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A new method for the removal of ammonium from drinking water using hybrid method of modified zeolites/catalytic ozonation

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ABSTRACT

Ammonia in the form of ammonium ion is toxic and could decrease the dissolved oxygen in water and endanger the aquatic life. The aim of this study is the removal of ammonium using a new method of oxidation and adsorption by catalytic ozonation and clinoptilolite zeolite, respectively. The research method is an experimental study. First, optimal pH of ammonium adsorption on carbon catalyst (5 g/L), Garmsar and Firoozkooh zeolites and oxidation process were determined. Then, in catalytic ozonation process, the effect of other variables on ammonium removal efficiency such as the concentration of carbonic catalyst (0.5–50 g/L) and the reaction time were investigated. Then, the effect of retention time and adsorbent concentration on adsorption of the remaining ammonium and nitrate production by the oxidation process using zeolites and their modifications were determined. The results showed that optimum pH for the ammonium adsorption process by carbon catalyst, catalytic ozonation and zeolite were 8, 9 and 8, respectively. However, the optimum pH of 4 was determined for nitrate removal. The highest ammonium absorption capacity was related to natural Firoozookh zeolite as 18.5 mg/g, and the effect of ligand and acid modification decreased the absorbed capacity by 12% and 14%, respectively. The highest nitrate removal efficiency was related to Garmsar ligand modified zeolite (98%) and an absorption capacity of 11.2 mg/g. In the catalytic ozonation process/absorption process, the concentration of ammonium was decreased to 0.6 mg/L. This method effectively eliminates ammonium, and the modification of zeolite with cationic surfactant increased the efficiency of nitrate removal and therefore the concentrations of all pollutants were below standards.

Keywords: Adsorption; Ammonium; Catalytic ozonation; Clinoptilolite; Nitrate; Water; Zeolite

1. Introduction

Ground water and surface water pollution by ammonium are considered as serious problems for many areas in the world. In one side, water reservoir limitation and in other side, increase in surface water and ground water pollution by ammonium, nitrate and other pollutants made by industrial and domestic wastewater, results in elimination of these pollutants from water bodies [1]. Ammonia is a type of nitrogen which can be found in water as ammonia, ammonia salts or free ammonia. It is possible that these pollutants

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have been occurred by sanitary wastewater penetration into groundwater, plant break down or nitrates revive by bacteria or crossing water from ground layers. According to the National Standards of Iran, the concentration of ammonia in water needs to be 1.5 mg/L and below [2]. According to the World Health Organization, the concentration of nitrate in drinking water is 50 mg/L; while Europe recommendations offer 5.6 mg/L of nitrate as N. Also, according to EPA, maximum concentration of nitrate in water needs to be 10 mg/L and below [3]. Since nitrogenous compounds such as nitrates are harmful for humans, health risk assessment of it with regard to its concentration should be evaluated in water sources [4,5]. Nitrogenous elimination from water is by physical, biological and chemical processes. These methods include ion exchange, nano-filter, reverse osmosis, biological nitrification, oxidation, chemical revive and electrochemistry [6–8]. Reverse osmosis and ion exchange do not work optionally for ammonium elimination and need continuous environmental revive. These two processes would not make any chemical change for nitrate and finally will be discharged as wastewater [9]. Also, in most of the times, biological nitrification is used for wastewater treatment which is not a common in water treatment, due to organic chemicals and system protection. Also, in biological wastewater treatment, elimination and denitrification process are difficult to be applied in treatment of the sewages having mineral chemicals because it needs some organic chemicals as electron receivers [10]. Ion exchange process is used for harmful anion and cation elimination of wastewater [9]. Researches show that cation exchange capacity is good for organic materials and ammonium removal from water [11,12]. On the other hand, the pollutant adsorption capacity can be improved by zeolite amending [13]. Zeolites are mineral crystalline aluminum silicate and hydrated alkali and alkali earth metals with three dimensional net. Their open skeleton includes caves and canals of water molecules and cations and because of the cation movements the ion exchange which is one of the properties of zeolite will be resulted [13]. The other properties of zeolite are their capability of irreversible dehydration and ion exchange without any change in the structure of zeolite [14]. Clinoptilolites are one of the most abundant kinds of natural zeolites in Iran which are found abundantly in areas as Firouzkooh, Semnan and Mianeh [15]. Heterogenous catalytic ozonation process (COP) is a new method of advanced oxidation processes (AOPs) which takes place more effectively in lesser time for pollutants oxidization by adding the catalyst, which are very effective in removal of pollutants [16–20]. Although transition metals and their oxides are common catalysts in ozonation process, but recently activated carbon was considered due to its efficiency and substitution for oxidization of pollutants. This is because of chemical properties of the surface of activated carbon and its superficial oxygenated groups which have a crucial effect in the mechanism of the interaction [21,22]. Activated carbon helps to decompose ozone and leads to the formation of reactive oxygen species that are responsible for the chemical oxidation improvement. Ozone can also oxidize the materials that are adsorbed on activated carbon after the adsorption process. As a result, the simultaneous use of activated carbon and ozone can increase the efficiency of removal [23].

In this study, ammonium oxidation was performed by COP with carbon catalyst and adsorption with natural and modified clinoptilolite zeolites of Garmsar and Firouzkooh in water purification in the batch and continuous reactors.

2. Materials and methods

2.1. Chemicals

All chemical substances in this project such as mineral stabilizer, polyvinyl alcohol, Nessler's reagent, sodium hydroxide, sodium thiosulfate, sodium sulfite, dihydrogen sodium phosphate buffer, ammonium nitrate (CAS: 101187), acetic acid, hexadecyltrimethyl ammonium bromide ligand and sulfuric acid have a lab purity degree. Clinoptilolite zeolite has been prepared from Kimia Gostar Co., (Iran) Ammonium and nitrate adsorbent and their characteristics have been shown in Table 1.

2.2. Experiments method

Table 1
Properties of clinoptilolite adsorbent and catalyst characteristics [16]

Clinoptilolite	
Parameters	Properties
Molecular formula	$Na_6[(AlO_2)_6(SiO_2)_3O]{\cdot}24H_2O$
Crystallization system	Monoclinic
Classification	Silica
Fracture	Nacreous-unequal
Transparency	Transparent-semitransparent
Apparent shape	Aggregate-crystal
Mineral's color	White
Crystal shape	Rhomboid-wide and small
Other properties	Having some uneven fractures
Root of the name	Kline in means lied on pitilon means feather or pencil and lithos is a Greek word which means stone
Density	Min.:3.5 max.:4
Apparent shape	 

Magnetic carbonaceous catalyst	
Parameters	Properties
Specific surface area (m^2/g)	814 (cm^3/g)
Pore volume (cm^3/gr)	0.26
pH_{pzc}	7.71
Assay (%) as carbon	89.2

Research method was conducted in lab scale and based on optimization method for ammonium removal from water sources. Ammonia removal efficiency by natural zeolites of clinoptilolite has been measured in Garmsar and Firouzkooh and their adsorption efficiency and its adsorption capacity defined before and after amending the zeolites. The adsorbents were modified by hexadecyltrimethyl ammonium bromide (HDTMA) and acid by impregnation common method and then used for magnetic activated carbon with ozonation for ammonium removal. Also, based on studies for acid modification of the surfaces of zeolites, the chloridric acid was applied [13,24]. Generally the experiments were done in three separate conditions.

2.3. Phase 1: Oxidation and then ammonium adsorption

In this condition, the ammonium adsorption with initial concentration of 10 mg/L by catalyst (5 g/L) for pH determination in the range of 4–10 has been used. Namely by research on COP for removing ammonia from water by magnetic activated carbon catalyst with concentration of 10 g/L, the effect of the initial pH on removal efficiency of ammonia in the AOP was calculated. The catalyst used in COP was a super-para magnetic activated carbon that was synthesized using iron salts and powder activated carbon according to the impregnation and calcination method reported in the previous study and based on the optimum conditions of oxidation, the catalyst concentration of 5 g/L was used in the COP process [16]. Also, the reusability of the catalyst was performed.

2.4. Phase 2: Catalytic ozonation of ammonium

After finding the optimum pH in ammonium COP in the range of 4 to 10, the effect of other parameters such as carbon catalyst concentration (five levels of 0.5, 5, 10, 25, 50 g/L) and retention time (nine levels of 0, 5, 10, 15, 30, 45, 60, 90 and 120 min) were studied on ammonium removal efficiency and procedure on the remaining ammonium concentrations, pH, nitrate and produced nitrate.

2.5. Phase 3: adsorption process and ion exchange of ammonium and nitrate by zeolites

In this part, at first we analyzed pH effect on ammonium adsorption process by natural zeolite. Then, the adsorption of remaining produced ammonium and nitrate took place by oxidation of Garmsar and Firouzkooh zeolites and their modifications. The effect of different parameters such as contact time (five conditions from 0 to 2 h), concentration of adsorbent substance (five levels of 0.5, 5, 10, 25 and 50 g/L) were selected and their isotherms and adsorption capacity of each of them were measured. Then, the other physical and chemical parameters such as pH, TDS, ammonium, nitrate, nitrite in continuous flow reactor were analyzed by standard method presented in "standard methods of water and wastewater examinations" [25]. Table 2 shows the conditions and the stages of experiments for adsorption and ammonium oxidation.

2.6. Properties of ozonation reactor

Pure oxygen flow with pressure of 1 atmosphere and a flow rate of 1 L/min were conducted to produce 40 mg/min of ozone gas flow. The pilot reactor in this research was a glass impinger with the volume of 250 mL and the flow type of this reactor was semi-batch. The real scheme of the pilot and its components is shown in Fig. 1.

3. Results and discussion

3.1. Effect of pH on ammonium removal in COP and adsorption by zeolites

Results of the efficiency of ammonium removal in different pH are shown in Fig. 2a. The best efficiency of ammonium removal was calculated about 30% for the ammonium concentration of 10 mg/L and the concentration of catalyst was 5 g/L at the pH of 8. In addition, the best efficiency for ammonium removal in COP process was 50% with the concentration of 10 mg/L and carbon catalyst concentration of 10 g/L in the pH of 9.

It is confirmed about the mechanism of the process that pH_{zpc} is one of superficial properties of catalyst and superficial potential of different adsorbents can be positive or negative depending on superficial agent groups and their components. pH_{zpc} is a point of pH that positive potential and negative potential of the surface of the catalyst have balance. According to researchers' results, pH_{zpc} of this carbon catalyst is 7.7 [26]. It should be mentioned that the acid and base constant (pK_a) of ammonium is 9.25 [27]. In other words, in higher pHs ammonium will change to ammonium anion (ammonia), and the best pH for catalyst adsorption is in the range of pH_{zpc} to pK_a, other words in the range of 7.7–9.25 which averages to the pH of 8. In other words, ammonium is neutral or positive and catalyst surface is negative and they can adsorb each other extremely.

In oxidation of ammonium with COP process most efficiency of ammonium removal in alkali pH of 9 is about 50%.

The mechanism of ozonation of ammonia as a method of oxidation is expressed as below [28]:

$$NH_3 + 4O_3 \rightarrow H^+ + NO_3^- + H_2O + 4O_2 \quad (1)$$

Researches show by increase in pH of ammonium, oxidation will increase, which it can be related to pH effect on transition of ozone from gas phase to liquid phase. Since the persistence of ozone molecules in solution is quite short, its rate of reaction with ammonia molecules is relatively slow [29].

Some chemical advanced oxidation potential methods are based on free hydroxyl radical generation and they can effectively oxidize ammonium anions to nitrate [30,31].

Increase of ozone decomposition and increase of active radicals result as a matter of increase in anions, which has more oxidation potential in comparison with ozone [32], because, hydroxyl radicals have more oxidation potential in comparison with ozone (1.34) and make an effective oxidation of ammonium. Also, another reason can be increase of ozone break down rate in distilled water by increasing pH that one of the most important reasons of

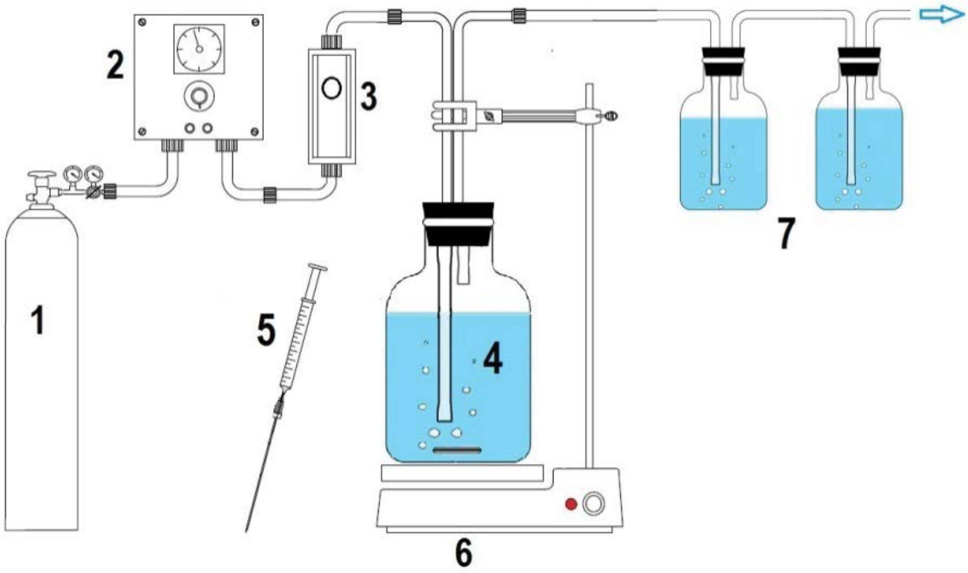

Fig. 1. Scheme of ozonation reactor with zeolite catalyst; (1) pure oxygen capsule; (2) ozone generator; (3) rotameter; (4) reactor; (5) sampling syringe; (6) mixer; (7) ozone gas trapper (KI 20% v:v).

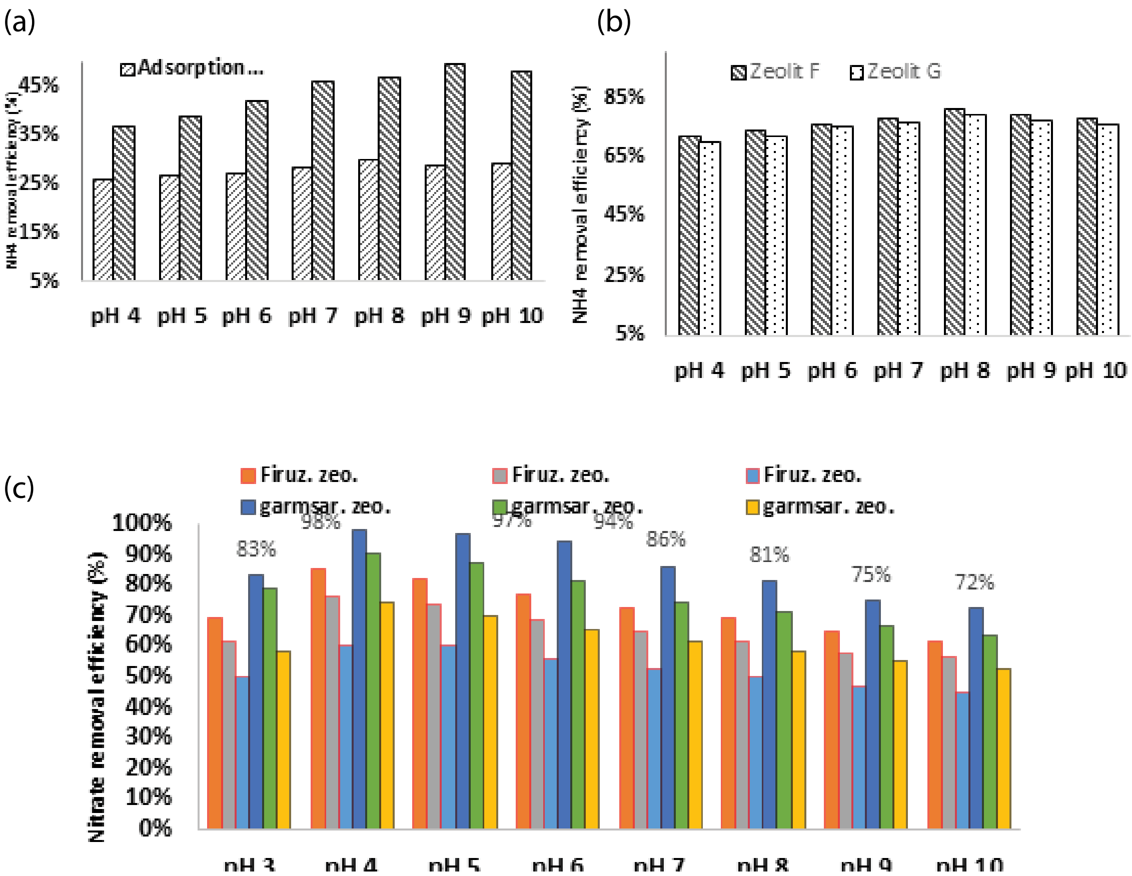

Fig. 2. (a) Comparison of efficiency of ammonium removal in diverse pHs of COP and catalyst adsorption. Rotation of the mixer: 200 rpm, process time: 120 min, ozone stream: 40 mg/min; (b) comparison of efficiency of ammonium removal in diverse pHs in ammonium adsorption process by natural zeolite of Garmsar and Firouzkooh; initial concentration of ammonium: 10 mg/L, zeolite concentration: 5 g/L, 200 rpm, reaction time of 120 min; (c) nitrate adsorption using various adsorbent and pH; initial concentration of 10 mg/L, zeolite concentration: 5 g/L, 200 rpm, reaction time of 120 min.

ozone break down in pure water is hydroxyl radicals $(OH^{\bullet})$ that can be offered as the beginner of ozone break down reaction. Thus, with increase in pH and hydroxide ion, the quantity of produced hydroxyl radicals by ozonation operation will increase and thus, ozone break down will increase [33]. Such that, carbon catalyst surface have some agents such as hydroxyl and carboxyl agents that have a crucial function on ozone break down to hydroxyl radicals causing more ozonation break down rate [34]. But, according to Eqs. (1) and (2) with increase of pH equivalent goes to the direction of proton consumption and ammonia production and solution phase will be lesser and efficiency of ammonium removal will increase [35]. Also, other researches show the same result. For example, Zhao et al. [36] presented that in COP with Mn crystals by increasing pH from 3 to 11 nitrobenzene removal efficiency will increase. In addition, some researchers reported that with increasing pH from 3 to 10 will cause decreasing mineralization of organic substances in COP with Mn Ce O catalysts [37]. Also, the reports showed the optimum pH for decolorization and mineralization of a dye by ozonation in COP with nanoparticles of MgO in alkali condition is more than 8 [38]. According to Fig. 2(b), in ammonium adsorption process by natural zeolite of Garmsar and Firouzkooh, the optimum efficiency of ammonium removal is 81% which for Firouzkooh zeolite reaction takes place in pH of 8. With due attention to this note that the ammonium concentration related to the pH value (Eqs. (2) and (3)) and properties of surface of adsorbent, the optimum pH for adsorption of ammonium by zeolite is in the range of pH_{zpc} to pK_a, or in the range of 5.3–9.25 [27], in other word, averaging in pH = 8. Since, ammonium is neutral or positive zeolite, has negative potential, so they attract each other extremely. Although, optimum pH of adsorption process is based on other researches [39], Dianati et al. [40] offered the pH of 7 as an optimum condition and also in another research reported the optimum pH of 6 for ammonium adsorption by natural clinoptilolite zeolite [35]. In Table 3 the ammonium adsorption capacity by different zeolites are presented.

$$NH_3 + H_2O \leftrightarrow NH_4^+ + OH^- \quad (2)$$

$$NH_4^+ \leftrightarrow NH_3 + H^+ \quad (3)$$

Researches show that the effect of pH on nitrate adsorption with Firouzkooh and Garmsar natural and amended zeolites resulted in optimum efficiency of nitrate removal of about 98% for Garmsar ligand modified zeolite (HDTMA) in an acidic condition (pH = 4) and adsorption by Firouzkooh natural zeolite at pH = 10 had the least efficiency of about 45%. Also, results showed at pH = 4 Garmsar amended ligand and acidic zeolite resulted in 24% and 16% increase for nitrate elimination, respectively. In Chabani et al.'s [41] research about the effect of Amberlite resin on nitrate removal maximum nitrate removal occurred in pH = 6.8.

Results indicated that the ligand and acid amending of zeolites effect the ammonium adsorption by Firouzkooh and Garmsar zeolite. Results of the effect of the ligand of hexadecyltrimethylammonium bromide (HDTMA) and acid modified of Garmsar and Firouzkooh zeolite on ammonium adsorption are shown in Fig. 3 at optimum pH of 8 which shows Firouzkooh natural zeolite has optimum efficiency of 81%, while its ligand and acid modified types have efficiencies of 66% and 62%, respectively.

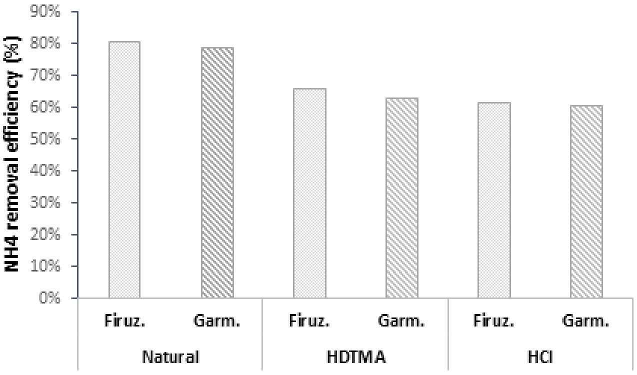

Fig. 3. Ammonia removal of Firouzkooh and Garmsar zeolite by ligand and acid modification; initial ammonium concentration: 10 mg/L; zeolite concentration; mixer velocity of 200 rpm, retention time of 120 min; and pH 8.

Also, the most efficiency in ammonia removal was by Garmsar natural zeolite which has been calculated about 79% and for ligand and acid amended were 63% and 61%, respectively. In general, results showed that the maximum quantity in ammonia removal occurred in two untreated (not amended) kinds of both zeolites and in comparing both adsorbents, Firouzkooh natural zeolite had a higher efficiency.

In other words, ligand and acid treatment have reductive effect on ammonium adsorption's capacity and both adsorbents of Firouzkooh and Garmsar. The reason of these phenomena is the potential of treated adsorbent surface. Because usually cationic surfactants such as HDTMA have a long chain of alkyl and a quaternary ammonium›s group at the end of their chains which increase their capability of interaction with ions and we can see this phenomena on the surfaces of zeolites in acid treatment (because of protons covering) so their interest of attracting some cations such as ammonium will decrease [42,43].

3.2. Effects of adsorbent concentration of Firouzkooh natural zeolite on NH_4 adsorption

Results of ammonium removal efficiency of Firouzkooh natural zeolites in different concentrations and optimum pH of 8 are shown in Fig. 4. Results show that ammonium concentration of 10 mg/L, pH = 8) maximum ammonium removal efficiency occurs in 50 g/L concentration of adsorbent which equals to 90% and minimum ammonium removal efficiency occurs in 0.5 g/L of zeolite concentration which equals to 39%. Since ammonium removal efficiency in 5 g of zeolite's concentration is just 6% less than 50 g/L of concentration of zeolite but is 45% more than 0.5 g/L so it can be considered as optimum concentration of adsorbent.

Also, maximum nitrate removal efficiency was about 98% which occurs by Garmsar ligand treated zeolite in concentration of 50 g/L and minimum removal of ammonium which was about 22%, occurs at zeolite concentration of 0.5 g/L with initial nitrate concentration of 25 mg/L and an optimum pH of 6.

In general, in adsorption processes with increase of adsorbent concentration, adsorption efficiency will increase which is because of increase in active sites on the adsorbent surface and quick adsorption of ammonium ions existing in water by zeolite catalyst surface takes place due to potential difference [44] which has been observed in other studies about adsorption, while excessive increase of adsorption concentration causes reduction on adsorbent capacity [45].

3.3. Ammonium and nitrate adsorption by Firouzkooh and Garmsar zeolites

Results of ammonium adsorption capacity by treated and untreated zeolites of *Firouzkooh* and *Garmsar* in optimum pH (pH = 8) are shown in Fig. 4. Results of the experiment showed that Garmsar acid-treated zeolites and Firouzkooh natural zeolites have minimum and maximum adsorbent capacity, respectively (Garmsar: 12.7 mg/g, Garmsar: 18.5 mg/g). It is a good statistic in comparison of other capacities of adsorption of adsorbents which are shown in Fig. 3. Also, Dianati et al. [40] measured ammonium adsorption by zeolite 6 mg/g. Also, Lin and Wu [35] calculated ammonium adsorption capacity of about 3.2 mg/g by Dowex SAR kinetic resin with concentration of 5 mg/L.

On the other hand, with due attention to this note that treated zeolite with ligand has maximum efficiency for nitrate removal, which occurs in acidic pH and also, since after ozonation process pH will become 6.3, so, the conclusions in optimum pH (pH = 6) showed Firouzkooh natural zeolite and Garmsar treated zeolite with ligand have minimum and maximum adsorption capacities which are 4.9 and 11.2, respectively. Results shown in Fig. 2c indicate that in pH = 4 ligand and acid treatment of Garmsar have 24% and 16% increase of nitrate eliminate and removal.

In general, cationic surfactants improve intense and capacity of the anions. Guan et al. [24] showed treated zeolites by organic surfactants (hexadecylthreemethyl ammonium) causes nitrate adsorption to increase. Also, in a research by Faghihian et al. [47] which were about nitrite and nitrate ions adsorption by Kerman zeolites showed that using tetramethyl ammonium and tetraethyl ammonium increases the adsorption of these ions by these minerals from polluted water. Also, Soleymani et al. did their experiments by zeolites of Semnan and Firouzkooh for elimination of nitrate and ammonium ions. These zeolites have been treated by organic surfactant of hexadecylthreemethyl ammonium for modifying their adsorption properties. Results showed that Semnan natural zeolite has maximum ammonium adsorption and Firouzkooh treated zeolite has minimum ammonium adsorption. Also, using surfactants, doubled nitrate removal up to 9.92 [1]. In Table 4 the adsorption capacity of natural and modified *Firouzkooh* and *Garmsar* zeolites are shown.

3.4. NH_4 and nitrate adsorption isotherms by of Firouzkooh and Garmsar zeolites

Results showed (Fig. 5) that ammonium and nitrate adsorption (or absorption) by Firouzkooh natural zeolite and Garmsar modified ligand zeolite follow Langmuir

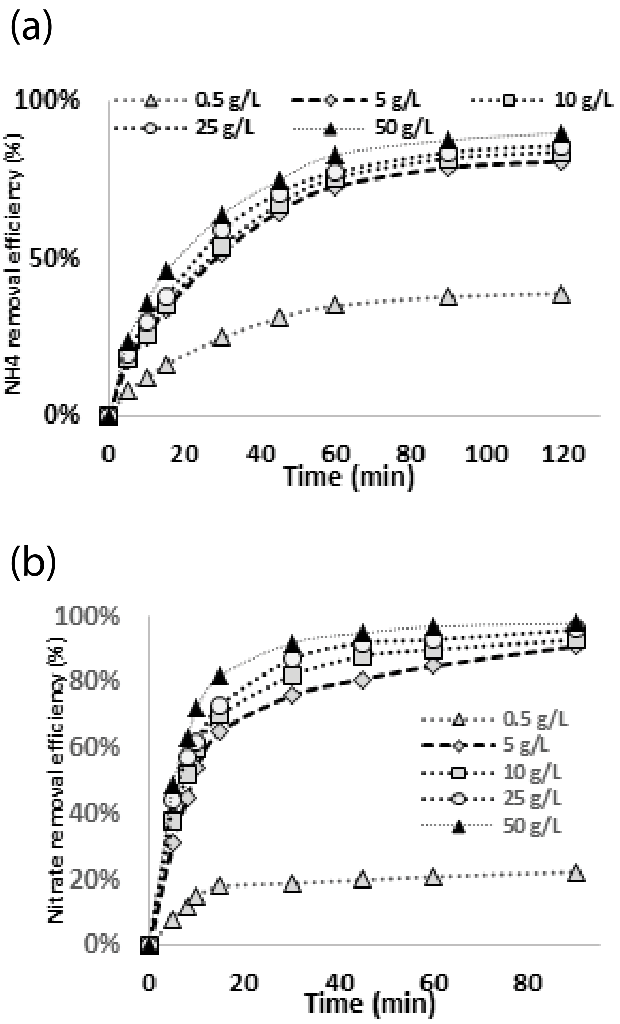

Fig. 4. (a) Diagram of ammonium removal in different concentrations of natural zeolite of Firouzkooh; initial concentration of ammonium: 10 mg/L, pH = 8; (b) nitrite removal in different concentrations of Garmsar ligand treated zeolite; initial concentration of nitrate 25 mg/L, pH = 6, rotation of the mixer = 200 rpm.

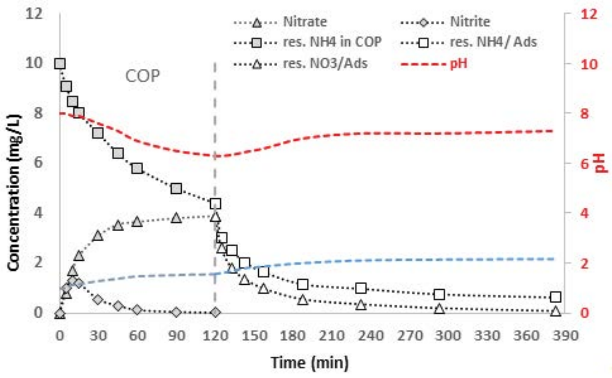

Fig. 5. Concentration procedure of ammonium, nitrate, nitrite and pH in integration process of COP and Garmsar ligand modified zeolite concentration, initial concentration of ammonium of 10 mg/L, carbon catalyst 10 g/L, Garmsar ligand modified zeolite 5 g/L, ozone flow rate of 40 mg/min, initial pH of 8.

Table 2
Conditions and stages of experiments of adsorption and ammonium oxidation

Stage	Effects of operational conditions on removal efficiency of ammonium	Initial concentration of ammonium (mg/L)	Catalyst concentration (g/L)	pH	Time (min)
1	Defining pH effect on ammonium adsorption in catalyst	10	5	4–10	0–120
2	Defining pH effect on ammonium oxidation in COP	50	10	10–4	120
3	Effect of ligand and acid treatment on NH4 adsorption by Garmsar and Firouzkooh zeolite	10	5	8	0–120
4	Defining optimum pH effect on ammonium adsorption by zeolite of Garmsar and Firouzkooh	10	5	10–4	120
5	Effect of adsorbent's concentration on NH_4 by G and F untreated zeolites	10	0.5–50	8	0–120
6	Defining effect of NH_4 by G and F treated and untreated zeolite	50	0.5–50	8	120
7	Defining optimum pH in nitrate adsorption process by natural and treated zeolite of Garmsar and Firouzkooh	10	5	10–4	90
8	Effect of concentration of Garmsar ligand treated zeolite on nitrate adsorption and defining adsorption capacity	25	10	6	0–90
9	Ammonium, nitrate, nitrite and TDS removal in COP integration process and Garmsar ligand zeolite adsorption	10	10	8	0–390

Table 3
Ammonium adsorption capacity by different zeolites [46]

Ion exchanger	q_m (mg NH_4^+/g) (cmol kg^{-1} in parenthesis)
Natural Hungarian zeolite	11.72 (64.93)
New Zealand zeolite	7.39–7.43 (40.94–41.16)
Natural Chinese clinoptilolite	14.42 (79.89)
Natural Turkish clinoptilolite	8.12 (44.99)
Natural Akita clinoptilolite	16.06 (88.98)
Natural Iranian zeolite (millimeter)	11.31 (62.66)
Natural Iranian zeolite (nanometer)	13.27 (73.52)

Table 4
Adsorption capacity of natural and modified Firouzkooh and Garmsar zeolites

Adsorbed	Type of zeolite	pH	Modification	Q_m (mg/g)
NH_4	FiroozkoohZeo.	8	Natural	18.5
			Zeo./HDTMA	16.28
			Zeo./HCl	15.91
	GarmsarZeo.	8	Natural	15.2
			Zeo./HDTMA	13.22
			Zeo./HCl	12.77
NO_3	FiroozkoohZeo.	6	Natural	4.93
			Zeo./HDTMA	9.8
			Zeo./HCl	7.4
	GarmsarZeo.	6	Natural	5.5
			Zeo./HDTMA	11.2
			Zeo./HCl	8.3

adsorption function because squared of data are nearer to each other and maximum adsorption of them are 18.5 and 11.2 mg/g, respectively. Since, ammonium and nitrate adsorption models follow Langmuir isotherms, adsorption energy of pollutants is the same and does not depend on the quantity of adsorbed material by adsorbent, in other words adsorption capability of all active locations is the same and existence of adsorbed substances does not have any effect on another place. Also, adsorption bonds are reversible and the adsorbed substances form a layer with the thickness of one molecule and the absorption is not multilayer. In addition, considering the two parameters of $q_{\max}$ and b, b is determinant of desirability of adsorption isotherm. If $b > 1$, adsorption process is undesirable, if $b = 1$, the process is linear and if $0 < b < 1$, the process is desirable, and if $b = 0$, the adsorption process is irreversible. Since adsorptions by b for ammonium and nitrate are 0.07 and 0.121 L/mg, respectively, the processes are desirable. In Table 5 the results of isotherms parameters of Langmuir and Frondlich for ammonium and nitrate adsorption by natural zeolite of *Firouzkooh*.

Chatterjee and Woo [48] analyzed the effect of treated chitosan by sodium bisulfate on nitrate absorption. Adsorption model data followed Langmuir isotherm and adsorption capacity of treated chitosan was more than natural chitosan. Ren et al. [45] showed heavy metals adsorption process by zeolite followed Freundlich and Langmuir isotherms but was closer to Freundlich while according to research by Demir et al. [9] Langmuir model was closer to ammonium adsorption by zeolite.

According to research of Alidadi et al. [49], nitrate adsorption by zeolite followed Freundlich isotherm and K_f and $1/n$

Table 5
Results of isotherms parameters of Langmuir and Freundlich for ammonium and nitrate adsorption by natural zeolite of Firouzkooh

	Freundlich isotherm parameter				Langmuir isotherm parameter			
Pollutant	$\ln K_f$	R^2	N	K_f	$1/ab$	R^2	b or K_L (L/mg)	q_m (mg/g)
NH_4	0.33322	0.970	0.665	1.40	0.739	0.990	0.07	18.54
NO_3	0.137	0.980	1.012	1.147	0.737	0.990	0.121	11.22

are 4.8 and 0.43, respectively, that their adsorption bonds are stronger than nitrate and ammonium.

3.5. Ammonium, nitrate, nitrite removal and TDS concentration in COP/zeolite process

Results of elimination of ammonium, nitrate, nitrite, TDS, pH changes in COP syncretistic process and Garmsar ligand modified zeolite adsorption are shown in Fig. 5. Results showed that initial concentration of ammonium after COP process and reaction time of 120 min. and carbon catalyst concentration of 10 g/L with efficiency of 56% became 4.4 g/L (initial concentration = 10 mg/L) and then at the end of adsorption process by zeolites (5 g/L) and time of 90 min became 6 mg/L. Generally total efficiency of ammonium was 94%. According to the same researches, ozonation just can change nitrite to nitrate and could not eliminate ammonium efficiently such as efficiency for the contact time of 20 min. which was just reported 25% and ammonium was exchanged to byproducts such as nitrate; while in ozonation column at the first times of reaction nitrite changed into nitrate [35]. Also the reduction in catalytic properties of the catalyst was negligible after five times of reuse. The finding revealed that this catalyst is proven to be suitable for the oxidizing of ammonium from contaminated waters.

At this condition after 120 min catalytic ozonation, concentration of nitrate from 0 increased up to 3.9 mg/L and at the end of adsorption process decreased down to 0.1 mg/L. Also, nitrite concentration decreased differently in oxidation production process, such that in this adsorption process concentration process could not be measured. Initial pH of the process was 8, which at the end of ozonation decreased down to 6.3 and at the end of adsorption process increased up to 7.3. According to other researches, decrease in pH of ammonium ozonation process can be due to changing of ammonium or nitrate into nitric acid which is a strong acid [35]. According to other researches about catalytic revive of nitrate, some byproducts such as nitrite, ammonium and nitrogen gas have been formed [50].

Also, initial quantity of TDS after COP process increased up from 98 to 156 mg/L; then at the end of adsorption process by Garmsar ligand zeolite increased up to 217 mg/L. Results showed that ammonium elimination by integration process was very crucial such that fell under the standard line and initial TDS parameter had a little increase, which was under the standard line again. Also, according to the same researches except reduction of initial EC and TDS at the beginning of extracting from adsorption tower, their improving procedure during the extracting time was obvious [51].

Generally results showed that ammonium removal by this integration process was so strict such that fell into under the standard line and three parameters of EC, TDS and initial turbidity had a little increase were in the standard regulations [52].

Also, in the research by Mažeikiene et al. [53] with increase of nitrate concentration, the electrical conduction of water increased up and therefore, the quantity of EC and pH of refined water increased up by clinoptilolite's adsorbent column. In addition, quantity of chlorine and sulfate ions increased up in the extracting times [54], that this phenomenon approves our findings. In other words, in wastewater treatment by zeolite, with increase of adsorbent concentration, the present quantity of TDS will decrease, such results show that by using zeolite for wastewater treatment decreases the solid particles of solutions and promotes its quality.

4. Conclusions

In this research, oxidation by catalytic ozonation, carbon catalyst and adsorption of clinoptilolite for elimination and removal of ammonium from water in batch and continuous reactors have been analyzed. Oxidation process causes elimination of ammonium or changing them into byproducts and zeolite treatment by cationic surfactants increases the efficiency of nitrate removal.

The high ammonium oxidation efficiency in the COP process is due to the presence of free hydroxyl oxidizing radicals that converts the ammonium to nitrate anions that subsequently being adsorbed to zeolite adsorbent.

In general, as the results show, this process is a good way for treatment of waters which are polluted by ammonium because its efficiency and time is desirable. Also, this process does not have any problems such as high consumption of substances, remaining new combinations in treated wastewater and complexities of process and operation.

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