

Full Length Research Paper

Removal of 2-Nitrophenol by Linde Type A (LTA) zeolites

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Accepted 02 January, 2013

The adsorption of 2-nitrophenol on zeolites 3A (KA) and 5A (CaA), the general name of which is Linde Type A (LTA), have been investigated by using fourier transform infrared (FT-IR) spectroscopy and scanning electron microscope (SEM) analysis. Nitrophenols can be regarded as both occupational and environmental pollutants. In this work, LTA zeolites which are commercially suitable media for environmental pollutants are used to remove nitrophenols. FT-IR spectroscopy can give useful and often definitive information on the structure and surface properties of zeolite before and after the adsorption. The spectral data showed that the source of adsorption of the 2-nitrophenol on zeolites 3A and 5A is the interaction between the hydroxyl (OH) group of the adsorbent and the surface silanol groups of the zeolites by means of a hydrogen bond.

Key words: Adsorption, Linde Type A (LTA) zeolites, 2-nitrophenol, IR spectroscopy.

INTRODUCTION

Zeolites are widely known as molecular sieves. Considering the penetration and adsorption of molecules onto the zeolite channels are important. This is shown in the investigation of adsorption onto zeolites using molecular spectroscopic procedures (Little, 1966). Phenols and phenolic compounds are a kind of typical organic contaminants in wastewaters and drinking water. These contaminants are generated from a number of industrial manufacturing processes such as pesticide, paint, solvent, pharmaceutical, wood preserving chemicals, and pulp industries (Pi et al., 2007). Specific adsorbents are used for the removal of phenols from aqueous solution (Abburi, 2003; Furuya et al., 1997; Dargaville et al., 1996; Shu et al., 1997; Ku and Lee, 2000; Dutta et al., 2001; Shen, 2002; Denizli et al., 2001).

Nitrophenols are of interest due to their inclusion as priority toxic pollutants by agencies such as the United States Environmental Protection Agency. The industrial growth and population increase have resulted in the release of different pollutants in the

environment and the treatment of effluents has become a challenging topic in environmental sciences (Ely et al., 2009).

Synthetic zeolites are interesting from the point of view of their usability as efficient adsorbents for removal of many pollutants from the environment (Bardakçı and Kaya, 2009; Abu-Lail, 2010). Because aromatic nitro compounds represent a group of highly toxic pollutants, study of the method of their removal from environment represents the highest degree of interest in environmental technologies.

Adsorption is an effective technique for removing low level of organic pollutants out of drinking water, waste water, and other aqueous solutions. Toxic organic pollutants such as phenolic compounds can effectively be removed by means of adsorption. In this study, the adsorption of 2-nitrophenol on 3A and 5A zeolites are examined by infrared spectroscopy and scanning electron microscopy (SEM).

EXPERIMENTAL

3A and 5A zeolites are chosen by the facility of same structure but different cavity sizes which allows comparing their adsorption characteristics. The synthetic zeolites KA (type 3A), and CaA (type 5A) were obtained from the Aldrich Chemical Company. The unit cells of zeolites contain:

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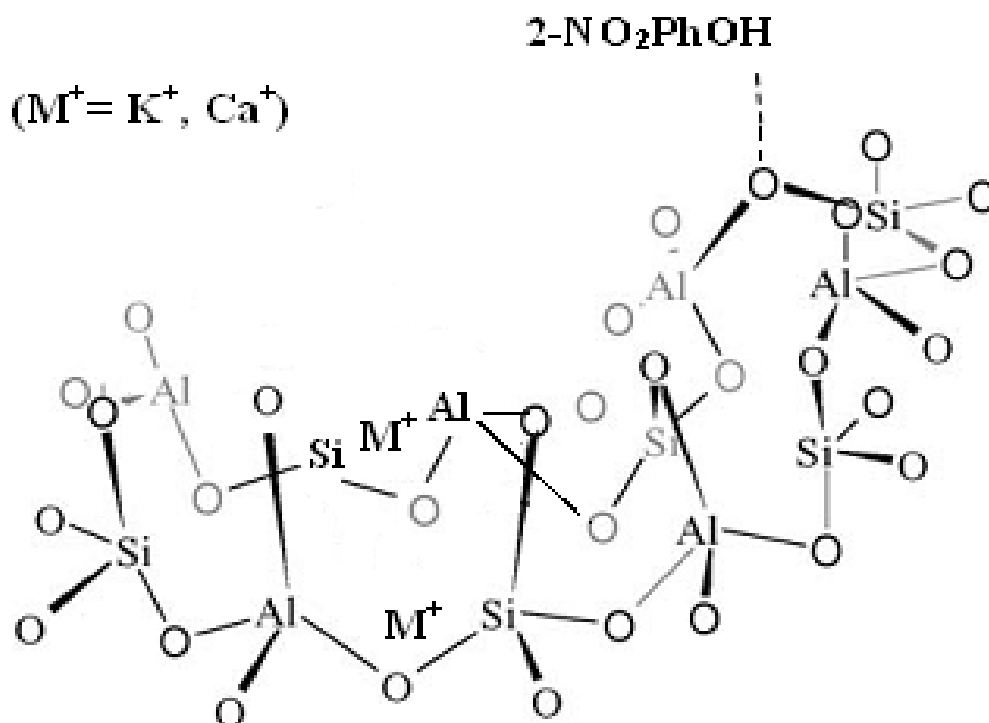
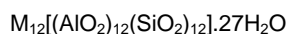


Figure 1. Schematic representation of zeolite-2-nitrophenol interaction.



Where, M = K, or Ca.

2-nitrophenol ($HOC_6H_4NO_2$) was used without purification. As for the preparation of the samples, the mentioned zeolites were activated at 623K for 4 hours then 0.1 g of each zeolite was placed into 40 mg of 2-nitrophenol. After stirring and storing for 72 h, the mixtures were filtered and washed twice with ethyl alcohol to remove the residues and then filtered again and dried at room temperature.

The samples were compressed into self-supporting pellets and introduced into an Infrared (IR) cell equipped with KBr windows. The IR measurements were performed at room temperature on a Perkin-Elmer BX FT-IR (Fourier Transformed Infrared) spectrometer at a resolution of 4 cm^{-1} in the transmission mode. Scanning electron microscopic analyses were taken by using a Zeiss model scanning electron microscope.

RESULTS AND DISCUSSION

FT-IR analysis results

Schematic representation of zeolite-2-nitrophenol interaction was given in Figure 1. The excess oxygen in the alumina molecules gives the framework of a negative charge which can be balanced by trapping positively-charged ions (cations) in cages of structure. IR spectra of pure 3A zeolite and 2-nitrophenol adsorbed on 3A zeolite were given in Figure 2. IR spectra of pure 5A zeolite and 2-nitrophenol adsorbed on 5A zeolite are given in Figure 3. All IR spectral data were summarized

in Table 1.

We refer to the work of Chiş (2004), Srinivasan et al. (2007), Sundaraganesan et al. (2007), Zych et al. (2007), Clarkson and Smith (2003), Wang et al. (2009), Kovacs et al. (1998), Refat et al. (2007), Sundaraganesan et al. (2006, 2008) and Pei et al. (2006) for vibrational assignments of 2-nitrophenol.

The hydroxyl (OH) stretching vibration frequency for pure 2-nitrophenol is observed at 3467 cm^{-1} . This band is observed at 3438 and 3434 cm^{-1} after 2-nitrophenol adsorption on zeolites 3A and 5A, respectively. As can be seen from these results, there are considerable decreases in OH vibration band for the zeolite complex. The fact that OH group of 2-nitrophenol and surface silanol groups of zeolites interact with each other through a hydrogen bond can explain the reason of decrease at OH band vibrations (Öztürk et al., 2009). As a reason for this; OH group has a weak hydrogen bond with surface silanol groups and decreased force constant of OH group.

For 2-nitrophenol, asymmetric nitro stretching band was observed at 1532 cm^{-1} . After the adsorption of 2-nitrophenol on zeolites 3A and 5A, it was observed at 1533 cm^{-1} for both the zeolites. Symmetric nitro stretching vibration band for 2-nitrophenol, which was observed at 1312 cm^{-1} , was observed at 1313 and 1312 cm^{-1} , after the adsorption on zeolites 3A and 5A, respectively. As can be seen in Figure 2, there is a little frequency changes in asymmetric and symmetric NO_2 stretching bands. This gives a clue that interaction between nitrophenol and zeolites cannot occur through NO_2 .

The C-O stretching vibration band for 2-nitrophenol

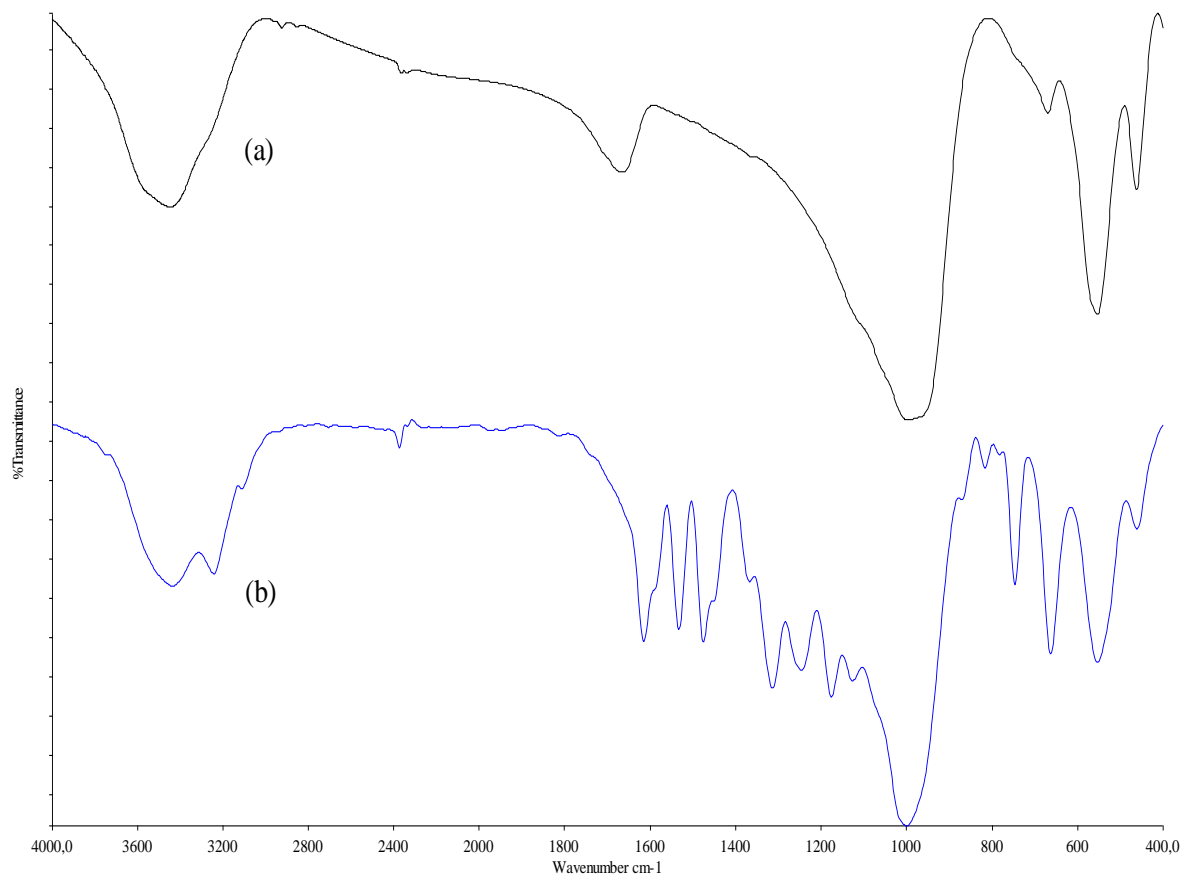


Figure 2. (a) IR spectra of pure 3A zeolite, (b) 2-nitrophenol adsorbed on 3A zeolite.

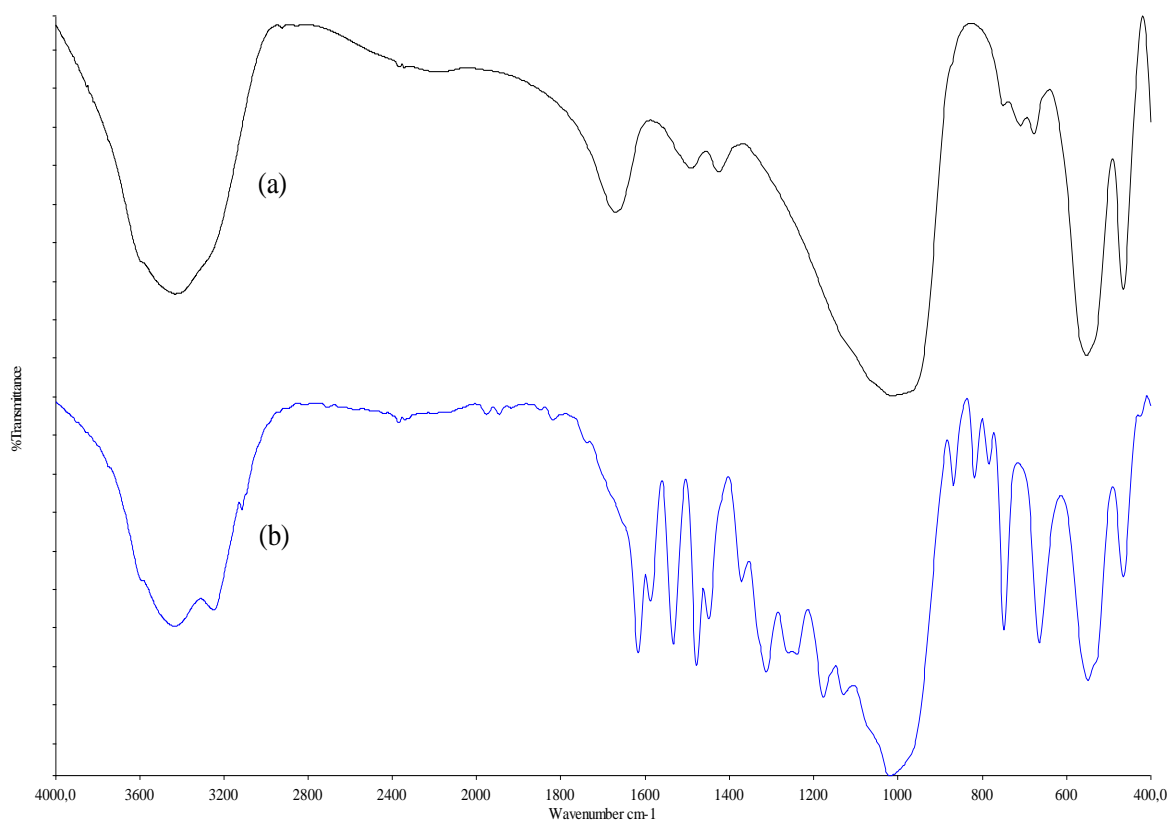


Figure 3. (a) IR spectra of pure 5A, (b) 2-nitrophenol adsorbed on 5A zeolite.

Table 1. IR results of zeolites + 2-nitrophenol (vibrational frequencies in cm^{-1}).

2-nitrophenol	2-nitrophenol-3A	2-nitrophenol-5A	Assignments
3467 ^w	3438 ^b	3434 ^b	$\nu(\text{O-H})$
3236 ^w	3245 ^b	3248 ^b	$\nu(\text{O-H})$
3113 ^{vw}	3113 ^w	3114 ^w	$\nu(\text{C-H})$
3091 ^{vw}	3092 ^w	3094 ^{sh}	$\nu(\text{C-H})$
1614 ^{vs}	1616 ^s	1615 ^s	$\nu(\text{C=C})$
1589 ^b	1589 ^m	1587 ^m	$\nu(\text{C=C})$
1532 ^{vs}	1533 ^s	1533 ^{vs}	$\nu(\text{NO}_2)$ as.
1477 ^b	1478 ^{vs}	1477 ^s	$\nu(\text{C=C})$
1312 ^m	1313 ^m	1312 ^s	$\nu(\text{NO}_2)$ s.
1266 ^w	-	-	$\beta(\text{C-H})$
1236 ^w	1248 ^w	1239 ^w	$\nu(\text{C-O})$
1177 ^m	1177 ^m	-	$\beta(\text{O-H})$
1027 ^w	-	-	$\gamma(\text{C-H})$
868 ^m	872 ^m	868 ^m	$\gamma(\text{C-H})$
818 ^m	816 ^s	817 ^s	$\beta(\text{NO}_2)$
784 ^m	784 ^m	784 ^m	$\gamma(\text{C-H})$
748 ^b	748 ^{vs}	748 ^{vs}	$\omega(\text{NO}_2)$
664 ^{vs}	-	-	$\beta(\text{CCC})$

ν = stretching; δ = bending; β = in plane bending; γ = out of plane bending; ω = wagging; as = asymmetric; s = symmetric; vs = very strong; s = strong; m = medium; w = weak; vw = very weak; sh = shoulder; b = broad.

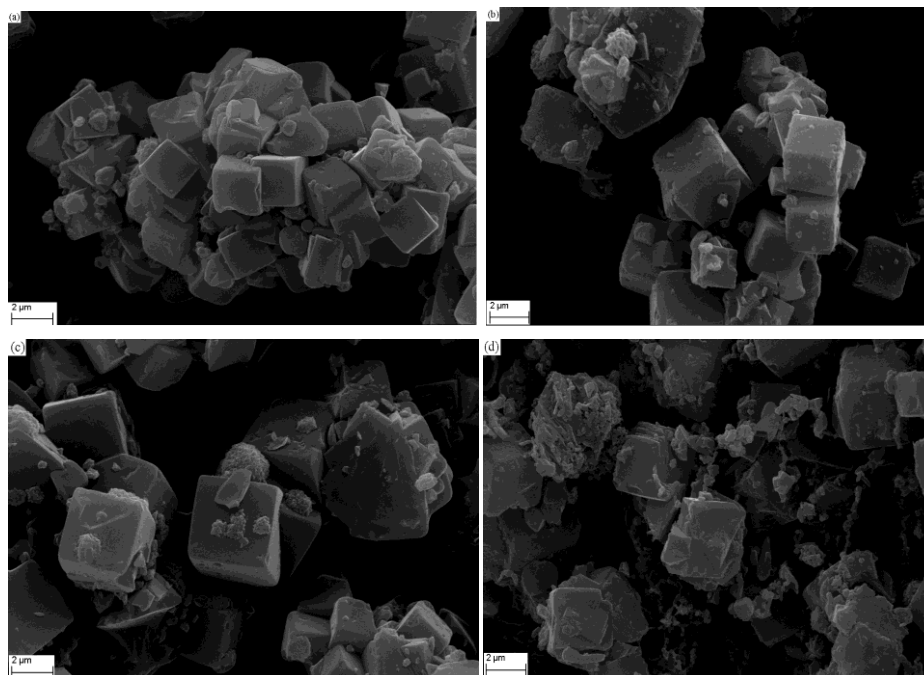


Figure 4. SEM images of (a) pure 3A zeolite, (b) pure 5A zeolite, (c) 2-nitrophenol and 3A zeolite, (d) 2-nitrophenol and 5A zeolite.

is observed at 1236 cm^{-1} , this band is observed at 1248 cm^{-1} after the adsorption on zeolite 3A of 2-nitrophenol and at 1239 cm^{-1} after the adsorption on zeolite 5A of 2-nitrophenol. So, there are red frequency shifts on C-O stretching vibration band for 2-nitrophenol adsorbed on 3A and 5A zeolites, respectively.

Scanning electron microscopy (SEM) results

SEM images of samples were given in Figure 4. The images of pure zeolites 3A and 5A and those taken after the 2-nitrophenol adsorption show the structures. Cubic forms of zeolite 3A and zeolite 5A are observed in their naked state. The SEM images

of zeolites after adsorption of 2-nitrophenol on zeolites predicated that no impressive results were obtained in the scale of 2 μm . Cubic forms of zeolites still stay in the same shape. After the adsorption, it is possible to talk about no formational change on the surface of the zeolites. This result can be attributed to stable zeolite surface after adsorption.

Conclusion

From these results we can say that the OH group of the 2-nitrophenol interacts with the silanol groups on zeolites 3A and 5A. The interaction reveals the existence of a hydrogen bond between them. After the adsorption, there are blue frequency shifts for OH groups of 2-nitrophenol adsorbed on zeolite 3A and 5A, respectively. In zeolites, the oxygen atom of Si-O-Si bond, acts a hydrogen bond acceptor, which tends to make a bond of OH part of 2-nitrophenol.

FT-IR spectroscopy was used to study the molecular scale interaction of nitrophenol compound with sorbent. Little change was observed in vibrations of nitro group after the adsorption. These data can be explained that $-\text{NO}_2$ functional group has no effect in adsorption process.

The results are very important for the application of zeolites as sorbent for the adsorption of organic pollutants from environment. Results show that LTA type synthetic (3A and 5A) zeolites are effective sorbents for the removal of 2-nitrophenol.

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