

original article

Effectiveness of nanozeolite modified by cationic surfactant in the removal of disinfection by-product precursors from water solution

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ABSTRACT

Aim: In this study the performance of a natural nanozeolite, modified with a cationic surfactant, on the adsorption of humic acid from water was investigated in a batch system.

Materials and Methods: Clinoptilolite as a natural nanozeolite was modified with different doses of a cationic surfactant solution, hexadecyltrimethylammonium bromide (HDTMA-Br), at dosages from 0.5 to 10 g/l. The modified adsorbents were individually added to synthetic water samples containing a known amount of humic acid and put on the shaker for two hours, at room temperature. Humic acid (HA) concentrations, turbidity, and pH were measured before and after the adsorption process.

Results: According to the results obtained, and based on the statistical analysis (Pearson correlation statistical test), there was a clear correlation between the cationic surfactant dosage and HA removal ($P_{\text{value}} < 0.001$, $r = 0.87$). By increasing the HDTMA-Br dosage, the ratios of turbidity/turbidity_{initial} and $UV_{254}/UV_{254\text{-initial}}$ adsorbance by HA (after/before adsorption process) were decreased. In HDTMA-Br dosages of 7 and 10 g/l, the maximum removal efficiency for HA was 96 and 86%, respectively, with a slight variation in the pH value and turbidity unit.

Conclusions: This study showed that modification of nanozeolite by cationic surfactants, to reduce its negative surface charge, could markedly improve its efficiency in the adsorption of disinfection by-product precursors from an aqueous solution. The HDTMA-Br/Clinoptilolite nanozeolite (CNZ) ratio of 0.07, pH have to coincide in iso-electric point, can be an optimum ratio for the modification.

Key words: Cationic surfactant, clinoptilolite, humic acid, nanozeolite, water pollution

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INTRODUCTION

The growth of population and thereby an increase in different industrial and agricultural activities has resulted in the

contamination of surface and groundwater. Natural organic matter (NOM), the most important constituent of water pollution, is known as a precursor for disinfection chlorinated by-product formation (DBPs). These emerging products are harmful and their adverse effects on human health have been proved. In most developing countries chlorine is applied to remove microbial pollution from drinking water.^[1]

Trihalomethanes (THMs), haloacetonitriles (HANs), and haloacetic acids (HAAs) are common compounds formed as a result of NOM and chlorine reaction, which are toxic and have a carcinogenic property.^[2,3] The NOM in water is

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comprised of hydrophilic acids, carboxylic acids, amino acids, and carbon hydrates. About 50% of the NOM is comprised of humic substances, including humic acids and fulvic acids.^[4] These complex macromolecules are produced via chemical and biological decomposition of plant and animal residues.^[5] These substances can make a metal complex with some of the trace elements, such as, copper, cadmium, mercury, and zinc, which play a specific role in the chemical properties of water. Among them, the mercury complex is exceptionally more toxic than its ionic state in the ligands formation.^[6,7] The common methods of removing the natural humic substances in water treatment systems are: (i) physical or physicochemical separation processes; such as, coagulation and flocculation, ion exchange, adsorption by activated carbon or natural zeolite, on the nano- and macroscale, and membrane filtration^[8] and (ii) chemical decomposition processes; such as applying strong oxidants, UV irradiation, and ozonation.^[9]

On account of the health concerns of DBPs, several researches have been carried out to enhance the performance of the adsorption methods for removing these compounds. In a research, a cationic surfactant-modified zeolite was applied for fulvic acid removal from water, using a fixed-bed reactor. The optimal efficiency for fulvic acid removal occurred with the hexadecyltrimethylammonium bromide (HDTMA-Br) surfactant in the range of 120% external cationic exchange capacity (ECEC) and 5 BV/hour (volume bed in time) of the flow rate through the bed.^[10] In another study, when the removal of humic acid from water by TiO₂ was examined, a removal efficiency of 70% was achieved in the optimum conditions.^[11] Nanozeolite A was applied in a study for cadmium and humic acid removal. The results showed that the adsorption efficiency of nanozeolite was more than that of other types of zeolites.^[12] By application of poly aluminum chloride (PACl) for humic acid removal from water, a removal percentage of more than 90% was achieved at pH ranges of 5 to 6.^[13] The capacity of nanofiltration in removing humic acid from water was examined, and a high removal efficiency was attained.^[14]

Nowadays, according to the literature cited, the application of natural adsorbents on a nano scale for elimination or reduction of organic pollutants from water seems to be an encouraging method.^[15] The main aim of this study was to modify a natural nanozeolite by a cationic surfactant (HDTMA-Br) and investigate its efficiency in the removal of trihalomethanes' precursors from aqueous solutions.

MATERIALS AND METHODS

Characteristics of the applied nano-adsorbent

In this research, a type of clinoptilolite nanozeolite [CNZ: (NaK₃) (Al₆Si₄₀O₉₆)24H₂], the most abundant and inexpensive natural zeolite^[16] was applied; It was purchased from the American Nanoshel Company. According to the company's certificate, the size of this nanozeolite was 30 to 60 nm

[Figure 1a]. It had a specific surface area of 160 m²/g. Table 1, specifies the chemical compositions of the CNZ used.

Modification of the nanozeolite

As a negative charge is present on the surface of natural zeolites, they have a high tendency to adsorb or exchange cations rather than anions.^[17] To increase the positive charge on their surface they must be modified by cationic agents [Figure 1b].^[18] In the present research for the modification of CNZ, it has been primarily treated with one molar sodium chloride solution by stirring at 150 rpm for 24 hours. Subsequently, the CNZ is separated from the solution in a centrifuge (Sigma 3K30) at 16000 rpm, until the silver-nitrate test becomes negative. The separated solid phase of CNZ is rinsed with distilled water and dried in an oven at 105°C for 24 hours. For the final modification, 100 g/l of pre-treated CNZ is contacted with different concentrations of HDTMA-Br solutions, including 0.5, 1, 3, 5, 7, and 10 g/l, in a shaker, for 24 hours, by continuously mixing at 150 rpm. Ultimately, it is separated in the centrifuge at 16000 rpm, rinsed with distilled water, and dried in the oven at 105°C for 24 hours.^[19,20]

Adsorption experiments and analysis

In this study, humic acid purchased from Sigma-Aldrich Ltd. was used as a representative of the organic precursors, for DBP formation. A synthetic water sample was prepared by dissolving humic acid in organic-free deionized water, with a concentration of 100 mg/l. Each of the nanozeolites modified with various concentrations of the cationic surfactant, with an identical concentration of 800 mg/l, was individually added into the synthetic water samples containing 100 mg/l humic acid to reach a adsorbent/adsorbate ratio of 8:1. The mixtures were then contacted on a shaker (IK® KS 260 BASIC) for two hours. Following the adsorption process, modification of the CNZ was fractionated from water using an ultra centrifuge at 16000 rpm, as low speed centrifuging was not able to completely separate the fraction. All the experiments were conducted in triplicate, at room temperature (20 ± 2°C), and the average of the results was reported. Sampling and analysis of humic acid concentration and other parameters of interest, such as, turbidity and pH were conducted before and after the adsorption tests according to the methods described in the standard methods for the examination of water and wastewater.^[21]

Table 1: Chemical compositions of clinoptilolite nanozeolite

Compositions	Weight %
SiO ₂	69.44
Al ₂ O ₃	11.87
Fe ₂ O ₃	1.3
Ti ₂ O	0.18
K ₂ O	1.31
Na ₂ O	0.68
CaO	3.28
MgO	0.99

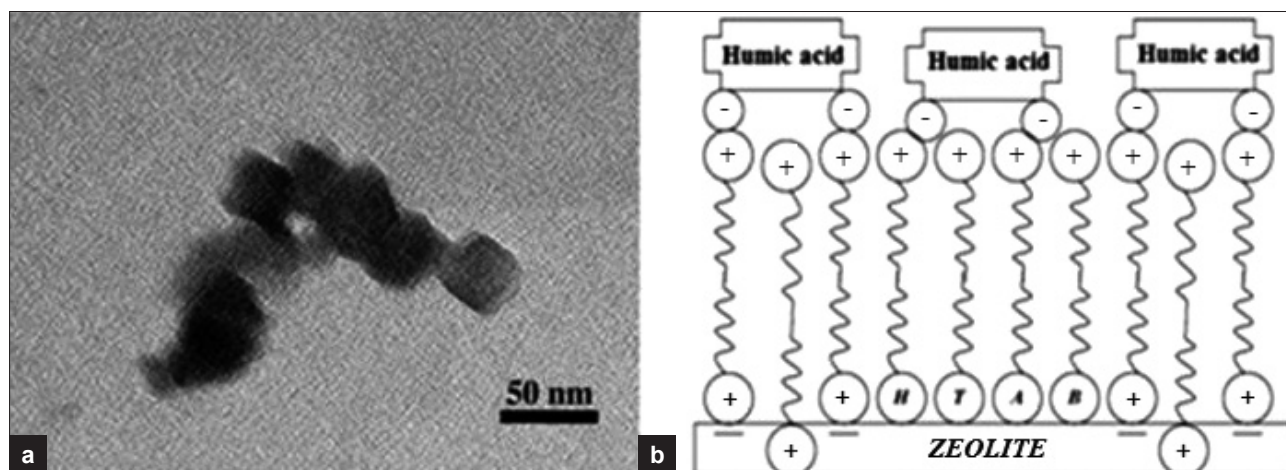


Figure 1: (a) TEM image of the nanozeolite, (b) Schematic of adsorption phenomenon of the nanozeolite modified by the cationic surfactant

The humic acid concentration was analyzed according to method 5910B,^[21] by spectrophotometer DR-5000 (HACH-LANGE), at 254 nm ultraviolet wavelength (UV_{254}). For drawing a standard calibration curve, the five known amounts of humic acid concentrations ranging from 1 to 100 mg/l were introduced to the DR-5000, in a 10 ml quartz cell, and the corresponding UV_{254} absorbance was plotted with the standard humic acid concentration values.

Figure 2 shows the relationship between humic acid concentrations and UV-ray absorption in the wavelength of 254 nm. There is a good correlation between the humic acid concentration and UV_{254} absorption ($r^2=0.9994$).

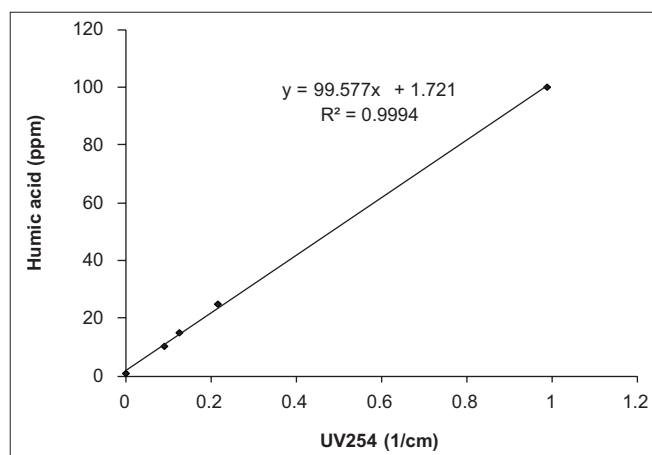


Figure 2: The relationship between humic acid concentration and UV_{254} absorption

RESULTS

The applied nanozeolite naturally had a negative surface charge and preferably adsorbed cationic compounds. To produce a cationic charge on its surface and thereby enhance its potential for adsorbing both cationic and anionic compounds, it was modified by a cationic surfactant (HDTMA-Br). Figure 3 illustrates the X-ray diffraction (XRD) patterns and surface charge changes of the nanozeolite before (a) and after (b) modification by the cationic surfactant.

Figure 4 shows the relation between the dosage of HDTMA-Br for modifying the nanozeolite and UV_{254} adsorption by humic acid (which is proportional to the humic acid concentrations).

The relation between HDTMA-Br concentration for modifying the nanozeolite and residual turbidity is illustrated in Figure 5.

Figure 6 indicates the pH variation in the beginning and at the end of the adsorption process with the application of nanozeolite, modified by various dosages of the surfactant.

Comparison of changes in pH, turbidity removal efficiency, and UV_{245} absorption, with increasing concentrations of the

surfactant used to modify nanozeolite, is shown in Figure 7. By increasing the surfactant concentrations, there are variations in the ratios of turbidity/turbidity_{init} (init=initial) and UV_{254}/UV_{254} init.

DISCUSSION

The X-ray diffraction (XRD) image of the particle adsorbent [Figure 3] clearly shows that the nanozeolite structure is not changed by the adsorption of HDTMA-Br, as the HDTMA-Br is adsorbed on the external surface of the zeolite, and only increases its positive charges.^[18]

By increasing the concentrations of HDTMA-Br for nanozeolite modification, the UV_{254} absorption of the water samples decreased [Figure 4]. In other words, the nanozeolite modified with a high dose of surfactant resulted in higher humic acid removal, and thereby, lower UV_{254} adsorption in the solution. Based on the statistical analysis (Pearson correlation), there was a linear correlation

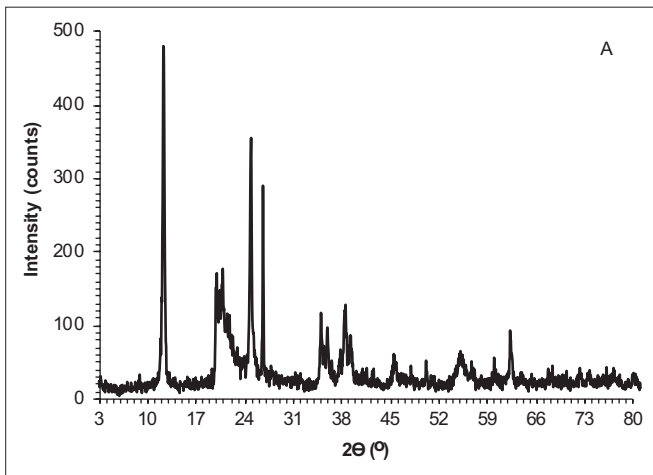


Figure 3a: XRD pattern of the nanozeolite, before modification

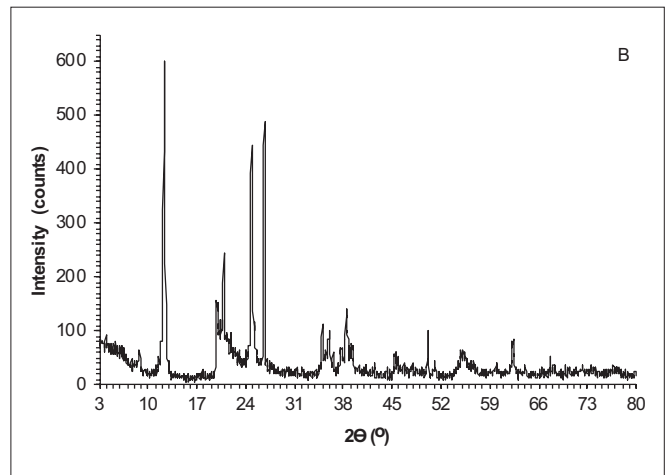


Figure 3b: XRD pattern of the nanozeolite, after modification

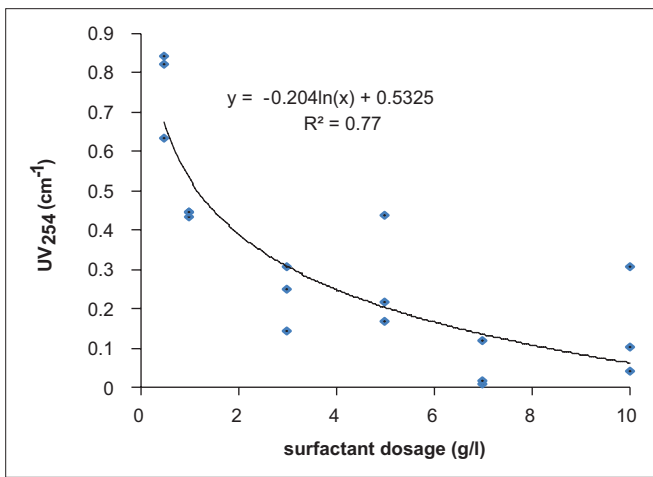


Figure 4: The relationship between the concentration of HDTMA-Br for modification of nanozeolite and absorption of UV_{254} by humic acid

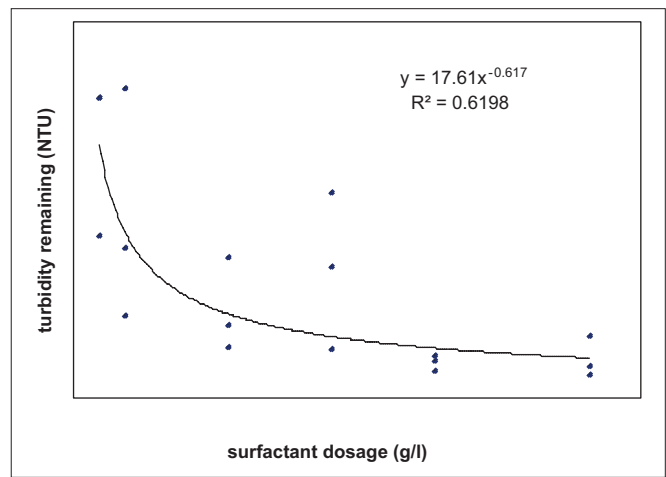


Figure 5: The relationship between the concentration of HDTMA-Br for modification of the nanozeolite and the remaining turbidity

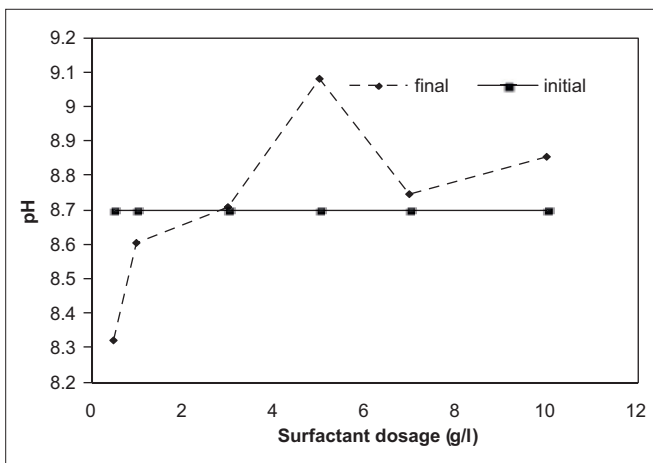


Figure 6: pH of water before and after addition of the nanozeolite modified by various dosages of surfactant

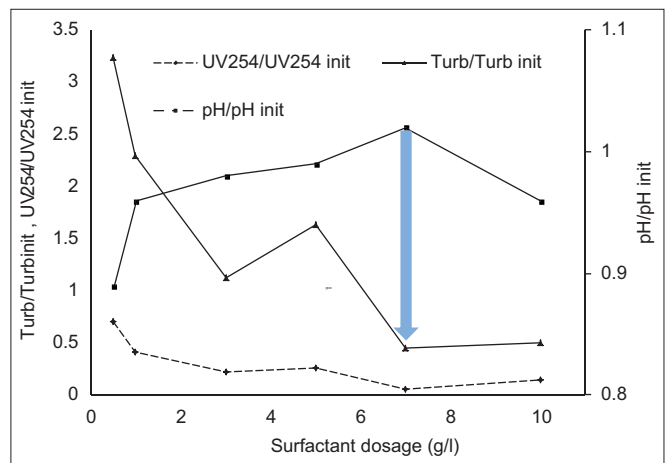


Figure 7: Comparison of changes in pH, turbidity removal efficiency, and absorption of UV_{245} with increasing the concentration of surfactant for nanozeolite modification

between the surfactant concentrations and the remaining humic acid concentrations, in terms of the UV_{254} absorption index ($P_{value} < 0.001$, $r = 0.87$). In a similar study, removal of chromate by natural clinoptilolite, modified by two

kinds of surfactants, HDTMA-Br and cetyl pyridinium bromide (CPB), was investigated. Increasing the dosage of HDTMA-Br from 0.17 to 7 g/l caused more removal of

chromate, which was consistent with the finding of the present study. This was due to the fact that the surfactant molecules made two layers on the zeolite surface; one side was hydrophilic and the other side was hydrophobic. Therefore, they could adsorb the pollutants and remove them from the solutions.^[22]

According to Figure 5, by increasing the dosage of the surfactant applied for the modification of nanozeolite the turbidity that remained in the water sample was notably reduced. There was a reverse correlation between the cationic surfactant and the turbidity that remained. Therefore, increasing the dosage of the used surfactant caused a decrease in the amount of remained turbidity in the water sample. The Pearson correlation showed that there was a significant correlation between the concentration of the applied cationic surfactant and remained turbidity in the water solution ($P_{\text{value}} < 0.001, r = 0.78$). The performance when submerging a membrane reactor with surfactant-modified zeolite in the removal of organic matter from potable water was investigated. Proper turbidity removal occurred at the optimum surfactant dosage of 3 g/l, which was nearly in agreement with the results of the present research.^[20] However, by increasing the surfactant dosage, the pH values of the initial and final solutions were varied [Figure 6]. The statistical test (paired t-test) showed that there was no significant relationship between the average of the initial and final solutions' pH ($P_{\text{value}} = 0.187$). It meant that the initial and final pH values were the same. On the other hand, lower pH variations were at surfactant dosages of 3 and 7 g/l. Hence it was concluded that in the surfactant dosages mentioned above, the net surface charge of the zeolite could be close to zero. In other words, pH_{zpc} (pH at zero point of charge) was achieved based on the dosages, and its zeta potential could also possibly be equal to zero.^[23] According to similar studies, by increasing the dosages of the applied surfactant, the zeta potential was increased. However, in pH_{zpc} , the zeta potential was minimum. Therefore, the adsorption value would be maximum. Thus, in the optimum dosages of the applied surfactant, the variations of pH and pH_{init} values were negligible.^[10]

However, at surfactant dosages of 7 and 10 g/l, there was maximum removal and minimum variations in the turbidity produced. Also there were no specific differences in the ratio of $\text{pH}/\text{pH}_{\text{init}}$ [Figure 7]. According to the data, the optimum dosage of the applied HDTMA-Br for modifying the nanozeolite, in this study, was 7 g/l, which gave a maximum removal of humic acid, and thereby, turbidity. In theory this concentration for the modification could be an iso-electric point (IEP) with a solution pH value equal to pH_{zpc} . Other experiences showed that the maximum removal efficiency of the arsenic anion by a modified zeolite was at the optimum dosage of the cationic surfactant at pH_{zpc} . As the size of the pollutant ions when adsorbing on the zeolite surface at pH_{zpc} were suitable, they had maximum pK_a . Thus, in the present study, the variations of pH and pH_{init} values were negligible

and the percentage of pollutant removal was maximum.^[18] The results of another study, on removing arsenic from water by a modified zeolite, showed that removing the pollutants at pH 6-10 had high efficiency, but the value of the $\text{pH}/\text{pH}_{\text{init}}$ was decreased to the acidic range, which was contradictory to other studies. It might be because of the bad selection of pH value.^[24]

Humic materials are present in the surface water resources in no more than 100 mg/l on the size of nanoscale. Due to their colloidal properties, removing them from water treatment plants is not easy. Application of the modified nanozeolite with a concentration of 0.8 g/l, shows a higher potential of humic acid adsorption from water. However, its modification by 0.5 to 10 g/l HDTMA-Br can remove 70% of humic acid (25 to 96%) on an average. The maximum removal efficiency for humic acid is 96% and 86% for the surfactant dosage of 7 and 10 g/l, respectively. Also the results show that in experiments with surfactant dosages less than 3 g/l, the turbidity is increased. As the pH values are in the potable water standard range (6.5 to 9), the variations in pH values, in this research, may be acceptable. The amount of HDTMA-Br absorption on a zeolite depends on the zeolite's external cationic exchange capacity, and hence, gravimetric tests must be performed.^[18] A research on color removal from textile wastewater by a modified zeolite shows an optimum concentration of 1 g/l for HDTMA-Br. However, the zeolite is in the macroscale and a higher dosage of the zeolite has been used.^[19] In the same study, the macro- and micro-zeolites, with a size fraction of 250 – 350 micrometers, modified by HDTMA-Br, with a dosage of 3 g/l, had been applied for natural organic matter removal from water. The results show that particle size and size fraction of the zeolite play an important role in adsorbing organic matters. This is partly due to the increase of contact surfaces and their modification for adsorbing the aliphatic groups.^[20] Therefore, application of natural zeolites in nanoscale and their modification by cationic surfactants show a high potential in adsorption of organic precursors, and can be applicable in the water treatment process.

CONCLUSION

Clinoptilolite nanozeolite, modified by HDTMA-Br surfactant, was utilized for humic acid removal from water. The surfactant dosages of 3 to 10 g/l were used in this study for the modification. The results showed that application of the surfactant in a concentration less than the optimum range (7 g/l) for nanozeolite modification provided a product with insufficient removal efficiency. Thus, the surfactant with a concentration of 7 g/l at conformity pH on IEP could be applied as the optimum concentration for CNZ modification, which could be used for removal of disinfection by-products in water purification systems. Also, the removal of humic acid and turbidity has acceptable removal efficiency and correlation by surfactant dosage for nanozeolite modification. The authors suggest that to use this new adsorbent in water

treatment industry more studies need to be done.

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