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Dedicated to the memory of
Professor Candin Liteanu on his 100th anniversary

MODIFIED CLINOPTILOLITE USED FOR REMOVING AZOMETHINES FROM WASTEWATERS. II. ADSORPTION OF AZOMETHINES FROM WASTEWATERS ON CLINOPTILOLITE

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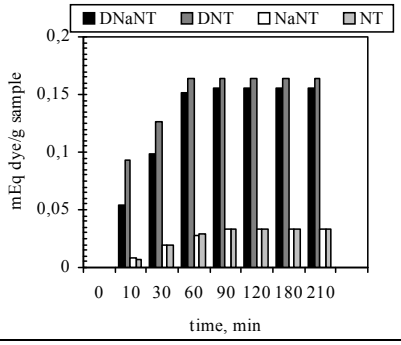
The native clinoptilolite volcanic tuff (NT) and its Na form (NaNT) as well as dealuminated clinoptilolite (DNT) and its Na form (DNaNT) were investigated as efficient adsorbents for separating the 2,2'-dihydroxy-diphenyl azomethine from wastewaters. The effect of parameters such as the pH dye solution, contact time and temperature of adsorption process was examined. The studies show that the DNT and DNaNT samples have a higher capacity of adsorption in comparison with the NT and NaNT samples. Also, the amounts of azomethine dye retained on the dealuminated clinoptilolite are much higher at 60°C than at 40°C. Thus, the adsorbed amount of azomethine dye on DNT sample was about 85% at 60°C, pH=4 and contact time 60 min.



INTRODUCTION

Textile industries spend large amounts of water and chemicals for the dyeing processes. These industries discharge large amounts of colored wastewaters which can be dangerous for environment due to their toxicity. Thus, these wastewaters containing small amounts of dyes can affect the aquatic life[1,2] or causing allergy and skin irritation[3] etc.

In order to remove dyes from wastewaters, many chemical, physical or biological treatments have been used either separately or in combination. Among these removal methods, adsorption process is a prominent method.[4,5]

The removal of dyes from industrial wastewaters using different adsorbents is always of great interest.[6-12] Among the adsorbents, the natural zeolites are the most suitable due to its selectivity for certain pollutants. Intensive research has been done on the application of natural clinoptilolite as adsorbent in special in removing heavy metal cations,[13-20] organic and inorganic anions,[21-23] etc. Also, the application of clinoptilolite in removing dyes from wastewater has been reported.[24-28] The reported studies made evident that the values of the adsorption capacity is strongly influenced by several factors regarding both chemical and structural properties of the zeolite (composition, porosity, pre-treatments, etc.)

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as well as the adsorption process parameters (ion concentrations, temperature, contact time, presence of other ions, etc.).

In a previous study we showed that dealumination of the clinoptilolite accomplished by 24 hour treatment with nitric acid give a material with properties much improved which can be used as adsorbent in order to remove organic compounds with higher molecular mass, such as azomethines from wastewater.[29]

These reasons support the necessity of the present study, aimed to investigate a removal method for 2,2'-dihydroxy-diphenyl azomethine, from wastewaters by adsorption on the modified clinoptilolitic volcanic tuff by acid treatment. The 2,2'-dihydroxy-diphenyl azomethine is an orange dye which can be used in textile industry as a disperse dye for coloring natural and artificial fibers. But its presence in wastewaters for long time can be dangerous to the environment due to its toxicity. For this reason we have investigated the influence of the temperature, the pH solution of dye and the contact time of adsorption process, which are the most significant parameters in the purification process of wastewaters.

EXPERIMENTAL

1. Preparation of zeolitic material

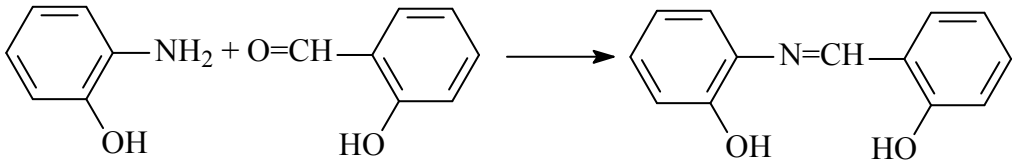
The volcanic tuff under study was mined from the Mirsid deposits in Roumania and had a clinoptilolite content of 70%. The detailed study of the preparation, ionic exchange and dealumination process of the clinoptilolite and the characteristics of these materials were presented in first part of our study.[29] The samples obtained and used for this study were following: NT (native volcanic tuff), NaNT (native volcanic tuff in Na form), DNT (dealuminated native tuff) and DNaNT (dealuminated native tuff in Na form).

2. Azomethine dye obtaining

All chemicals used in this study are of analytical grade, were obtained from commercial sources (Fluka, Merck, etc.), and used without further purification (salicylic aldehyde) or after recrystallization (ortho aminophenol).

In order to obtain the azomethine dye we started from ortho aminophenol and salicylic aldehyde. The synthetic method for the azomethine is presented as follows: 4 g ortho aminophenol was solved in 100 mL warm ethanol and then 3.88 mL salicylic aldehyde were added, using as catalyst few drops of acetic acid and the mixture was refluxed for 2 hours. The azomethine crystallize by cooling and is filtered, washed with cold ethanol and purified by recrystallization from ethanol. Finally, 7.1704 g orange crystals were separated.

The azomethine of the following structure is finally obtained:



3. The adsorption techniques of azomethine dye on the obtained samples

All samples were put into contact with 0.005N azomethine dye solutions (1:10 ratio by vol). The adsorption process for each sample separately was carried out in both 40°C and 60°C, for 3 hours. The pH of azomethine dye solution was between 4-9.0. After the adsorption period, the mixtures were centrifuged for 5 min at 4500 rpm and the phases were separated.

The equilibrium concentration of azomethine dye in the solution phase was determined spectrophotometrically by measuring the absorbance at the maximum wavelength at 439 nm for the azomethine dye through a Uv-vis spectrophotometer. The dye amount in the wastewater was estimated by using the calibration curve previously registred.

RESULTS AND DISCUSSION

1. Characterization of the azomethine dye

The IR spectra were recorded on a Fourier Transform Digilab Scimitar Series spectrometer, in KBr pellets in the range 4000-400 cm^{-1}. The NMR spectra were recorded on a Brücker WM 400 MHz spectrometer. The UV-VIS spectra were obtained using a Shimadzu UV-1601 Spectrophotometer and 1 cm quartz cells.

The 2,2'-dihydroxy-diphenyl azomethine was characterized by the means of FTIR spectroscopy in order to verify that the condensing reaction occurred (by the presence of the signal between 1645 and 1650 cm^{-1} corresponding to the -CH=N- bond). In Fig. 1 is presented the FTIR spectra for the analyzed azomethine dye.

From Fig. 1 we notice the bands with medium intensity at 774 cm^{-1} due to 1,2-disubstituted benzene ring. Other characteristic signals are: the band at about 3642 cm^{-1} characteristic for the OH phenol and that at 1672 cm^{-1} specific for the azomethine bond. Also, the 2,2'-dihydroxy-diphenyl azomethine was characterized spectrophotometrically by UV-VIS spectrophotometer. The obtained spectrum is presented in Fig. 2.

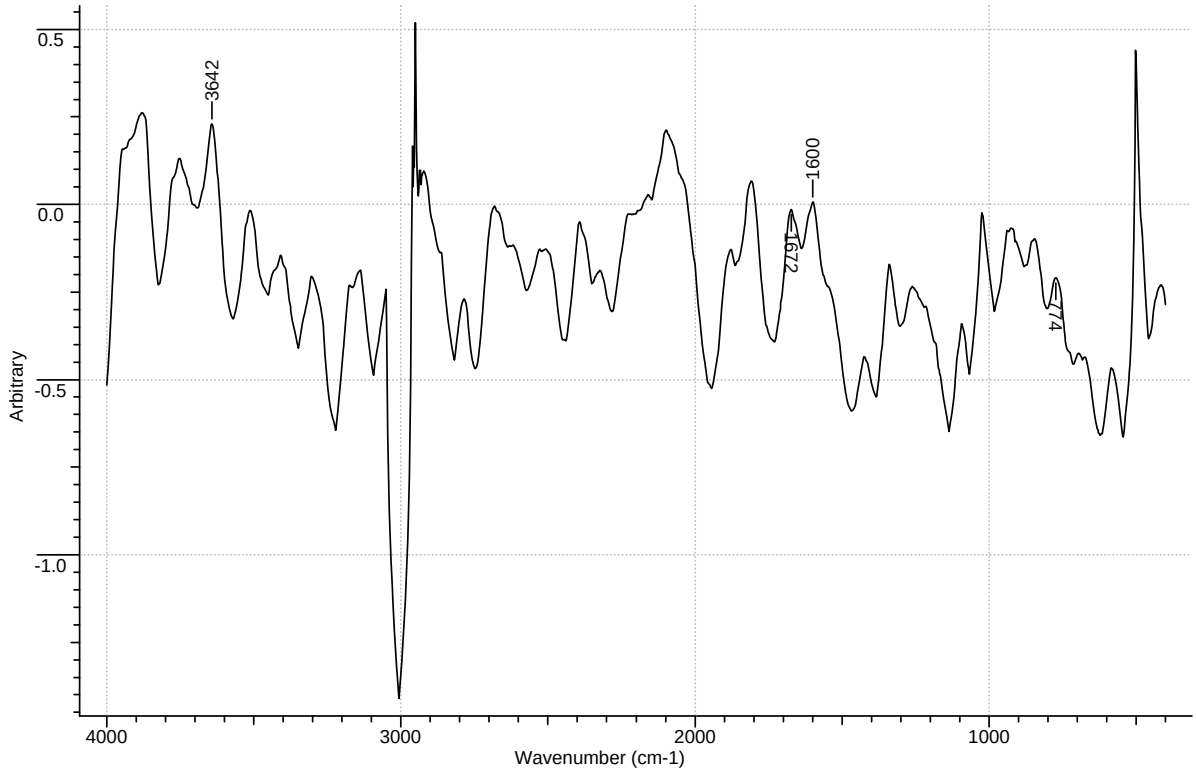


Fig. 1 – FTIR spectrum for the azomethine dye.

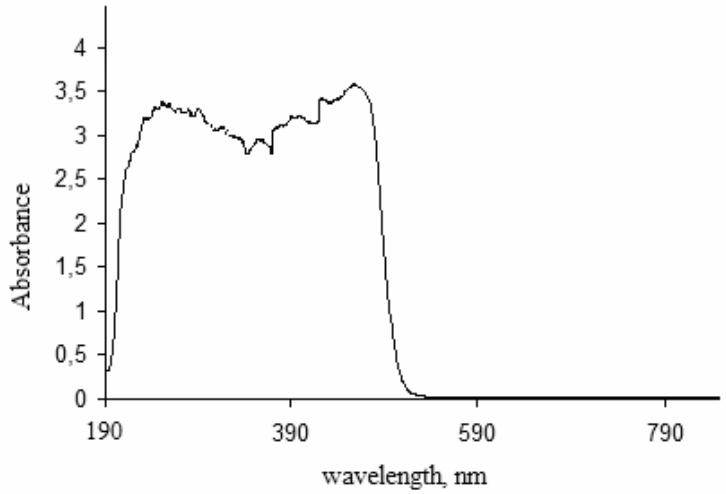


Fig. 2 – The UV-VIS spectrum for the synthesized azomethine dye.

From Fig. 2 we observe two different zones, the first one in near UV area being characteristic for the aromatic ring (at about 254 nm). The second zone is at the beginning of the VIS field and appears due to the chromogenic effect of the azomethine group coupled with the effect of the OH groups in ortho to the azomethine bond.

The obtained azomethine structure was confirmed by the H-NMR spectral analysis. In the spectrum the specific signals for all the protons of the azomethines were identified. For example, the H-NMR spectrum for azomethine the signal for OH proton appears at 8.707 while the aromatic protons give bands between 7.934-6.890 ppm (Fig. 3).

2. The effect of temperature on the adsorption process

In Fig. 4 is presented the variation in time of azomethine dye adsorption by all the adsorbent samples, the process occuring at 40˚C.

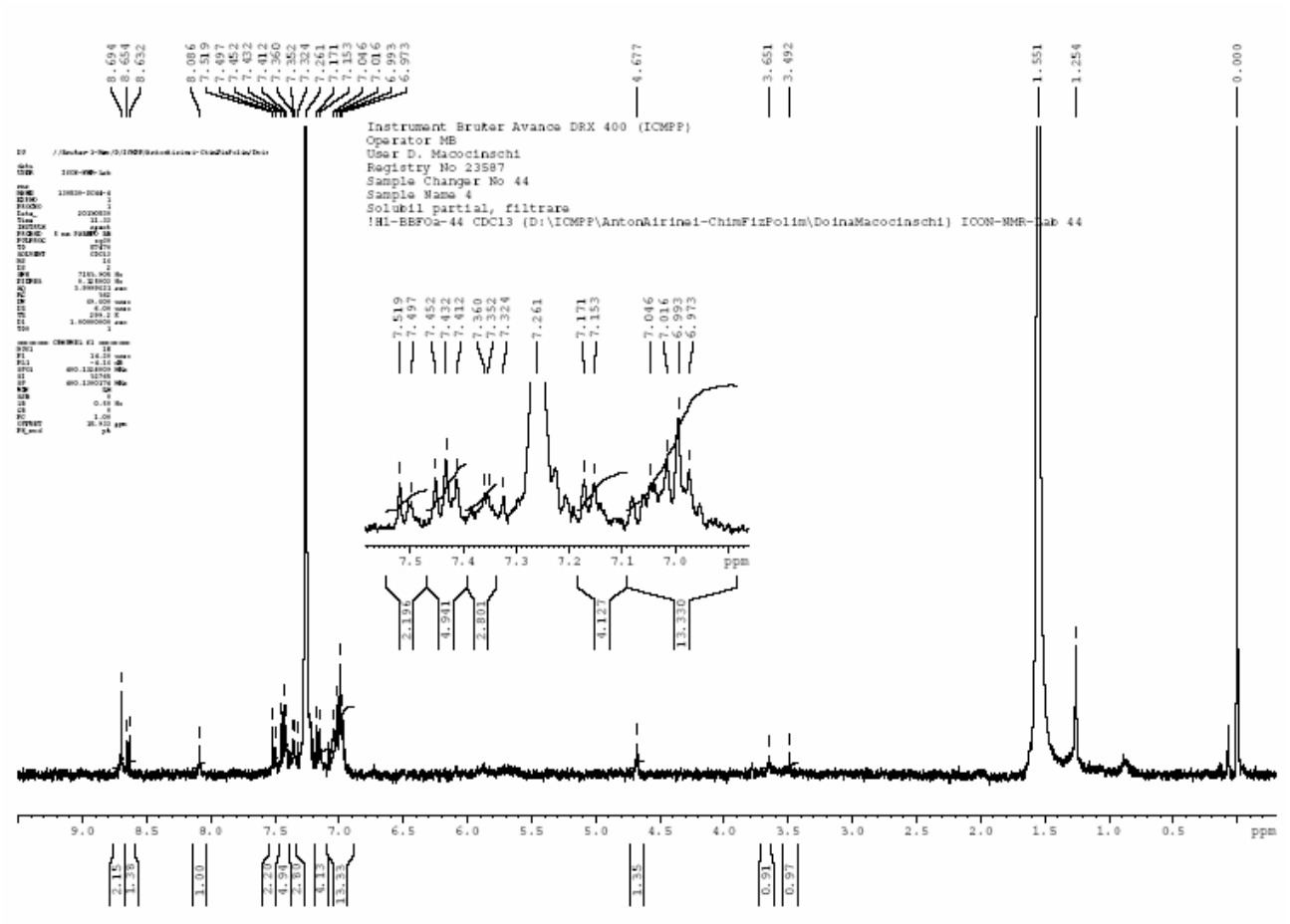


Fig. 3 – H-NMR spectrum for the azomethine dye.

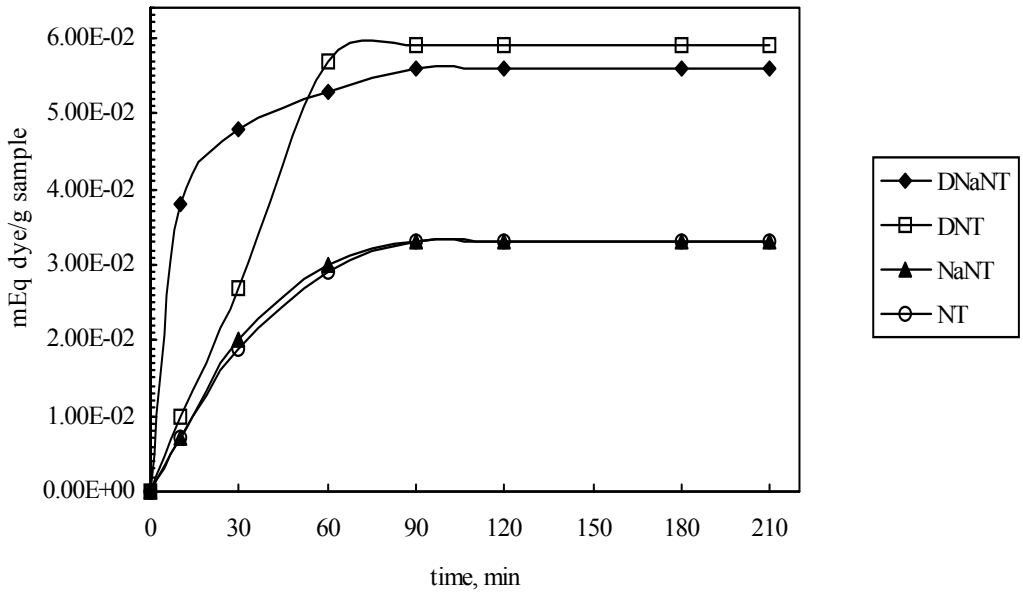


Fig. 4 – Kinetic curves of adsorption process for the azomethine dye on all the samples at 40˚C.

As shown in Fig. 4 we could observe that the adsorption process for the two samples (NT and NaNT) reached an equilibrium after aproximately 60 minutes. The experimental data presented in Fig. 4 make evident that the adsorbed amount of the dye is insignificant in the case of the two samples (NT and NaNT) and it increased in the case of the dealuminated samples (DNT and

DNaNT). Nevertheless, the sample DNT showed a higher capacity of adsorption in comparison with the DNaNT sample. This is because the dealumination, treatment leads to decreasing of the crystallinity and aluminium ratio and increases the specific area and porous volume, which is more acute for the native tuff than for its Na form. This fact was demonstrated in the first part of our research.[29] Another situation is observed when the adsorption process took place at 60°C (Fig. 5).

As shown in Fig. 5 the adsorption capacity of dealuminated samples for azomethine dye increased at 60°C and the adsorption process for the two samples reached an equilibrium after aproximately 60 minutes. It is also worth noting that the amount of azomethine dye removed by the two samples DNT and DNaNT at 60°C was much higher than the quantities removed at 40°C (Fig. 4). For a better comparison, the variation of the adsorption capacity of all sample for azomethine dye at the two temperatures is represented in Fig. 6.

The increases of the adsorption capacity of the native clinoptilolite for other dyes with increasing temperature have been observed in many studies.[30-34] Compared with these results, in this case the dealuminated clinoptilolite has a good adsorption capacity for the azomethine dye.

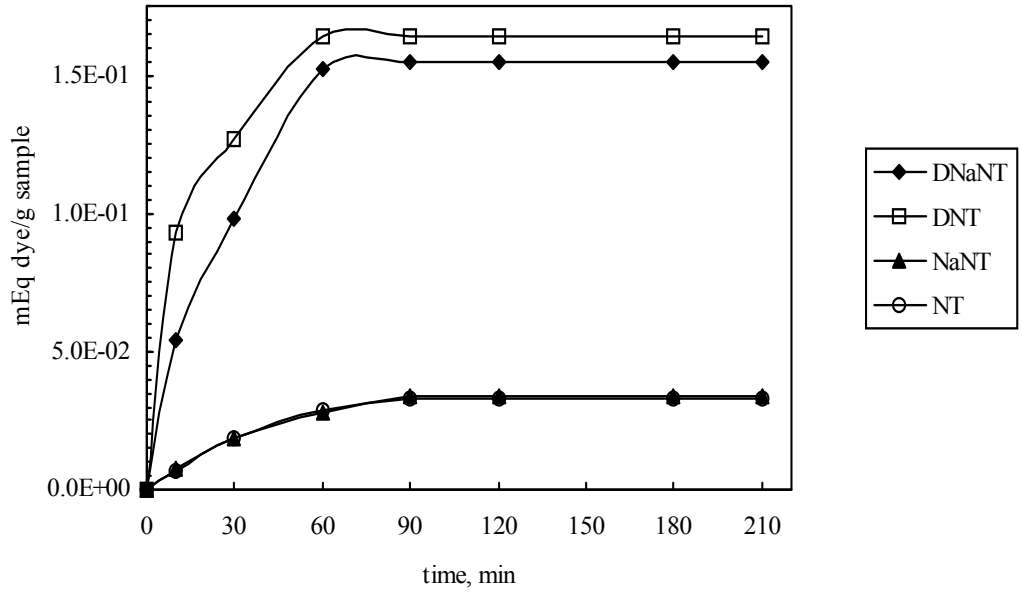


Fig. 5 – Kinetic curves of adsorption process for azomethine dye on all the samples at 60°C.

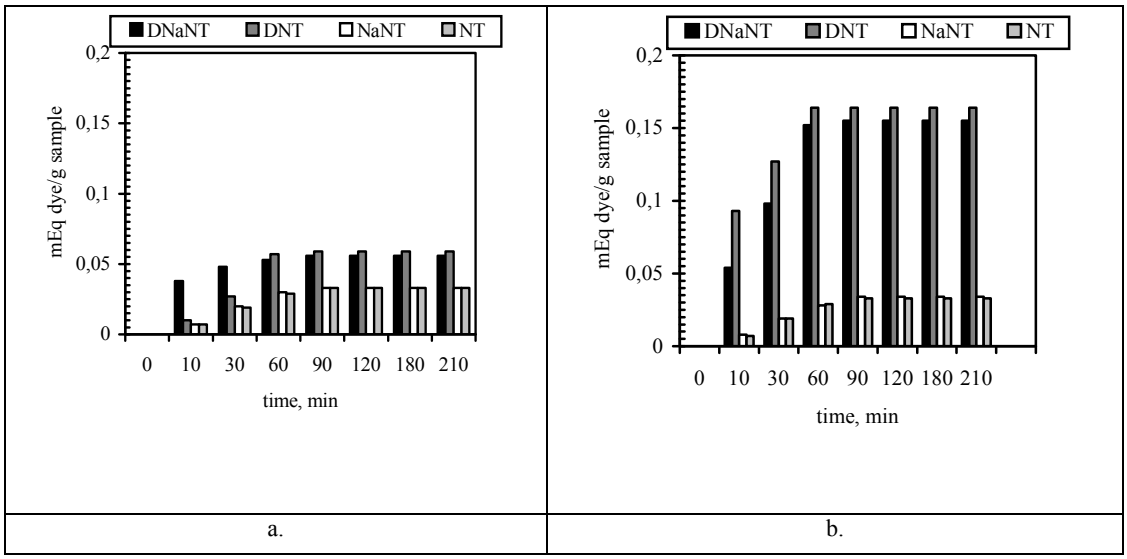


Fig. 6 – Variation of the adsorption capacity of all the samples as a function of temperature. a. 40 °C; b. 60 °C.

3. The effect of the pH of the dye solution on adsorption process

According to the literature data[30-33] the adsorption of dyes onto the zeolitic surface is primarily influenced by the solution pH. In this way, we have investigated the effect of the pH dye solution (pH=4 and pH=9) on adsorption process on DNT sample at 60°C because it presented the best results. The variation adsorption capacity with the contact time at the two values of pH dye solution is depicted in Fig. 7.

As can be seen in Fig. 7, the dealuminated sample show high adsorption capacity at pH=4, probably because the strong acid sites that appear through the long acid treatment.

The azomethine dye due to its structure has a zwitterionic character because of the migration of a proton between the OH group and the N atom from the azomethine bond.

The dual charge allow our dye to have a slightly buffer action on the solution pH value. The decreasing of the adsorption with the increasing of pH value (pH=9) could be explained by the blocking of acid sites of dealuminated sample by the free hydroxyl group presented in the alkaline solution.

We can say that the information obtained upon these investigations give us important suggestions toward the effect of pH of the azomethine solution on adsorption process onto dealuminated clinoptilolite which are unique in literature.

4. The effect of the contact time on adsorption process

The variation of contact time with adsorption capacity of samples is depicted in Fig. 8.

As can be seen in Fig. 8 the amount of azomethine dye adsorption on the dealuminated samples increased with increasing the contact times. The adsorption of azomethine onto dealuminated clinoptilolite (DNT) reached equilibrium after 60 min. The amount of azomethine adsorption was found of $2{,}1\times10^{-4}$ mol/g sample at pH of 4.0.

Compared to the other investigations related to adsorption of some dyes, our results were in good agreement. The dealuminated clinoptilolite is the best solution to be used as adsorbent for the removal of the azomethine dye due to its low cost and adsorption characteristics.

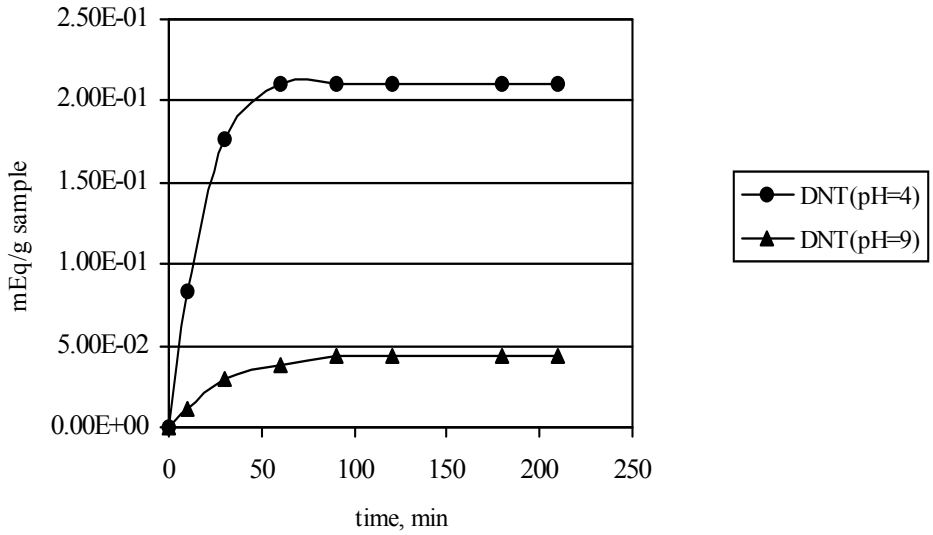
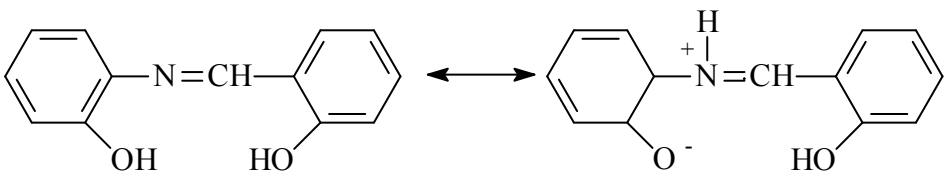


Fig. 7 – The effect of the pH dye solution on adsorption process.



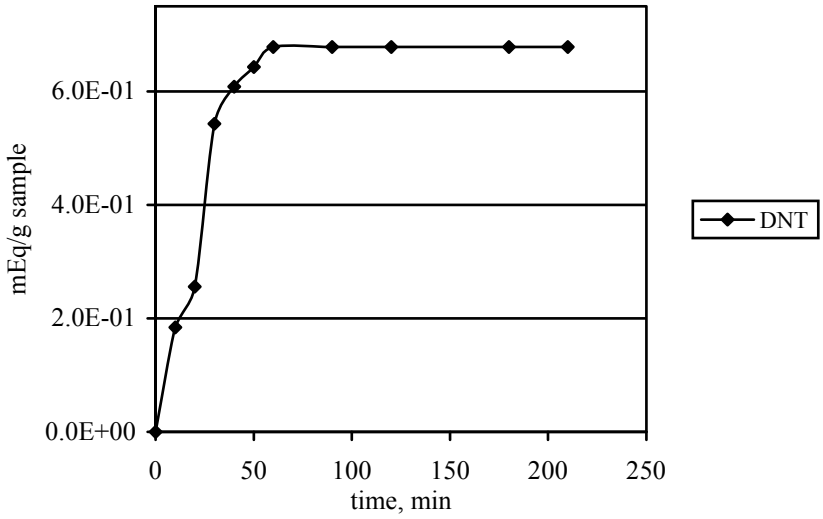


Fig. 8 – The effect of the contact time on adsorption process.

CONCLUSIONS

Dealuminated clinoptilolite which is presented for the first time in our studies has been proved to be the most efficient adsorbent for azomethine dye adsorption in wastewaters. The 2,2'-dihydroxy-diphenyl azomethine is an orange dye used in textile industry and can be dangerous in wastewaters due its toxicity. The adsorption of the azomethine dye was found to be dependent on temperature of process, pH and contact time. Thus, the amounts of azomethine dye retained on the dealuminated clinoptilolite are much higher at 60°C than at 40°C. Also, the adsorbed amount of dye decreased at higher values of pH at the short contact time (the maximum adsorbed amount of azomethine dye on DNT was about 85% at pH=4 and 60 min.)

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