sup>-3</sup>, respectively, which follow an inverse trend to their maximum uptake on ZSM-5. It is certainly intuitive to infer that a higher solubility of a given molecule in water will reduce its maximum uptake. A high solubility indicates a relatively strong interaction between solute and solvent, which runs counter to the requirement of breaking bonds to enable adsorption. Previous studies show a correlation between  $q_{\max}$  and the solubility of adsorbate for a range of chloro- and nitro-substituted phenols, where  $q_{\max}$  was found to decrease linearly with increasing solubility (Koubaissy *et al.* 2011). For the adsorption of nitrophenols, a tenfold increase in solubility brought about a 40% decrease in the number of moles of maximum uptake, whereas for the chlorophenols, a sixfold increase in solubility brought about a 30% decrease. For the results presented here on ZSM-5, the magnitude of change in maximum uptake as a function of solubility is vastly more pronounced than that for either the nitro- or chlorophenols. An increase in solubility of a factor of only a half, going from 2-NA to 4-NA, that is, 0.08 to 0.12 g dm<sup>-3</sup>, produced over a 700% increase (265/37.2) in maximum uptake, which greatly exceeds that observed for either the nitro- or chlorophenols. As already mentioned, no such differences in maximum uptake were observed between 2-NA and 4-NA on either activated carbon or dealuminated Faujasite (Derylo-Marczewska and Marczewski



2002; Koubaissy *et al.* 2011). While the variations in solubility between the NAs studied here could potentially explain the differences in the maximum amounts adsorbed, the extent of these differences strongly suggests that an additional, much more influential parameter, that is, shape-selective adsorption, is responsible.

Another variable to consider is  $pK_a$ . All  $pK_a$  values in Table 1 are lower than the pH of the deionized water used in these experiments, and therefore, it seems appropriate that in all cases the amine group of each molecule was in its non-ionized form in the solution. Considering that the quantities of maximum uptake increase as one proceeds from 2-NA to 3-NA to 4-NA, and that no such trend exists for the  $pK_a$  values,  $pK_a$  is not considered to be responsible for the adsorption profiles. It should be further noted that the shape-selective effect observed here is not due to any 'slower' adsorption of 2-NA or 3-NA into the pores, relative to either aniline or 4-NA. Our experiments conclusively showed that equilibrium was reached in the adsorption of each of the four molecules onto ZSM-5, that is, all experiments conducted are reported here at equilibrium concentration.

#### 4. CONCLUSIONS

Aniline, 2-NA, 3-NA and 4-NA were successfully adsorbed from an aqueous solution using ZSM-5. All four molecules obeyed Type I Langmuir adsorption, which was confirmed by linear analysis with  $R^2$  values of 0.997 or greater. The maximum uptake varied considerably due to shape-selective adsorption based on molecular diameters. Aniline and 4-NA had similar adsorption properties, whereas the amounts of 3-NA and 2-NA were significantly reduced due to the bulky nitro group at the 2- and 3-positions of these molecules.

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