A STUDY OF THE REMOVAL OF NATURAL ORGANIC MATTER (NOM) BY ZEOLITES CLINOPTILOLITE AND SYNTHETIC TYPE A LOADED WITH TITANIUM DIOXIDE WITHOUT DIRECT RADIATION OF LIGHT

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ABSTRACT

Background: *Titanium dioxide as an effective semiconductor used in the process of photocatalyst to easy recover and isolate it from the water on passive porous matters. The study aimed to determine and compare the removal of dissolved organic matter from water by zeolites clinoptilolite and synthetic loaded with titanium dioxide in non-loaded state.* **Methods:** *Zeolites clinoptilolite and synthetic type A covered by titanium dioxide nanoparticles via co-precipitation method using titanium tetraisopropoxide and ethanol was prepared. Studied concentrations were organic carbon dissolved in the water 3, 5 and 10 milligrams per liter. Discontinuous experiments has been performed at different contact time, different adsorbent dosage and conditions of acidic, neutral and alkaline at room light (Klux3-2). Reaction kinetics and isotherm were studied. Continuous experiments in the column containing the adsorbent used with Dbi 1.66 ml/min were studied. Dissolved organic matter by dissolved organic carbon analyzer was measured.* **Results:** *In the study, optimum pH was determined 7, optimum and maximum time of removal of clinoptilolite and modified synthetic type A for 10 minutes and, the best adsorbent dosage, was 20 g/l and 50 g/l, respectively. Absorption kinetics was pseudo-second degree and in the isotherm experiment, zeolite clinoptilolite and synthetic loaded follow by Langmuir and Freundlich isotherm. In the continuous experiments in clinoptilolite column and modified synthetic after 90 BV, 130 failed respectively.* **Conclusions:** *In the presence of natural light the removal of zeolite clinoptilolite and synthetic loaded with TiO2 has higher efficiency in the removal of dissolved organic matter than non-loaded showed.*

INTRODUCTION

Photocatalysis is rate of photodegradation that in the presence of a catalyst increased. Transition and semiconductors metal oxides (TiO_2, ZnO, ZrO_2, CdS, WO_3, etc) are the most common Heterogeneous light catalysts. They are mainly used in water treatment, waste, air and energy production are used. Semiconductors to destroy photocatalytic organic molecules are usually oxides and metal sulphides[1]. TiO2 is neutral substance, non-toxic, suitable photocatalyst that can be used in water and wastewater treatment due to having the photocatalyst property considered [2].

Matter removed by TiO2 into two mechanisms adsorption TiO_2 and photocatalyst oxidation occurred. The process of removal by TiO_2 should be noted that absorption occurs faster than photocatalytic oxidation. However, application of TiO_2 as attractants or photocatalytic due to a problem retrieving in water was limited. For this reason, various passive methods are examined [3]. The use of preservatives is one method of increasing of photocatalytic activity of photocatalyst which can increase the effective surface area or form photocatalytic in the structure of the nanofibers [4]. The combination of zeolite and TiO_2 to remove many substances, such as humic acid, nitrogen oxides and volatile acetone, 2-propanol in the presence of visible and ultraviolet light is used [3,5].

Mixture natural organic matter derived from organic compounds with different molecular weight and diverse chemical nature such as humic acid with high molecular weight and fulvic acid with low molecular weight [6]. This is a complex mixture of organic compounds containing both hydrophilic (phenolic and carboxylic) and hydrophobic humic substances (HS) (aromatic, aliphatic) [7]. Humic substances consists the bulk of organic matter dissolved in water and it is about 90% soluble organic carbons [2]. NOM can influence smell, taste and color of raw water as well as the growth of bacteria in drinking water and reduce the efficiency of water treatment [8].

The potential of formation of Disinfection By-Products (DBPs) such as trihalomethanes (THMs) and Haloacetic acids (HAAs) are suspected to carcinogenic [9, 10]. Health risks such as Bladder cancer and other have been attributed to the consumption of water containing DOC and DBPs [11]. Properties of NOM including structure (aromatic, aliphatic, hydrophilic and hydrophobic nature), Average Relative Molecular Mass (RMM), distribution RMM, distribution and density load are the most important factors in the formation of DBPs [12].

Concentrations of organic matter in the exhaust secondary treatment are typically about 6-10 mg/l in terms of total organic carbon (TOC) [13].

Thus, effective removal of NOM in water increasingly in water treatment systems is important and coagulation and flocculation is common method for removal of NOM and large particles during treatment processes [6]. Also several methods of removing NOM from natural water sources, such as ozonation, advanced coagulation, membrane separation, carbon adsorption, biodegradation and advanced oxidation processes (AOP) has been carried out [14].

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Most of these methods have high cost and sludge disposal resulted of treatment is difficult [15]. Of these absorption methods has wide application and a wide range of absorbents such as activated carbon, Granular ferric hydroxide, natural minerals such as zeolite, Iron oxide and silica and carbon nanotubes have been used and examined [3]. Three-dimensional Aluminosilicates zeolites with porous structure has physical properties such as cation exchange, screening molecules, and as they catalyze and attract negatively charged on their surface, are dominant which thus had the high cation exchange capacity and organic matters tend to absorb a little while anions in the aquatic environment [3].

Zeolites also to remove pollutants, such as heavy metal ions, ammonium, inorganic anions, phenols, pesticides and color placed in the studied water. Zeolite to remove hydrophobic and anionic pollutants because of the negatively charged and surface is inappropriate. These reactions are modified to improve energy surface modification of particles reduces hydrophobic properties. In order to improve performance of zeolite to remove water-soluble organic surfactants, Zeolites modified by cationic surfactants and have achieved satisfactory results [16, 2]. Neary et al (2015) in a study using modified clinoptilolite via cationic surfactant HDTMA to remove NOM found that the sorbent for the removal of NOM is very effective aqueous solutions [17].In the removal of soluble and homogeneous organic matter from industrial wastewater using natural zeolites and active and passive synthetic zeolite found that passive synthetic zeolite has further removal efficiency (93%) of natural species (85%) and active synthesis (89%) [18]. Clinoptilolite is a crystalline aluminosilicates which its usual molecular structure is $Na_6[(AlO_2)_6(SiO_2)_{30}].24H_2O$.

Ion exchange capacity (CEC) is 100 to 300 meq/100g [19]. Zeolite Type A is zeolite with a small pore and eight-ring pore with diameter free 0:30 to 0:45 nm [20,21].

One of the disadvantages of Modified Zeolite with cationic surfactant is production of waste in the process of recovery. Accordingly modified zeolite using nanoparticles of titanium dioxide was used to remove water-soluble organic matters which does not produce using side waste photocatalytic recovery [3]. Liu et al (2013) conducted an experiment using the modified zeolite with titanium oxide, 80% removal of humic acid during 5 minute in primary contact reported [3].
Mansouri et al in a study in 2015 on the removal of humic acid by nano-particles TiO2-SiO2, the removal efficiency of 85% and 97% respectively for synthetic and real samples at concentrations l mg/1 humic acid in pH =3 on contact time 30 minutes was obtained [2].

According to different studies of direct of sunlight and ultraviolet radiation in activating the photocatalytic properties of semiconductors this study aimed to determine the performance of remove the dissolved natural organic matter (NOM) using zeolites clinoptilolite as modified natural zeolite (MNZ) and Modified Synthesis Zeolite type A (MSZ) with nanoparticles of dioxide titanium and comparison with the natural zeolite (NZ) and synthetic (SZ) in concentration, pH and diverse dosage of adsorbent in indirect sun light.

MATERIALS AND METHODS

This study is an experimental study at laboratory scale as discontinuous and continuous experiment was performed. All tests in the light 2-3 Klux by photometer TES1335 were measured.

Preparation of zeolite covered with titanium oxide

In the study, the natural zeolite clinoptilolite zeolite in Semnan mines and synthesis Zeolite in DAE JUNG company (Zeolite, synthesis, A-3 gronular) with ion exchange capacity 80 meq/100g was used as the first zeolite is washed several times with distilled water to the impurities to be removed. Then, using a sieve shakers, size range of mesh 18X30 (that passes through the sieve 18 and retained on sieve 30) of zeolite was chosen. The zeolite as natural zeolite were used and its feature in [Table 1] shown [22].

To modify it ten grams of zeolite added to a solution containing 957.5 ml ethanol and 7.5 ml water and then the suspension was stirred at 500 rpm. The absorption of the nanoparticles of titanium dioxide on zeolite by hydrolysis of tetra-iso propoxide titanium (TTIP) was prepared from Sigma-Aldrich Company. TTIP diluted solution by adding 1.75 ml TTIP to 33.25 ml ethanol produced from Merck Company. Then dilute solution of TTIP was added into the zeolite suspension drop by drop. After 3 hours, the product repeatedly with distilled water to remove free TiO_2 particles don't sticking to zeolite washed. Zeolite/TiO_2 sample at 80˚C dried and in 45˚C for 3 hours at the furnace was heated [23].

Table 1: Feature of natural clinoptiloli

Compounds	The amount of natural clinoptilolite%
SiO_2	66.5
Al_2O_3	11.81
Fe_2O_3	1.3
CaO	3.11
MgO	0.72
Na_2O	2.01
K_2O_3	3.2
P_2O_3	0.01
MnO	0.04
TiO_2	0.21
L.O.I*	12.05

* Waste due to heat

Construction of dissolved natural organic matter (NOM)

In order to construct NOM stock solution of contact 100 grams of soil plant with distilled water for 24 hours on the shakers were used and solution first by paper filter to smoothing and to separate the soluble from filter 0.45 micron was passed [23].
DOC by Shimadzu TOC analyzer device was determined and the concentration of 25 ppm was obtained.

The stock solution in concentration of 3, 5 and 10 mg were prepared. Tests at different pH and adsorbent dosage were different. To change the pH of HCL and NaOH, a normal was used. All tests at ambient temperature of 25° C were conducted.

Determining the optimum pH to remove natural organic matter

Using a solution of NOM, concentration of 5 milligrams per liter of dissolved organic matter NOM were made and the amount 30 ml was poured in the bottle and its pH using HCL and NaOH, a normal were set on 10,9,7,6,4,3. Then adsorbent with dosage 20 g/l was added to the bottle and for 10 minutes put on a shaker with speed 180rpm. After the end of touch time, 0.45 samples by micron filter was separated. Sample by Shimadzu TOC analyzer device was read.

Determine the kinetics of absorption

In order to determine the optimal time of solution NOM with concentration of 5 ppm with dose of absorption 20 g/l and the optimum pH of previous step was used. At the time of the touch 20, 15,10,5 1440,360,300,240,180,120,60,30,25 minutes, remaining concentration of dissolved organic matter using a Shimadzu TOC analyzer device was determined. To describe the kinetics, pseudo-first and second models were used.

The first linear kinetics following equation $\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2/303}$

Here qe and qt respectively the adsorption capacity in balance and time t (mg/g) and k1 is Velocity factor (min-1).

The values k1, qe are the intercept and slope of the linear Fig ln (qe-qt) vs. t are calculated [22]
Second-degree kinetics linear equation is $\frac{t}{q_t} \quad \frac{1}{k_2 q_e^2} \quad \frac{1}{q_e}$

qe and q1 is similar to the first equation. In equation k2 pseudo-second reaction constant is according to min (mg/g). Qe and k2 values can intercept and the slope of the linear Fig. t/qt against t be determined.

Determine the optimal dose of adsorbent

In the optimal time and optimal pH, different doses to determine the optimal dose were used. 50, 40, 33, 26, 20, 13 doses grams per liter were examined and concentration of dissolved organic matter remaining in the solution was measured.

Determine the adsorption isotherm

In this study, Langmuir and Freundlich isotherm mathematical model to attract natural dissolved organic matter were used. Using the optimal contact time of 10 minutes, optimum pH 7 and optimum doses 20 g/l at concentrations of 1, 5, 10, 15, 20 mg/l, isotherm tests were conducted.

Freundlich isotherm

Freundlich mathematical equation is as follows:

$$q_{e=}\ K_f\ C_e^{1/n}$$

qe: the amount of absorption per unit mass of sorbent (mg/g)
Ce: matter equilibrium concentration in solution (mg / l)
k and n: are Freundlich constants
Linear equation of Freundlich isotherm is as follows:

$$ln\,q_{e=}Lnk_f + \frac{1}{n}LnC_e$$

Langmuir Isotherm model

Mathematical model of isotherm shown in the following equation:

$$q_{e=}\frac{q_0\ bc}{1+kc_e}$$

q_0 : The maximum adsorption capacity (mg/g)
Kl: fixed Langmuir (L/mg)
Parameters qe and Ce are similar to Freundlich isotherm [33]
Langmuir isotherm linear model is as follows:

$$\frac{c_e}{q_e} = \frac{1}{K_1 q_0} + \frac{1}{q_0}$$

Absorption column tests

To perform continuous testing of the glass column with a diameter of 6 mm and length of 50 cm was used that a solution of Nom with dbi 1.66 ml per minute passed and two columns with modified zeolite clinoptilolite and modified synthetic type A was filled and sampling after each 10 BV with an average time of 170 minutes and the concentration of dissolved organic matter was measured [25].

RESULTS

Optimum pH of removal of dissolved organic matters

[Fig. 1] shown the effect of pH change solution on the removal of dissolved organic matter from water using adsorbents was tested. As you can see for all absorption at neutral pH the maximum of organic absorbents can be seen. In all studied pH absorption efficiency dissolved organic matter by MNZ was more than NZ for MSZ in the range of pH <5 and pH = 10 has higher energy efficiency compared to the SZ in the removal of dissolved organic matter is shown. But in the range of 5> pH <10 removal of synthetic zeolite was more than modified synthetic zeolite and therefore attract more absorption in neutral pH, as the optimum pH selected and to continue testing the pH 7 were used.
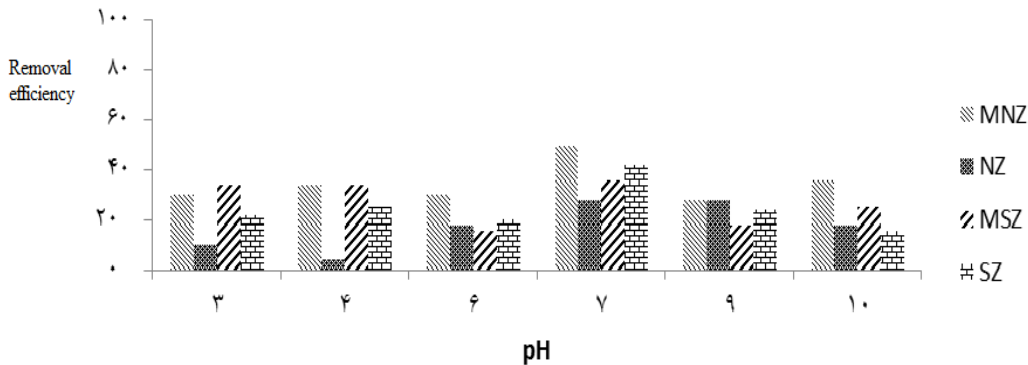

Fig. 1: The removal efficiency of MNZ, NZ, MSZ and SZ in different pH for concentration of dissolved organic matters ppm 5 and adsorbent dosage 20 g/l

Contact time and kinetics of removal

Different contact times of removal of NOM in [Fig. 2] shown. As can be seen in Fig. for all four tested absorbent time from 30 minutes to above reached to equilibrium status and for absorbent MNZ highest removal efficiency at 10 minutes 52% is obtained. And after 15 minutes decreased, and then absorption

rate has been fixed. For NZ the removal of time 10 to 15 minutes was same and increase at 20 minutes and after the absorption rate constant reached to equilibrium after which the removal efficiency is 30%. Optimum time for MSZ at 10 minutes reach to 33% observed at after 10 minutes reduced the absorption rate and has been fixed. In absorbent SZ highest removal efficiency at 10 minutes and the rate of 23% was observed and that this trend will continue in 15 minutes and then dropped until it has been proven performance. Kinetics coefficients in Pseudo-first and second degree in [Table 2] was shown.

As can be seen the process of adsorption of pseudo-second degree kinetics followed for every four adsorbent has been tested and does not correspond to pseudo-first degree.

The effect of different concentrations of dissolved organic matter on removal at pH =7 and adsorbent dosage 20 g/l is shown in [Fig. 3]. As can be seen with increasing concentrations removal efficiency by MNZ is decreased and similar efficiency at a concentration of 3 and 5 ppm a rate of 48% was obtained. Reducing the removal amount with increasing concentrations by NZ observed and highest removal efficiency at 3 milligrams per liter appeared and 42% is obtained and at the concentration of 5 milligrams per liter, MSZ lower absorption than the concentration 3 and 10 mg that this process is inconsistent with the other adsorbents tested. While the concentration of 5 mg per liter in the SZ maximum removal efficiency shows amount 40%. In general, MNZ in different concentrations had maximum removal rates compared to other absorbents.
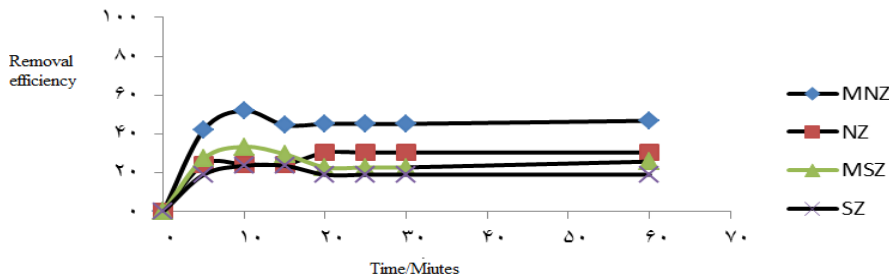

Fig. 2: The removal efficiency MNZ, NZ, MSZ, SZ to the concentration of NOM 5 ppm at 7 pH.
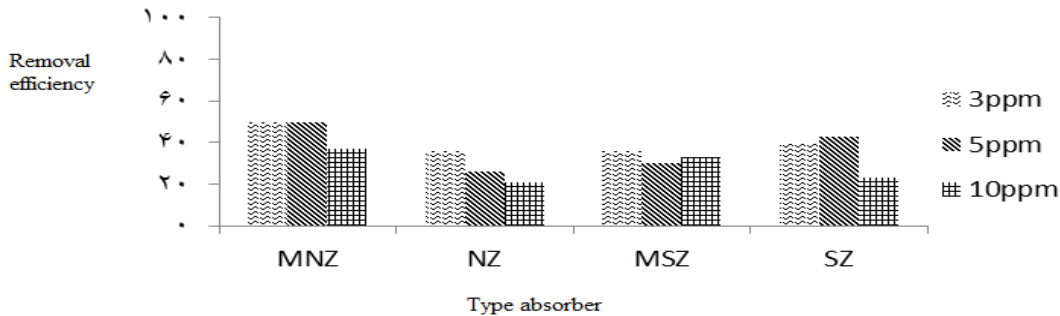

Fig. 3: The removal efficiency MNZ, NZ, MSZ, SZ for different concentrations of NOM at pH 7 and adsorbent dosage 20 g/l.

Table 2: Adsorbent kinetics parameters of dissolved organic matter by MNZ, NZ, MSZ, SZ

Pseudo-second degree		Pseudo-first degree				Type absorber
K2	qe	R2	K1	qe	R2	
6.0	117.0	9858.0	04.0	13.0	2649.0	MNZ
07.2	079.0	9139.0	075.0	076.0	4599.0	NZ
11.3	0625.0	09834	024.0	0835.0	0995.0	MSZ
68.2	046.0	09759	04.0	059.0	1598.0	SZ

Determine the optimal adsorbent dosage

Suitable dosage results are shown in [Fig.4]. Due to the dosage change, different performance appear to the best dosage for MNZ rate of 20 grams per liter by 50% and at dosages of 33 and 50 grams per liter the same performance was observed at a rate of 48%, while highest absorbance values for NZ in 33 g/l was about 30%. SZ similar MNZ maximum removal rates in 20 g/l showed while such synthetic modified sample he maximum removal at dose l50 g/l appeared. Similar efficiency in the removal of adsorbent dosage of 20 and 33 grams per liter by MSZ was observed. In doses 13-26 g/l by increasing the removal adsorbent by synthetic zeolite was further modified in doses of 33-50 grams per liter, while the removal rate by modified synthetic zeolite was higher.

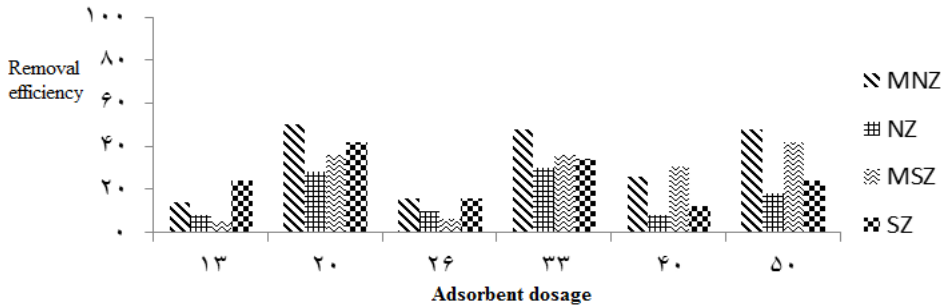In general, the maximum removal in different doses than the dose 13 g/l by MNZ obtained.

Fig. 4: The removal efficiency MNZ, NZ, MSZ and SZ at absorbent different dose at concentrations in 5 ppm

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Results adsorption isotherms

In [Fig. 5] the results of commissioning columns for MNZ, NZ, MSZ and SZ are shown. The column contains MNZ and the removal in 10-20 BV reached 35% and a maximum rate of removal in the 30 BV has been reached to 40% and later with the reduction of removal to 90 BV reduced by 10% and in the 130 BV input and output was same and column is completely saturated. Maximum removal in column containing NZ in 10 and 30 BV can be seen and then reducing the 30 BV in 100 BV is saturated and MSZ column in 20 BV maximum removal efficiency 40% emerged and the same amount was the maximum removal by MNZ in 30 BV. In column 30 BV removal efficiency reduced and in column 90 BV were saturated and in the column containing SZ the maximum removal in 40 BV emerged and in column 70 BV was saturated.

Table 3: Adsorption isotherm model coefficients of dissolved organic matter by MNZ, NZ, MSZ, SZ

Langmuir isotherm			Freundlich isotherm				Type absorber
Parameters	R2		Kf	R2		qm	Kl
0.57	0.24	0.9897	0.08	0.4		0.9876	MNZ
0.107	0.24	0.7862	0.027	0.63		0.9868	NZ
0.046	0.58	0.455	0.026	0.85		0.9688	MSZ
0.179	0.27	0.719	0.045	0.57		09267	SZ

The results of continuous experiments using column

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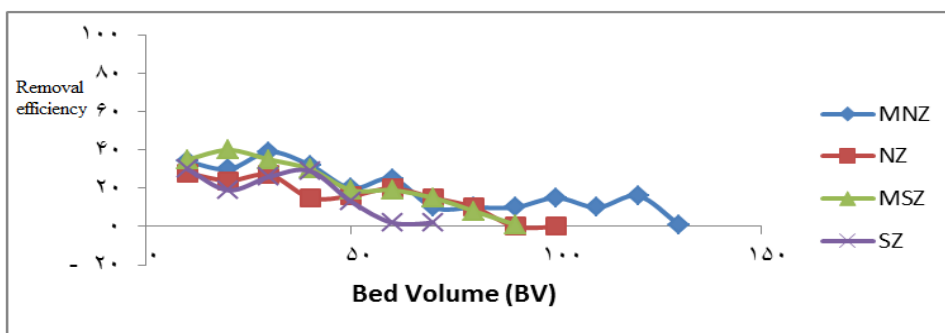
Fig. 5: The performance of the fixed-bed column filled with MNZ, NZ, MSZ and SZ at concentration 10ppm NOM at pH 7

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DISSCUSSION

The results obtained from continuous experiments show that the removal efficiency of NOM by all four adsorbent used in the neutral PH than other pH is higher.

NOM compounds are weak organic acids and their ionization is highly dependent on the PH solution. In low PH solution, NOM molecules are neutral. Un-ionized NOM adsorbent positively charged surfaces, by electrostatic attraction force is small, so the bands of hydrogen bonds and other organic products to absorb NOM in PH solution are low. NOM molecules completely are ionized at higher PH. Increasing PH in solution from 3 to 11 leads to reduced hydrogen bonding of NOM [17].

Natural zeolite in various PH has a negative surface charge, but in the zeolite coated with Tio2 in low PH surface charge is positive with increasing PH positive charge decreased and Electrostatic point was 6 is equal to Tio2 which is compatible with Tio2 particle deposition on the core zeolite. Reducing the negative charge to absorb HA on the surface of Tio2 on the zeolite is supported. The study found that humic acid is absorbed mainly by the Tio2 carboxyl groups [3]. The major adsorption of HA occurs at neutral PH (point above zero Tio2 charge) that shows in addition to electrostatic interactions, adsorption mechanisms occurs for zeolite such as hydrogen bonding reaction with the surface hydroxyl groups Tio2 or hydrophobic reaction [3]. Nirri et al in 2015 investigating the effect of PH on NOM removal by modified zeolite via surfactant HDTAM, PH 5 as the most effective PH in the removal of NOM and electrostatic reactions to major mechanism to remove NOM to SMZ in addition to hydrophobic interactions and hydrogen bonding announced [17]. The removal of humic acid by SiO2 the best removal efficiency in pH, 4 was observed [26].

Karimi Pasandideh et al in a study on the removal of humic acid as natural organic matter by magnetic iron oxide nanoparticles coated with silica concluded PH changes is effective in removal and increase the PH from 7 to above and increased removal efficiency and maximum rates occurred at around 10-11 PH because of two active removal mechanisms that is the hydrophobic absorption by nano-particle and hydrogen groups reactions are known [24]. The removal of natural organic matter by TiO2 loaded on glass labyrinth increase the pH of 3 to 9 that increase removal which it attributed to hydroxyl ion and increase the photocatalytic power [27]. While the removal of humic acid with activated carbon composite with TiO2 found with the increase in pH due to the reduced amount of removal are known to reduce the activity of photocatalytic [28]. Liu et al in 2013 zeolite covered with Tio2 used for quick removal of humic acid and in PH 7, best efficiency for removal observed [3]. The study according to different organic contaminants matched Liu study.

In continuous experiments best absorb dosage for modified clinoptilolite and modified synthetic 20 and 50 g/l while for the two unmodified absorbent was 33 g/l. For the removal of humic acid by zeolite covered with Tio2, the best performance in the range of 20 to 50 g/l was observed [3]. NOM removal by modified zeolite with surfactant by increasing the absorption dosage increased and absorption capacity decreased [17]. The use of modified zeolite with cationic surfactant alkyl dimethyl benzyl ammonium chloride was 20 g/l [29]. At present study efficiency variable was observed at different doses and dose of 20 to 50 g/l per liter has higher efficiency for the modified zeolite that is consistent with the study of Liu et al. In the present study reaction kinetics for zeolite/TiO2 and non-modified zeolite is pseudo-second degree and optimum time during four absorption used except usual clinoptilolite was 10 minutes. Liu et al in 2013 in their study of 10 minutes in removal efficiency 80% to remove humic acid by zeolite/TiO2 compared with 20% by conventional zeolite were mentioned by its free absorbent surface modification due to rapid absorption after 5 minutes after touch was declared [3]. Mansouri et al in 1393 in the removal of humic acid by removal of nanoparticles SiO2 best time to removal is time 10 minutes and adsorption kinetics is pseudo-second degree [30]. The removal of humic acid by magnetic iron oxide nanoparticles coated with silica, the best time to remove is 90 minutes and adsorption kinetics is pseudo-second degree [24]. NOM removal by modified zeolite with a cationic surfactant HDTMA, Kinetics is pseudo-second degree and optimal time to remove is 150 minutes [17]. The results of this study due to the different types of organic pollutants by Liu et al for humic acid and Mansouri for silica adsorbents for the removal of humic acid is compliant [3,30]. We can attribute to a difference in the removal efficiency to photocatalytic power TiO2 and loaded absorbent removed and the removal of non-absorbent surface to absorb is the photocatalytic effect. In continuous experiments with increasing concentrations decreased efficiency in the removal of methyl orange with clinoptilolite loaded with TiO2 photocatalytic activity was higher in low concentrations and zeolites have attributed it to higher-holder [31]. The removal of humic acid by composite zeolite/TiO2 photocatalytic activity was higher at higher concentrations [32].

In this study, removal of humic acid by zeolite/TiO$_2$, data with Freundlich and Langmuir isotherm is consistent [3] and in the study of Nirri et al Langmuir isotherm had a better suited to data [17] and removal isotherms of humic acid covered with silica nanoparticles and magnetized iron nanoparticles with silica of both Langmuir [24].

The removal of humic acid by TiO2-siO$_2$ the Langmuir isotherm is more fit [2] as for natural and active zeolites and passive synthetic, Freundlich isotherm is appropriate [18]. In this study, for zeolite / TiO$_2$ both Freundlich and Langmuir isotherm with r2 with 0.97 and 0.98 have a good match but for usual zeolite (NZ) Freundlich isotherm with r2, 0.98, has good match that shows the main cause of NZ, MSZ and SZ was multilayer adsorption while MNZ both single-layer and multi-layer adsorption mechanism with the dominance of a single layer can be seen. The removal of fulvic acid by column containing modified zeolite with surfactant column after BV200 with speeds 5, 8, 10 Bv close to input concentration that the value in the study for modified clinoptilolite 130 and modified synthetic was 90 [25].

CONCLUSION

The results of this study indicate that clinoptilolite modified with titanium dioxide increases removal efficiency in dissolved organic matter compared to the non-loaded and this increases in the load removal by synthetic zeolite can be seen in comparison with conventional synthetic generally, however, clinoptilolite loaded has more the removal efficiency than modified synthetic. Fixation TiO$_2$ on preservatives such as zeolite increase photocatalytic TiO$_2$ and increase access to positions of power absorbed.

CONFLICT OF INTEREST
There is no conflict of interest.

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