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PURIFICATION OF ANILINE AND NITRO-SUBSTITUTED ANILINE CONTAMINANTS FROM AQUEOUS SOLUTION USING BETA ZEOLITE

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Abstract. Aniline and 2-, 3- and 4-nitro substituted anilines were readily adsorbed from aqueous solution onto Beta zeolite. All four molecules adsorbed according to Type I Langmuir adsorption with maximum uptake calculated to be approximately 100 mg g^{-1}. At low adsorbate concentrations, both aniline and 3-nitroaniline were adsorbed in greater amounts than 2-nitroaniline and 4-nitroaniline. This variation in affinity was explained by differences in pKa values, which determined the strength and degree of attraction between the adsorbate and underlying zeolite substrate. The results show that zeolite acid strength can be studied by probe molecule adsorption in mild aqueous conditions using non-specialised laboratory facilities.
Keywords: wastewater purification, nitroaniline adsorption, zeolite

Introduction

Aniline, 2-nitroaniline (2-NA), 3-nitroaniline (3-NA), and 4-nitroaniline (4-NA), Fig. 1, are carcinogenic pollutants used in a variety of industrial processes. They are soluble in water, so their accumulation in groundwater is of major concern (Wang et al., 2008; Bhunia et al., 2003). Various methods have been used to purify wastewater containing nitro-substituted aniline viz. oxidation, membrane separation, and biodegradation (Lee et al., 1997; Sun et al., 2007; Gautam et al., 2005; Judd & Jefferson, 2003; Williams et al., 1999; Qureshi et al., 2007; Saupe, 1999).

Purification has also been conducted using solid materials as adsorbents, whereby simply filtering and washing the solid after adsorption allows its regeneration and subsequent reuse. Solids that have been used to successfully remove nitro-substituted anilines include activated carbons (Li et al., 2009a, 2009b; Derylo-Marczewska & Marczewski, 2002), polymer resin (Zheng et al., 2007), clays (Ko et al., 2007), and mesoporous oxides (Bibby & Mercier, 2003; El-Safty et al., 2012). Zeolites are microporous solid acids that have a variety of industrial applications including heterogeneous catalysis, water softening and as insulating layers in semi-conductors (Weitkamp, 2000). Beta
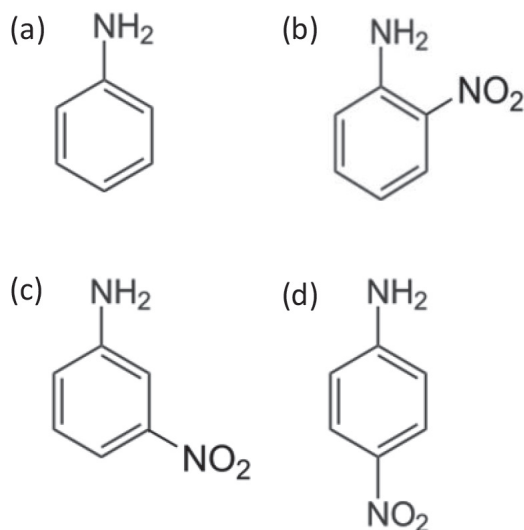
Fig. 1. Chemical structures of adsorbates; (a) aniline (b) 2-nitroaniline
(c) 3-nitroaniline and (d) 4-nitroaniline

zeolite, Fig. 2, has been used to remove aniline from aqueous solution, which was then decomposed by heating in the presence of a copper catalyst (O'Brien et al., 2004; 2008). Aqueous solutions of 2-NA and 4-NA were purified by treatment with dealuminated Faujasite zeolite (Koubaissy et al., 2011). We have recently reported the use of zeolite ZSM-5 as an adsorbent of substituted aniline compounds (Albayati & Doyle, 2013). Although each compound adsorbed on ZSM-5, the amount of material removed from solution varied greatly between adsorbates due to their shape-selective adsorption. Here, we report the adsorption properties of aniline, 2-NA, 3-NA and 4-NA on Beta zeolite. Each molecule was successfully removed from solution using Beta zeolite, while the amounts adsorbed at low concentrations were due to differences in the adsorbates' affinity for the zeolite.

Experimental
Adsorption isotherms were measured at room temperature by allowing Beta zeolite (Zeolyst, Si/Al = 25) to reach equilibrium with each of the adsorbates over a range of
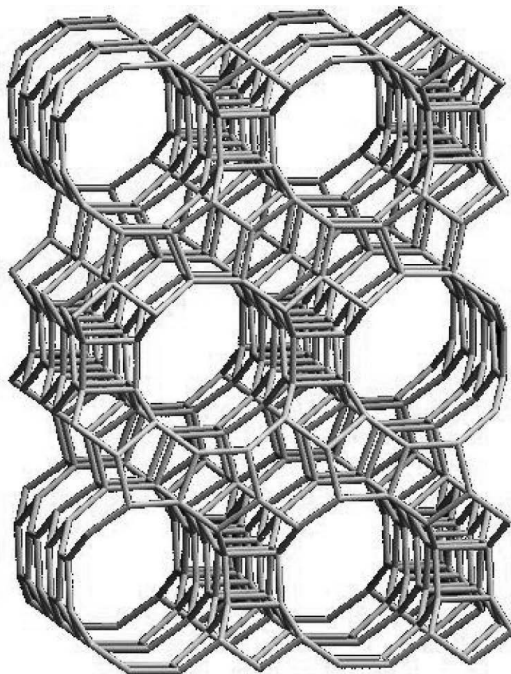
Fig. 2. Schematic diagram of Beta zeolite viewed along (100) axis

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 dm³ distilled water, which were then used to prepare solutions in the range 4-60 mg dm^{-3} for the adsorption experiments. 100 cm³ of solution was added to 0.01 g Beta zeolite in a glass beaker, which was stirred continuously for 1 hour at ambient temperature. At the end of the adsorption, the solution was extracted from the suspension by centrifuge (Hermle Z 200 A) at 3500 rpm for 5 mins, allowing for the analysis of 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.

Aniline, 2-NA, 3-NA and 4-NA loaded zeolite were isolated by centrifuge after adsorption, and then redispersed in 100 cm³ of deionised water to determine whether desorption occurs. The suspension was stirred for 1 hour at room temperature and the solution was extracted and analysed identically to that described above for the adsorption experiments. The extent of desorption was calculated by expressing the amount of ad-

sorbate present in solution, after desorption, as a percentage of the amount of adsorbate that was contained in Beta zeolite before desorption.

Results and discussion

Equilibrium time

Initial experiments were conducted to determine the time period required to reach equilibrium. This was done by measuring the quantity adsorbed on Beta zeolite, and that remaining in solution, as a function of adsorption time. The results (not shown) demonstrated that equilibrium was reached within ten minutes. The actual time required to reach equilibrium may be shorter in duration but an accurate determination of this time period was not achievable using the method described here due to the five minutes of centrifuge, during which adsorption can still occur. In any case, an exact value of equilibrium time is not needed, only that the time period is exceeded during experiments. Therefore, adsorption was allowed to proceed for 1 hr in all experiments.

Adsorption isotherms

Fig. 3 shows the adsorption isotherms of the four compounds, where q_e is the mass of adsorbate adsorbed per gram of zeolite and C_e is the equilibrium concentration of adsorbate in solution at equilibrium. Overall, each molecule was successfully adsorbed over the full range of solution concentrations. The profiles of the isotherms are consistent with Type I Langmuir adsorption (Brunauer et al., 1940); for all four compounds the amount adsorbed increased progressively until the adsorption isotherms reached values in the range 80-100 mg g^{-1}. These results agree very well with previous studies that show aniline adsorption from aqueous solution corresponds to Type I Langmuir adsorption on Beta zeolite (O'Brien et al., 2004; 2008).

Fig. 4 shows the *% Removal*, Eq. 1, of each compound as a function of initial concentration, C_0.

$$\%Removal = \frac{c_0 - c_c}{c_0} \; x \; 100\% \tag{1}$$

For an initial concentration of 4 mg dm^{-3}, approximately 70% of aniline and 3-NA, and 45% of 2-NA and 4-NA are removed from solution. At higher concentrations the *% Removal* values decrease and become approximately similar for all four compounds. The decrease of *% Removal* with increasing concentration is consistent with the use of a fixed mass of zeolite, which limits the amount of material that may be adsorbed from solution as concentration progressively increases. As the maximum uptake of the zeolite pores is approached, any further increase in concentration reduces the amount that may adsorb into the pores, which is recorded as a decrease in *% Removal*.
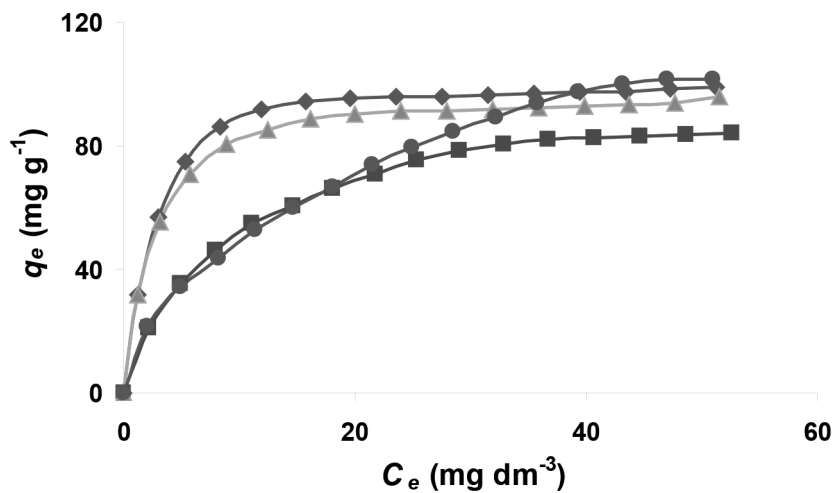
Fig. 3. Adsorption isotherms on Beta zeolite; (◆) aniline (■) 2-nitroaniline (▲) 3-nitroaniline (●) 4-nitroaniline
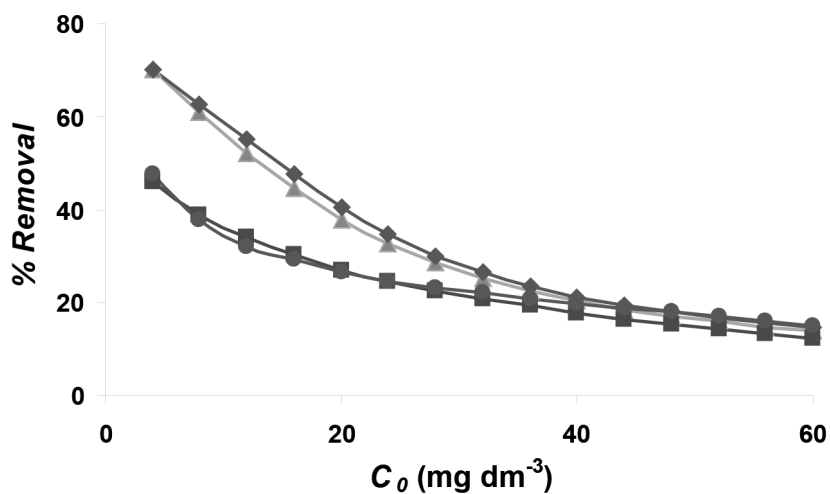

Fig. 4. *% Removal* on Beta zeolite; (◆) aniline (■) 2-nitroaniline (▲) 3-nitroaniline (●) 4-nitroaniline

The adsorption data were next tested to assess their fit to the Langmuir model in Eq. (2) (Langmuir, 1918).

$$q_e = \frac{K_L - C_C}{1 + A_L C_C} \qquad (2)$$

Type 1 adsorption was confirmed by plotting the linear form of Eq. 1 i.e. C_e/q_e vs. 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, Fig. 5, are all straight lines confirming Type I adsorption for each of the 4 compounds with R^2 values of 0.993 to 0.999, Table 1.
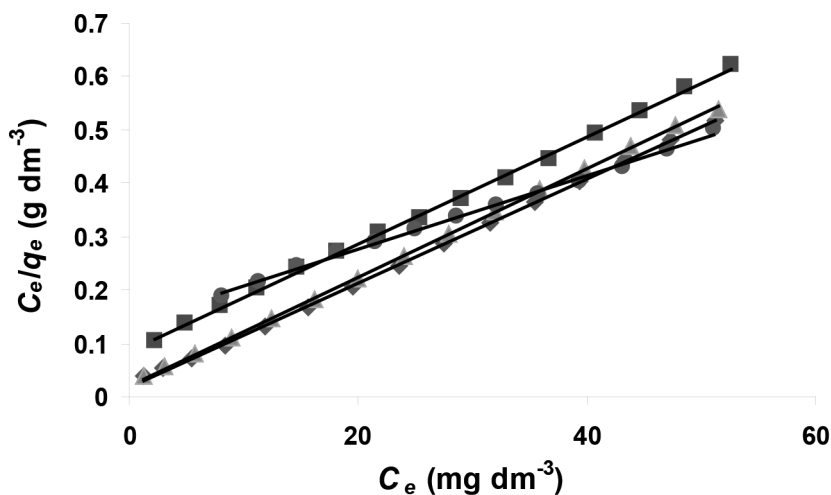

Fig. 5. Langmuir adsorption plots on Beta zeolite; (◆) aniline (■) 2-nitroaniline (▲) 3-nitroaniline (●) 4-nitroaniline

Aniline, 2-NA and 3-NA have almost identical maximum uptake values of approximately 100 mg g^{-1}, Table 1, which is close to the maximum uptake of approximately 110 mg g^{-1} reported for aniline on Beta zeolite (O'Brien et al., 2008). A value of 144 mg g^{-1} is calculated for 4-NA; inspection of the adsorption isotherms in Fig. 3 suggests that the true maximum uptake of 4-NA is more likely to be closer to those of the other molecules. The discrepancy may be a result of the maximum uptake K_L/A_L being calculated by extrapolation of results from the limited concentration range employed here.

Table 1. Langmuir constants and adsorption properties of aniline
and substituted aniline compounds on zeolite Beta

Adsorbate	pKa	K_L $(dm^3 \, g^{-1})$	A_L $(dm^3 \, mg^{-1})$	K_L/A_L $(mg \, g^{-1})$	R^2
Aniline	4.63	53.2	0.517	103	0.999
2-NA	-0.26	11.4	0.114	100	0.999
3-NA	2.47	45.5	0.460	99.0	0.999
4-NA	1.0	7.24	0.050	144	0.993

Although the adsorption isotherms are Type I for all compounds studied here, the profiles in the lower concentration range, 0-30 mg dm^{-3}, diverge in two separate directions; aniline and 3-NA adsorb in much greater quantities than 2-NA and 4-NA. This is also evident from the differences in K_L, Table 1, where the values for aniline and 3-NA are significantly higher (53.2 and 45.5 dm³ g^{-1}) than 2-NA and 4-NA (11.4 and 7.24 dm³ g^{-1}). The changes in the amounts adsorbed at low concentrations on Beta zeolite can be explained by the pKa values of the adsorbates. In solution, it is easy to predict whether a given molecule acts as an acid or base, given its pKa value. All four compounds used in this study have pKa values, Table 1, below the pH of deionised water (5.0-7.0) and therefore exist in their non-ionised form in free solution. However, it is their interaction with Beta zeolite that is relevant to the adsorption reaction. Unfortunately, a universally accepted scale of solid acidity directly comparable to pKa in aqueous solution is lacking. Therefore it is less straightforward to predict exactly how an alkaline molecule behaves in contact with a solid-acid than in solution. Nonetheless, knowledge about the strength and number of acid sites on the zeolite surface makes it possible to explore this interaction. Zeolite acid strength is typically measured by the adsorption of a probe molecule and subsequent analysis by UV-Vis (including Hammett method), IR, NMR, and temperature programmed desorption (TPD) (Farneth & Gorte, 1995; Haw 2002). These techniques have provided valuable information about the acid strength of zeolites that has contributed to deducing the mechanisms of numerous solid-acid catalysed reactions. Experiments on Beta zeolite show that it contains a mixture of strong and weak acid sites (Smirniotis & Ruckenstein, 1995; Camiloti, 1999; Miyamoto et al., 2000). For the results presented here, molecules with relatively high pKa values interact more readily with Beta zeolite,

which facilitates their adsorption. The pKa values of aniline and 3-NA are 4.63 and 2.47, respectively, which show increased adsorption at lower concentrations because of their interaction with both weak and strong acid sites on the underlying zeolite. In contrast, 2-NA and 4-NA have lower pKa values, -0.26 and 1.0, and are more likely to interact with a relatively small number of strong acid sites only, which reduces their adsorption. The adsorption of 2-NA and 4-NA on Beta zeolite is still a favourable exothermic process at low concentrations despite the lower pKa value. As a result, the adsorption reaction continues to proceed, albeit to a lower extent. At adsorbate concentrations 30 mg dm^{-3} and above, the increased presence of the molecules in solution becomes the dominant driving force pushing the reaction towards adsorption. The adsorption profiles of the four compounds become more similar to each other at higher concentrations used in this study. The method described here of adsorbing molecules with different pKa values on zeolites has further significance in that it could potentially be used to achieve a semi-empirical measure of acid strength using only basic 'wet-chemistry' laboratory facilities.

Desorption studies were conducted to confirm that the zeolite could be regenerated by removal of the adsorbates. It is important to confirm that desorption occurs if the zeolite is to be reused. The experiments showed that all four molecules were successfully desorbed into deionised water with over 90% efficiency in a single cycle. A more in-depth study could, of course, be conducted to explore desorption in more detail, i.e., effects of adsorbate loading, solution concentration, temperature etc., but this is beyond the scope of this paper.

Conclusions

Aniline, 2-NA, 3-NA and 4-NA were readily adsorbed from aqueous solution using Beta zeolite. All four molecules obeyed Type I Langmuir adsorption, which was confirmed by linear analysis with R^2 values of 0.993 or greater. At low concentrations, aniline and 3-NA adsorbed in greater quantities than 2-NA and 4-NA due to their greater interaction with Beta zeolite resulting from differences in pKa.

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