

Investigating the Effectiveness of Modified Clinoptilolite Zeolite on Nitrate Removal from Aqueous Solution

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Received: 20 April 2024 / Received in revised form: 22 August 2024, Accepted: 02 September 2024, Published online: 12 September 2024

Abstract

Nitrate ions are considered a serious threat to surface and underground water resources due to their high solubility in water. Therefore, it is necessary to remove them from water sources. There are many ways to remove nitrates from water, the simplest of which is to remove them with adsorbents such as zeolites. In this research work, particles of copper oxide and iron oxide were placed on natural clinoptilolite zeolite. The physical and chemical properties of the prepared nanosorbents were investigated by scanning electron microscopy (SEM), X-ray diffraction (XRD), measurement of the specific surface area of the adsorbents by the BET method, and diffuse reflectance spectroscopy (DRS). After choosing the appropriate adsorbent, other operating factors such as adsorbent amount, pollutant concentration, and solution pH were investigated for removal efficiency. The highest nitrate adsorption efficiency was obtained on clinoptilolite zeolite loaded with 5% copper oxide at a pH of about 4 to 9 at low nitrate concentrations and the adsorbent amount was 15 mg per liter.

Keywords: Clinoptilolite zeolite, Nitrate, Aqueous solution, Water

Introduction

Nitrate is a major pollutant widely found in water sources of many developed and developing countries. Water pollution with nitrates has reduced the quality of underground water so research shows that in many parts of the world, pollution of underground and surface water with nitrates has become a serious problem. Although nitrate is a mineral, nitrate pollution is grouped in the

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branch of pollution with organic substances, because nitrate is obtained from biological processes (Tyagi *et al.*, 2018; Dai *et al.*, 2023; Khatamian *et al.*, 2024).

The main source of nitrate entering water sources is agricultural fertilizers and irrigation of fields with domestic sewage. Among the dangers of excessive nitrate entering into drinking water sources, we can mention Blue baby syndrome, which is fatal and in adults also leads to stomach and digestive tract cancer due to the formation of nitrosamine (Salehi & Hosseinifard, 2020; Verma & Nadagouda, 2021). In livestock, the high level of nitrogen in water and fodder irrigated with sewage has led to problems in reproduction, abortion, and reduced milk production. Therefore, it is necessary to remove nitrate from drinking water (Bhatnagar & Sillanpää, 2011). Conventional methods for nitrate removal include several physical and chemical processes, including ion exchange, electrodialysis, biological treatment, reverse osmosis, adsorption coagulation with activated carbon or zeolites, and nitrification and mixing it with waters that have less nitrate (Goff *et al.*, 2023; Hidayat *et al.*, 2023; Hosseini Nami & Mousavi, 2023; Omorogie & Helmreich, 2024). In recent years, researchers have considered nanofiltration to be an efficient method, although some have described it only as a suitable pre-treatment for reverse osmosis. However, the simplicity of the process, easy access, low cost, and easy application in any system are the main advantages of the absorption process for water purification. With different adsorbent materials such as activated carbon or zeolite and silica, it is possible to remove or reduce a variety of inorganic pollutants such as fluoride, nitrate, bromate, and perchlorate (Orbuleț *et al.*, 2022).

Zeolites are crystalline aluminosilicates consisting of AlO_4 and SiO_4 structural units. These tetrahedra are connected by oxygen bridges and create a network of channels and holes with different sizes and shapes. Zeolites are formed by replacing several Si^{4+} ions with Al^{3+} in aluminosilicates. Placing Al^{3+} instead of Si^{4+} produces a negative charge in the zeolite network, which is balanced by metal cations. These metal cations are mobile and can be replaced by them in contact with solutions containing other cations (Jodaei *et al.*, 2011; Zhang *et al.*, 2023).

Clinoptilolite zeolite is an aluminosilicate whose cation exchange capacity varies between 100 and 300 micro equivalents per 100 grams. This adsorbent is suitable for applications due to its porosity, high resistance to extreme heat, and chemically neutral base structure. This material easily absorbs ammonia and other



toxic gases from the air and water, and as a result, it can be used as a filter for sanitary purposes and an odor absorber. It also can absorb some heavy metal cations such as lead, zinc, cadmium, and nickel and can be used as an ion exchanger to remove ammonium ions (Stylianou *et al.*, 2007; Wu *et al.*, 2017; Rajar *et al.*, 2018; Yahya *et al.*, 2023).

Considering the health problems caused by water pollutants, in this research, the removal of nitrate from aqueous solutions with natural clinoptilolite zeolite and its modified type with copper oxide and iron oxide was investigated by laboratory method. The structural features of several structures prepared by different device methods were identified and the effect of different operating factors such as initial nitrate concentration, adsorbent amount, pH, and contact time on the nitrate removal process was investigated.

Materials and Methods

Modification and Preparation of Clinoptilolite Zeolite

To prepare clinoptilolite zeolite, first, the zeolite was crushed and then washed with distilled water. After that, 50 mg of zeolite sample was stirred with 300 ml of 2 M hydrochloric acid solution at 70 °C for 24 hours to obtain the protonated form of zeolite. Finally, the desired sample was dried at 90 °C for 24 hours.

Preparation of Clinoptilolite Zeolites Loaded with Iron Oxide and Copper Oxide

To prepare these adsorbents, first, 5 grams of prepared clinoptilolite zeolite along with a certain amount of iron (III) nitrate, or copper (II) acetate were added to 50 ml of ethanol. The obtained mixtures were stirred for 12 hours under reflux conditions and then filtered. After that, the solid samples were placed at a temperature of 70 °C to evaporate the solvent. To remove existing nitrate and convert iron ions into oxide form, the corresponding sample is kept inside the furnace at 250 °C for 3 hours, and to remove existing acetate and convert copper ions into oxide form, the corresponding sample is kept inside the furnace at 250 °C for 3 hours. The temperature was set at 450 °C.

Investigating Sodium Nitrate Absorption Process with Prepared Adsorbents

In this phase of the research, all the experiments were done continuously. The equipment used included a 250 ml beaker as a reactor and a magnetic stirrer with a magnet. To perform the experiments, a suspension of 100 ml of a solution with a concentration of 10 ppm sodium nitrate and 0.2 g of adsorbent was prepared and stirred on a magnetic stirrer. At regular intervals, 5 ml of this sample was taken and collected. It was removed from the solution on top of the absorbent container with a syringe and its absorbance was measured with a UV-Vis spectrometer. The conversion fraction was calculated from Eq. 1. For each, a plot of conversion fraction versus time was obtained.

$$X = (C_0 - C) / C_0 \quad (1)$$

Where C_0 is the initial concentration of sodium nitrate and C is the concentration of sodium nitrate at any moment.

The Method of Measuring Sodium Nitrate Absorption

Different methods can be used to measure nitrate, and in this study, a UV-Vis spectrometer was used. To determine the maximum absorption wavelength, a solution of sodium nitrate with a concentration of 30 ppm was prepared and its absorption spectrum was measured with a double beam spectrometer, and the maximum wavelength was 296 nm. To calculate the residual concentration of nitrate in the samples, absorption was measured at a wavelength of 296 nm.

Results and Discussion

Examination of XRD Patterns

To evaluate the structure as well as the effect of the type of copper and iron particles loaded on clinoptilolite zeolite, the XRD patterns of the samples were investigated in the 2θ range from 6 to 61°. These patterns are shown in **Figure 1**. The XRD pattern of natural clinoptilolite zeolite used was in good agreement with the standard clinoptilolite zeolite XRD pattern, which proves the crystal structure of clinoptilolite zeolite. By adding copper and iron particles, peaks related to zeolite can be seen in all samples, which shows that the structure of zeolite is stable during the process of crystallization and calcination and the addition of copper or iron. The sample has not undergone a structural change.

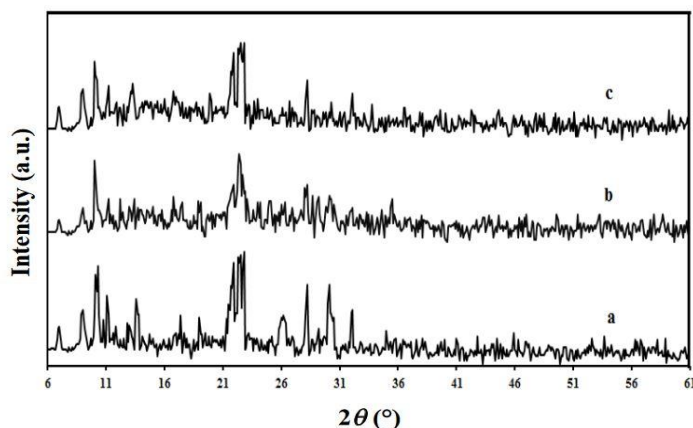


Figure 1. a) XRD patterns of clinoptilolite zeolite, b) copper-loaded clinoptilolite zeolite, and c) iron-loaded clinoptilolite zeolite.

Figure 2 shows the XRD pattern related to loading different amounts of copper and iron on clinoptilolite zeolite. As seen in the XRD pattern of these compositions, after loading zeolite with different percentages of copper or iron, the structure of the original composition has been preserved. However, the peaks related to the related oxides are also seen in the patterns of samples with high

percentages of copper and iron. The presence of peaks at 2θ equal to 36 and 38° confirms the presence of copper oxide according to the reported results (Nezamzadeh-Ejhih & Moenirad, 2011). Also, the presence of peaks at 2θ equal to 24, 33, 35.5, 41, 50, 54, and 58° confirm the presence of iron oxide in the form of α -Fe₂O₃ according to the reported results (Jodaei *et al.*, 2011).

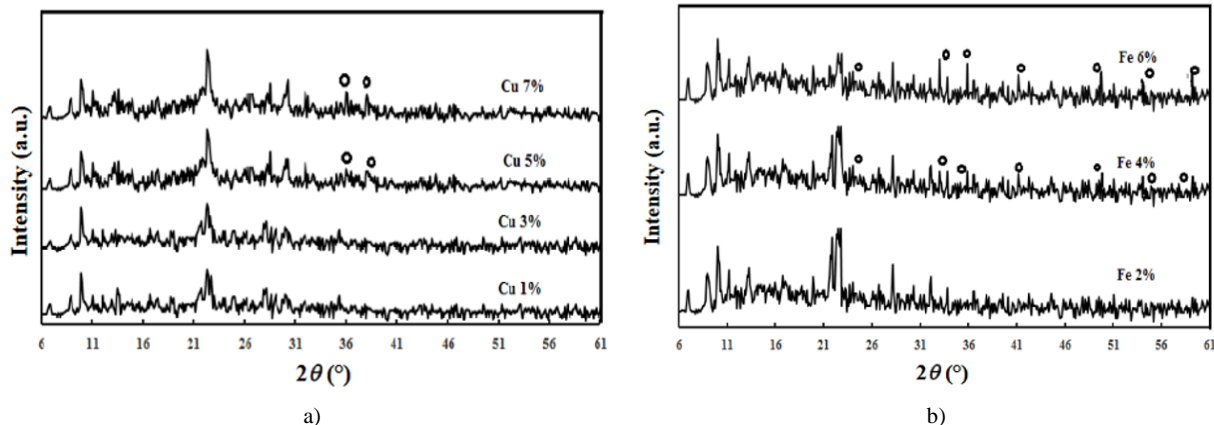


Figure 2. XRD patterns of clinoptilolite zeolites with different percentages of copper and iron (the peaks of the corresponding oxides are marked with O).

Measurement of the Specific Surface of Adsorbents

The specific surface area and volume of the adsorbents loaded with copper and iron and the specific area of clinoptilolite zeolite were measured, and the results are given in **Table 1**. As can be seen, with the loading of copper up to 7% and iron up to 6%, the specific surface area of clinoptilolite adsorbent has not changed significantly. This result can be attributed to the low level of zeolite used and the low loading percentage of the related chemical species.

Table 1. The specific surface area and the volume of the holes of the samples.

| Samples | Average diameter of pores (nm) | Total volume of pores (cm ³ g ⁻¹) | Surface area (m ² g ⁻¹) by single point BET method |
|-----------------|--------------------------------|--|---|
| Natural zeolite | 19.63 | 0.1136 | 23 |
| Cu 3% -Clin | 21.92 | 0.1247 | 23 |
| Cu 7% -Clin | 23.75 | 0.1356 | 22 |
| Fe 4% - Clin | 19.68 | 0.1174 | 22 |
| Fe 6% -Clin | 19.99 | 0.1266 | 20 |

Visible-Ultraviolet Reflectance Spectroscopy (UV-Vis DRS) and Band Cuff Energy of the Samples

The study of electron transitions, which is mostly carried out with the UV-Vis spectrometer, provides valuable information about the electronic structure of different materials, but in the case of polystructures and most semiconductors, due to the limitation in obtaining transparent solutions (insoluble or low their solubility) using UV-Vis spectrometer alone is not useful. Diffuse reflectance

UV-Vis spectrometry is a suitable fan that enables the study of electron transitions, absorption edges, and energy cuffs. The maximum wavelength of absorption and the energy of the tape cuff in the samples were calculated using Eq. 2.

$$\lambda_{\max} = 1240/E_g \quad (2)$$

Where λ_{\max} is the characteristic peak wavelength and E_g is the energy of the banded cuff.

As can be seen in **Table 2**, the maximum absorption wavelength for clinoptilolite zeolite is 307.46 nm and the energy of the band is 4.03 eV, while with increasing oxides of iron and copper in the zeolite, these values shift towards the wavelength higher and lower energy is shifted, which is 3.74 electron volts for copper oxide and 3.82 electron volts for iron oxide. Therefore, these loaded adsorbents can work under sunlight and even in catalytic processes, they have a better performance than basic zeolite.

Table 2. The maximum absorption wavelength and energy of the band cuff of the prepared samples.

| Catalyst | E_g (eV) | λ_{\max} (nm) |
|------------------------|------------|-----------------------|
| Clinoptilolite zeolite | 4.03 | 307.46 |
| Cu 3% - Clin | 3.74 | 328.04 |
| Fe 4% - Clin | 3.82 | 342.61 |

SEM Images

SEM images of zeolite loaded with copper oxide are shown in **Figure 3**. As can be seen in this figure, the size of the particles is about 100 nm. The EDS spectrum of the sample shows the presence of copper elements, which can confirm the presence and distribution of copper oxide on the surface of the catalyst.

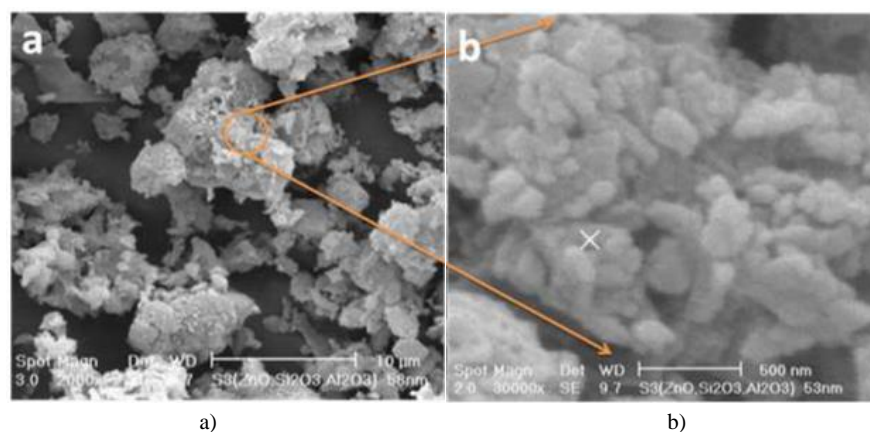


Figure 3. SEM images of clinoptilolite zeolite loaded with copper oxide at different magnifications.

Investigating the Nitrate Removal Process and the Efficiency of the Adsorbents Prepared

To check the efficiency of modified clinoptilolite zeolite, nitrate adsorption was investigated under the same conditions on unmodified clinoptilolite zeolite and zeolites loaded with copper oxide and iron oxide. The results of this study are shown in **Figure 4**. As can be seen, the ability of clinoptilolite zeolite to remove nitrate from the solution can be increased by adding copper and iron oxides. Of course, zeolites containing copper oxide showed higher absorption than zeolites containing iron oxide with the same percentage. This result can be related to the lower band energy of zeolites loaded with copper oxide compared to zeolites loaded with iron oxide. Therefore, the adsorption capacity of nitrate with clinoptilolite zeolite loaded with copper oxide is higher than that of clinoptilolite loaded with iron oxide.

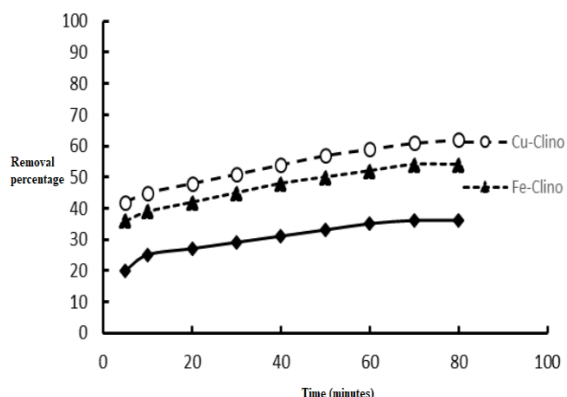


Figure 4. Nitrate absorption efficiency diagram of different adsorbents.

Investigating the Impact of Contact Time

Figure 5 shows the effect of contact time from 0 to 150 minutes on nitrate removal efficiency with CuO-loaded clinoptilolite adsorbent. As can be seen in the figure, with time, the amount of absorption increased so that the removal efficiency in 10 minutes was 46.9%, but after 80 minutes, this value reached 67%. Also, according to this figure, it is clear that after 90 minutes, the removal efficiency remains constant and does not change with increasing

time, and it is clear that the absorption equilibrium time is 80 minutes. By increasing the contact time, the opportunity and probability of nitrate ions encountering the adsorbent increases, and as a result, it increases the absorption efficiency. But after reaching the equilibrium time, the empty places on the adsorbent surface are occupied and the absorption efficiency remains constant (Llewellyn *et al.*, 1994; Hawash *et al.*, 2018; Senila & Cadar, 2024).

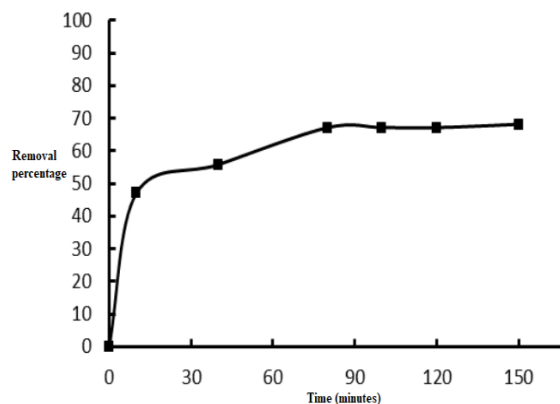


Figure 5. Effect of contact time on nitrate removal percentage with clinoptilolite adsorbent loaded with copper oxide (in initial concentration of 20 mg/L, adsorbent amount of 2 g/L, and initial pH of solution 7).

Investigating the Effect of the Percentage of Metal Oxides on the Amount of Nitrate Removal

To investigate the effect of the percentage of loaded metal oxides on the percentage of nitrate removal, 1, 3, 5, and 7% of copper oxide and 2, 4, and 6% of iron oxide were loaded on clinoptilolite zeolite, the result of which is shown in **Figure 6**. The graphs in **Figure 6** show that with the increase of copper oxide from 1 to 5%, the nitrate removal efficiency increases, but with a further increase of copper oxide (from 7% onwards), the removal efficiency decreases. In other words, increasing the loading of overlapping copper oxide on the vacant sites during the adsorption process leads to a decrease in the removal efficiency. Also, these graphs show that with the increase of iron oxide from 2 to 4 and 6%, the

percentage of nitrate absorption also decreases. Therefore, iron oxides do not show much tendency to absorb nitrates (Leyva-Ramos *et al.*, 2008; Castro-Castro *et al.*, 2020; Nasanjargal *et al.*, 2021).

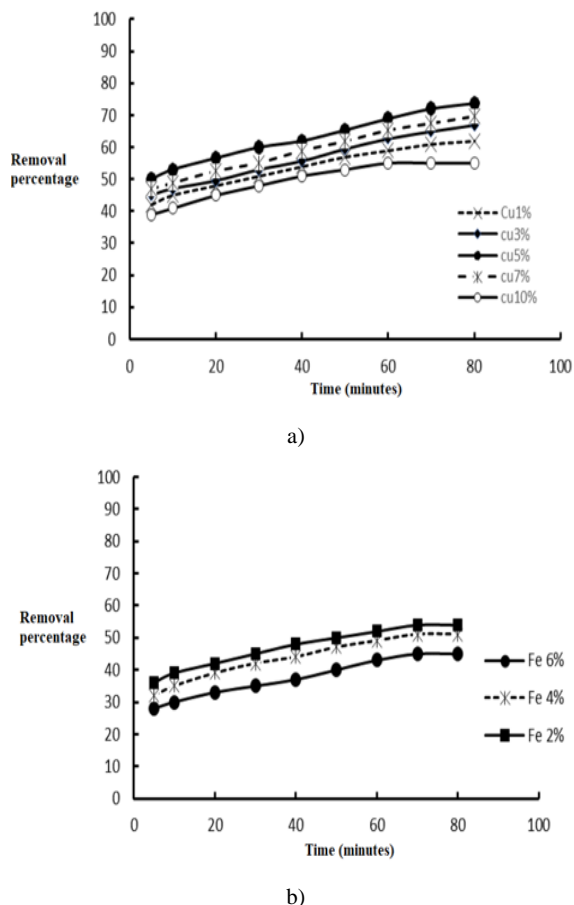


Figure 6. Effect of percentage of copper oxide and iron oxide loaded on nitrate removal efficiency.

The amount of nitrate desorption from loaded zeolites was also investigated. For this purpose, calcium chloride was used as the most abundant soluble ion in water and soil to evaluate the possible power of chlorine ions in replacement and exchange with nitrate absorbed on the surfaces. The amount of nitrate desorption for clinoptilolite zeolite loaded with copper oxide at the initial concentration of 40 mg/L nitrate was 0.98 mg, which was very low compared to nitrate absorption, while for clinoptilolite zeolite loaded with iron oxide in The initial concentration of 40 mg/l nitrate was equal to 1.99 mg/g. These results show that clinoptilolite zeolite loaded with copper oxide has a high ability to retain nitrate under natural conditions.

Investigating the Effect of pH on Nitrate Removal

To investigate the effect of pH, nitrate solutions with a concentration of 20 mg/liter were prepared with pHs of 1, 3, 4, 5, 7, 9, and 12. Also, 2 grams of adsorbent powder was added to 100 ml of sample and the contact time was 80 minutes. The effect of pH on nitrate removal efficiency with loaded zeolites is shown in

Figure 7. As can be seen in this figure, the highest nitrate removal in 80 minutes with clinoptilolite containing 2% Fe₂O₃ in the pH range from 4 to 9 is equal to 54%, and with clinoptilolite zeolite containing 3% CuO in the pH range from 4 to 9, 67% was obtained. With increasing pH from 2 to 9, nitrate removal efficiency increases, but with further increase in pH, nitrate removal efficiency decreases again. The reason for this increase and decrease in efficiency is determined by the pH of the zeta potential (Khan *et al.*, 2011; Yang *et al.*, 2017; Sato *et al.*, 2022). The pH of the zeta potential of clinoptilolite zeolite is equal to 8. Based on the study of Khan *et al.* at a pH higher than 8, the surface charge of nitrate is negative, therefore, at high pH, the number of negative charges on the surface of the adsorbent increases greatly, and due to the anionic nature of nitrate, the electrostatic force of attraction between the pollutant and the adsorbent decreases. It is found that, as a result, the amount of removal efficiency decreases gradually. Also, when the surface charge of the adsorbent becomes negative, there is competition between nitrate and hydroxide. As a result of the presence of more hydroxide, it prevents the absorption of nitrate on the adsorbent surface. But at low pH, the amount of hydroxide ions, which have a negative charge, decreases. Also, the surface charge of the adsorbent becomes positive and the conditions are prepared for more nitrate absorption (Jodaei *et al.*, 2011; Dharmapriya *et al.*, 2022). In very acidic environments, the competition of chloride and nitrate ions for absorption on the adsorbent increases, and according to the size of the ions, chlorides are absorbed more than nitrates on the surface of the adsorbent. In this research, at pHs of 4 to 9%, nitrate removal was approximately constant, and because the pH of water sources is in this range, there is no need to modify the pH of the incoming water on an industrial scale, because the pH in this range affects the amount of absorption. It did not have a significant effect.

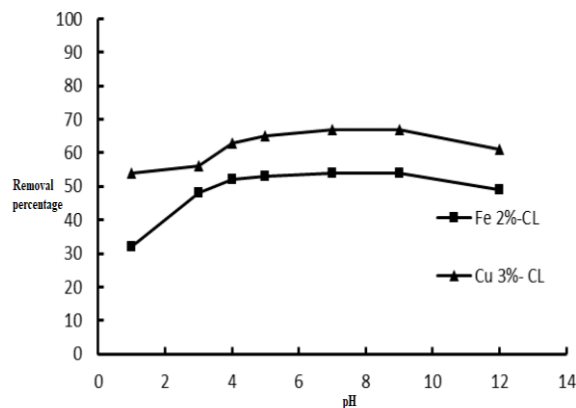


Figure 7. Nitrate removal efficiency at different pHs.

Effect of Amount of Adsorbent

To investigate the effect of the amount of clinoptilolite adsorbent containing 5% copper on the removal percentage of nitrate from the adsorbent in the range of 2 to 15 grams, for each liter in concentrations of 10 to 60 mg/liter of nitrate at a pH of 7 and a constant speed of 150 rpm stirring in time Calls from 0 to 80 minutes were used. The result is given in **Figure 8.**

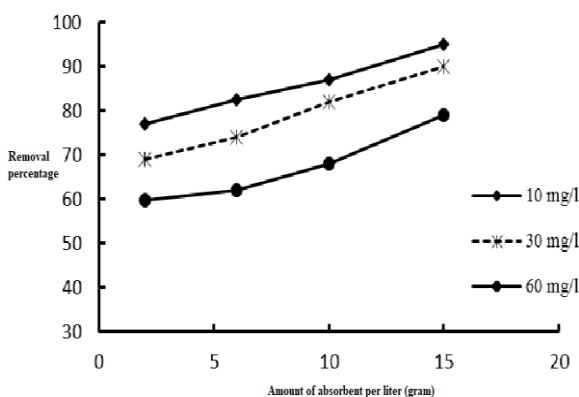


Figure 8. Nitrate removal efficiency at different concentrations of nitrate in the presence of different amounts of Zeolite Clinoptilolite loaded with copper oxide.

As can be seen in **Figure 8**, by increasing the amount of adsorbent from 2 to 15 grams per liter, the equilibrium concentration of nitrate in the environment decreases and for one sample, the removal efficiency reaches from 76 to 95%. By increasing the amount of adsorbent, the number of adsorption sites available for anion removal increases in a short time, which causes more contact of anionic nitrate with the cationic surface of the modified zeolite and thus leads to an increase in removal efficiency.

Conclusion

In this study, the existing zeolite alone could not reduce the nitrate in the water abundantly, so copper oxide and iron oxide were separately deposited on the zeolite by the co-precipitation method. Investigations showed that the adsorption capacity of clinoptilolite zeolite increased with the addition of copper oxide. For this reason, the percentage of loaded copper oxide was also checked. Among other influencing factors, solution pH, pollutant concentration, contact time, and adsorbent amount were also investigated. The results showed that in common pH, these prepared zeolites can remove nitrate in water.

Acknowledgments: None

Conflict of interest: None

Financial support: None

Ethics statement: None

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