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The detoxification nitrobenzene in waste water on zeolites

Abstract

Nitrobenzene has a high toxicity to warm-blooded animals and humans. It has been considered as very toxic compound for environment. In this paper it is been describe the possibility of detoxification of nitrobenzene through adsorption on zeolite. It is proposed to use of natural zeolite - clinoptilolite as a sorbent, which was saturated by quaternary ammonium salt. The activity of nitrobenzene removal from wastewater is shown on zeolite surface immobilized QUAT - N, N-dimethtyl-N-hexadecyl-N-2-hydroxyethyl ammonium bromide. The adsorption processes was investigated by calibration curve of UV spectrum of nitrobenzene in different concentration of water.

Keywords: detoxification, nitrobenzene, quaternary ammonium salt (QUAT), immobilization, removal, wastewater, toxicity, freundlich adsorption isotherm

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Introduction

Nitrobenzene - aromatic nitro compounds is produced in industry on the largest scale, the volume of production in the world is approximately 2million tons per year. It`s known to use nitrobenzene as a semi-product of organic syntheses, in the production of dyes, as reagent in analytical practice and as solvent. Nitrobenzene in the environment mainly comes from the wastewater of plants. A large amount of nitrobenzene is found in the wastewater produced by aniline dye, as well as insulating and glossy materials.[1]

Nitrobenzene contamination had been happened in case of accidents in chemical industry and storage depots. For example, in recent years environmental pollution with nitrobenzene in water systems has often occurred in China.[2] In this case nitrobenzene, as well as in combination with aniline, in waste water treatment studies have gained momentum in the last 10-15years by Chinese researchers, especially a number of emissions into the environment and the environment.[1–3] It is a very interesting study by Turkish authors, where there are large emissions of nitrobenzene and its derivatives, which are used by dye producers and those using it.[4]

Nitrobenzene is one of the representatives of the group of substances responsible for damage to the nervous system and red blood with the formation of methemoglobin, for the development of hemolytic anemia, hepatotoxic and nephrotoxic effects. The substance has a high toxicity to warm-blooded animals and humans. There are cases of poisoning with nitrobenzene, including fatal. The lethal dose of nitrobenzene for a person is 10mg/kg, but death can already occur from taking 1-2ml or a few drops of the substance. Nitrobenzene is slightly insoluble in water (0.19g/100ml water at 20°C).

Materials and methods

Here is used Armenian natural zeolite clinoptillite from north-east part of Armenia. Zeolite samples were thoroughly washed with distilled water and dried at 150°C for 3hours. Then they were rubbed into a powder with a particle size of 20-70microns. Here were prepared the next quaternary ammonium salts (QUAT) for zeolite saturation with them:

i. Catamín-AB - CAB (from Chemical reagent plant Kharkov, Ukraine)
ii. N, N-dimethtyl-N-hexadecyl-N-2-hydroxyethyl ammonium bromide - DMHDHEABR, (the synthesis had been made in our laboratory, the purity at 98% by titration)
iii. Thriethylbenzylamonium chloride – TEBACH, (the synthesis had been made in our laboratory, the purity at 99% by titration).

Clinoptilolite saturation with QUAT is reached at their concentration of 0.006mol/kg (Figure 1). Adsorption is comparatively higher for DMHDHEABR – 6,0-6,5mmol/gr. Almost the same value was obtained for CAB – 5,5-5,7mmol/gr. and 3,0-3,5mmol/gr for TEBACH. All the resulting QUAT-s on zeolite (clinoptilolite) exhibited stability in the heat treatment of up to 350°C. Moreover, the DMHDHEABR on zeolite is stable up to about 450°C, without any exposure to ammonium salts or Hofmann cleavage. The sorption of water on sorbents to determine hydrophobicity was also investigated. The coefficient of hydrophobicity increases almost linearly with an increase in the content of in the sorbent DMHDHEABR to 5% QUAT, which should be explained by the greater hydrophobicity of this modified sorbent compared to the initial one.

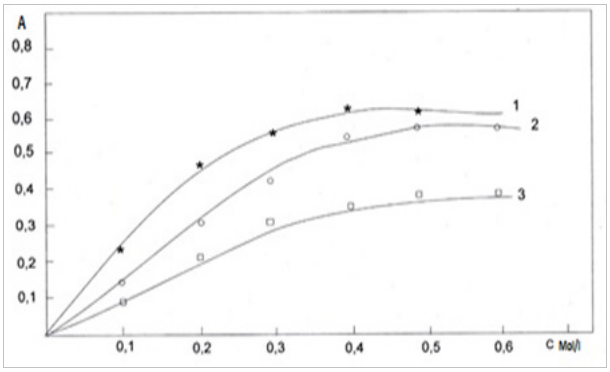

Figure 1 Adsorptive isotherms of -
i. DMHDHEABR
ii. CAB
iii. TEBACH

Nitrobenzene adsorption has been followed through this way

Below, the reduction of various concentrations of nitrobenzene

is 0.15grams in the sorption - up to 0.02grams in 100ml of water after 10hours batch sorption experiment. As sorbent here is used the zeolite with DMHDHEABR. The sorption activity is for zeolite with CAB about 80%, and 45% with TEBACH, in comparison with DMHDHEABR.

Nitrobenzene presences in water solution were analyzed by Liquid-Gaze chromatographic (GLCh) analysis. For GLCh method here are used with the heat conductivity detector; columns from stainless steel in the size 2mx3mm; the additionals-7%, silicon elastomer E-301 on chemosorbe AW-HMDS (0,26-0,36mm), 15% Carbovax 20M on Chromatone N-AW-HMDS (0,126-0,160mm) and 5% E-30 on Chromatone DMCS (0,400-0,630mm); gas-carrier-helium (speed of 30-60ml/mines) temperature of columns 40-240°. QUAT is identified using TLC method as well. Silufol UV-254 plates are used. The eluent for TLC was BuOH: EtOH: Acetic acid: water (7:5:1:3 volume ratio) mixture. The spots are developed by iodine vapors.

IR spectrum for zeolites is identified by IRS (Specord IR-75) and for nitrobenzene NMR (Varian "mercury-300" RS) methods. The chemical shifts are expressed by ppm with respect to $Si(CH_3)_4$, solvent was $CDCl_3$. For UV analysis of nitrobenzene in different concentration had using spectrophotometer "Specord-50" (Figure 2). The date of UV show the adsorption of nitrobenzene possibilities, then the absorption of molecules in 265nm beginning to evaporated after full sorption on sorbent.

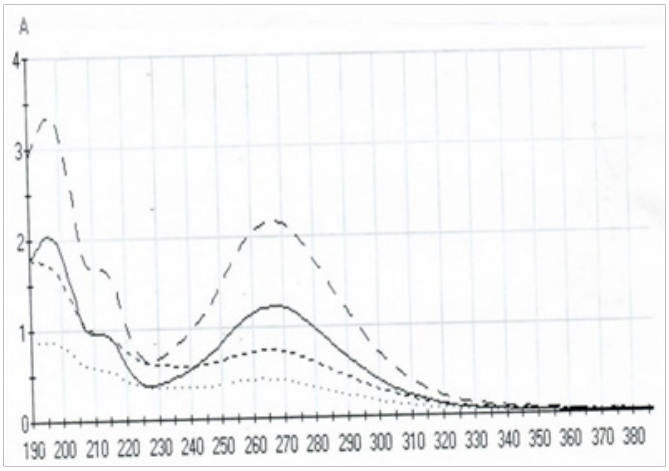

Figure 2 UV spectrum of nitrobenzene in difference concentration of water:

i. 0,15g/100 ml,
ii. 0,10g/100 ml,
iii. 0,05g/100 ml,
iv. 0,02g/100 ml

Results and discussion

The removal of nitrobenzene was primarily described by adsorption using activated carbon.[3] Detoxification of nitrobenzene was also studied as an adsorbent using wood residues, the sludge activated with ammonium salts, natural carbohydrates and other natural minerals, which are cheaper and widespread.[3] Our former study about aniline removal from waste water shows that zeolites with impregnated QUAT on surface is an effective sorbents for BTEX and aniline removal from wastewater.[5] It has been mentioned that all of that salts had been used as catalysts in the phase transfer catalysis – PTC processes.[6] In this case the mentioned immobilized with QUAT zeolites can be used in three-phase PTC system as catalyst.

An adsorption activity of nitrobenzene is very low on natural zeolite (0.5mg/kg) during the 8-12hour study of the static absorption process. In our opinion, this is due to the impossibility of nitrobenzene penetration into natural zeolite`s pores/molecular volume of nitrobenzene near 12Å, when clinoptilolite pore is about 4Å/and with none configured surface. In addition, the oxy groups that are present on the zeolite surface submerge nitrobenzene oxy-group. It is known that aromatic hydrocarbons (benzene, toluene, xylene, ethylbenzene-BTEX) as no polar compounds are most actively absorbed on inert solid bodies. In the case of zeolites such surfaces reach by surface quaternary ammonium salts.[5]

This is the reason why nitrobenzene is adsorpted on the investigated zeolites. The adsorption amount of nitrobenzene on the adsorbent 1 is 60mg/kg, on 2–54mg/kg, on 3-31mg/kg. The adsorption activity is particularly high in the case by DMHDHEABR -modified zeolite, since such salt is stronger immobilized with zeolite not only due to ammonium group, but also by the existing of hydroxyl group. Such immobilization also contributes to nitrobenzene adsorption activity on this zeolite. In our opinion, the adsorption activity of zeolite with such QUAT should be explained by the interaction of nitrobenzene with the hydrophobic surface of the zeolite by improving the interaction of the benzene and nitro- groups with the surface. The importance of quaternary ammonium salt surface activity in this process is once again confirmed in the case of TEBACH, when there the adsorption of nitrobenzene has a low level in comparison with other investigated QUAT – around two times lower. In the Figure 1 is presented the isotherms of quaternary ammonium salts adsorption on clinoptilolite.

The obtained results coincide with the Freundlich adsorption isotherm, which, in its turn, responds to the presence of the monomolecular layer of sorpted QUAT.

Conclusion

It has been shown that the adsorption ability for nitrobenzene removal from water solution by natural zeolite excessively increases after that saturation with QUAT. The absorption ability of such immobilized zeolite depends from surface activity of the used QUAT. It has been found that natural zeolite with quaternary ammonium salt -. N, N-dimethtyl-N-hexadecyl-N-2-hydroxyethyl ammonium bromide as efficient sorbent for detoxification of nitrobenzene from waste water.

Acknowledgments

None.

Conflicts of interest

Author declares that there is no conflict of interest.

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