Zeolite as a natural adsorbent for nitrosonous compounds being removed from water

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Abstract. Water is vital to the survival of humans and all other life forms, yet many sources of freshwater are being contaminated due to pollution, significantly limiting freshwater availability, and threatening human existence. Nitrates and ammonium are common water contaminants whose concentrations in water have increased significantly due to the excessive use of fertilisers. High concentrations of such contaminants in water can lead to multiple health issues, and thus controlling the concentration levels of these pollutants in water grows into the main task for environmental scientists. A natural zeolite filter was employed in this study to minimise traces of contaminants in water. Samples of synthetic polluted water were prepared that contained 50 mg/L of each contaminant for the laboratory tests. Testing natural zeolite doses ranging from 1 to 5 g/L at various pH levels (between 3 and 10) showed that a zeolite filter significantly improved the water quality from the initial concentrations of each pollutant by between 10 and 50 mg/l. In particular, more than 93% of both contaminants (nitrate and ammonium) were removed by using a 5 g/L dose of zeolite in a neutral pH level range for 120 minutes.

Keywords: nitrate, ammonium, water, zeolite filter.

1. Introduction
Massive amounts of water are available on earth, covering about 70% of its surface. However, freshwater represents only about 2.5% of this; all of the remaining water is salty [1, 2]. Further, less than 1% of the total quantity of fresh water theoretically available can be used for human consumption, as the majority of freshwater is captured in ice cover or groundwater [3-5]. Industrial sector expansion has also led to a significant increase in global pollution, creating huge quantities of polluted wastewater and significantly minimising the fresh water available for human use [6-8]. Recent studies have highlighted that fresh water is being polluted in an increasing rate with a range of pollutants, including biological pollutants [9, 10], heavy metals [11, 12], phosphates [13], nitrates [14, 15], fluoride [16, 17], turbidity [18, 19], phenols [20], and dyes [6, 21]. Nitrogenous ion pollutants such as nitrates and ammonium are among the main water pollutants creating serious health and environmental issues [22-24], and researchers are thus currently examining several different treatment
techniques, including biological [25, 26], chemical [27, 28], physical [29, 30], and combined techniques [14], to remove these contaminants from water or wastewater. Biologically, contaminants are converted into gaseous form using microorganisms, which removes them from water, and such biological approaches have been used by several researchers for water and wastewater treatment. For instance, Bidhendi, Nasrabadi, Vaghefi and Hoveidi [31] utilised anaerobic microorganisms to remove nitrates from water; they found that 120 minutes of treatment of the polluted water eliminated more than 75% of nitrates and about 80% of chemical oxygen demand (COD). He, Ye, Sun, Cai, Ni, Li, and Xie [32] employed anaerobic microorganisms to reduce nitrogenous contamination in water, with the result that more than 93% of nitrogenous contamination was removed. However, these biological methods have several drawbacks, such as required treatment duration, the required area for construction, sensitivity to ambient temperature, and the pH of water, which significantly limit their application [33, 34].

Chemical and physical de-nitrification processes are commonly used for nitrates removal from water. In these processes, chemicals such as iron or aluminium salts are used to convert nitrogenous ions into gases [29]. Although the chemical methods remove large quantities of nitrates, experiments have shown that these methods consume large amounts of metallic salts and produce large volumes of sludge [15], which in turn requires complex solid waste management plans [35-37]. Contaminants are removed in physical methods through trapping with filter media [1, 38]. The relevant literature has pointed out that many industrial constituents can be used to remove nitrogenous contamination from water, including clay adsorbents and activated carbon [39, 40].

Other scholars have combined both chemical and physical methods to remove pollutants from water. Dosta, Rovira, Galf, Macé, and Mata-Alvarez [41] employed coagulation-flocculation to improve rates of ammonium and other pollutant removal from wastewater. Dosta, Rovira, Galf, Macé and Mata-Alvarez [41] further highlighted that the application of coagulation-flocculation removed 1.17 kg/m$^3$.day of COD in their work. However, using this combination is expensive and requires appropriate controlled environments.

Researchers have noted that filtration techniques are an attractive option for removing nitrogenous ions due to cost-effectiveness and ease of operation [39, 42]. Rožič, Cerjan-Stefanović, Kurajica, Vančina, and Hodžić [43], for example, employed a mixture of zeolite and clay to remove ammonium from water, with 61.10 % of ammonium being removed after 120 minutes of filtration at a pH level of 5.5. Wang, Kmiya and Okuhara [44] also highlighted that ammonia could be efficiently removed from water using zeolite filters.

Filtration methods thus provide an attractive option for removing pollutants such as nitrogenous ions from water and wastewater. These methods can efficiently remove nitrogenous ions from water and wastewater in addition to offering other attractive advantages such as low cost, ease of operation, and eco-friendliness. The current research thus investigated the use of a natural zeolite filter (clinoptilolite) in the removal of nitrogenous ion pollutants from water. Clinoptilolite was used in this research as it is a readily available and inexpensive natural material [22, 23]; in addition, the isoelectric point for the natural zeolite filter is about 3 [45], maximising the adsorption capacity of the filter media at low pH levels (about 3).

2. Methodology

2.1. Materials

The chemicals and zeolite used in this study were provided by the Department of Civil Engineering, Liverpool John Moores University. All materials were implemented in the experiments without adjustment or decontamination. The filter used in this research was clinoptilolite, selected due to its wide application in water and wastewater treatment [13].
2.2. Solution
A polluted solution with 200 mg/L of nitrates and 50 mg/L ammonium was produced for the experiments. A suitable amount of KNO₃ was dissolved in four litres of deionised water to create a concentration of 200 mg/L of nitrates. The 50 mg/L concentration of ammonium in the solution was achieved by adding anhydrous ammonium-chloride salt, NH₄Cl. Subsequently, the prepared polluted water was cooled to produce the required samples with a range of pollution concentrations (10, 30, and 50 mg/L for both pollutants). HCl and NaOH were used to control the pH value of the solution.

2.3. Batch filtration process
Batch experiments were employed to examine the zeolite filter’s effects on the removal of both pollutants (nitrates and ammonium) from the polluted water. Initially, 500 ml of contaminated water was placed in a 1,000 ml plastic vessel with the filter media (zeolite) for one hour and 40 minutes. Samples of 10 ml were collected every 20 minutes to test the removal efficiency of the filter. The concentrations of both pollutants were measured using a Hach-Lange spectrophotometer (DR-2700), standard nitrate cuvettes (LCK 339 and LCK 340), and standard ammonium cuvettes (LCK 304 and LCK 303).

The impact of pH level on the removal efficacy of the filter media was studied by altering the pH level of the polluted water from acidic (3) to neutral (6.5), and then to basic (10). The impact of both pollutants’ initial concentrations on the elimination competence of the filter was also examined by changing the concentrations from 10 to 50 mg/L while the influence of filter dose was analysed by adding several doses of zeolite including 1, 3, and 5 g/l.

Finally, the removal efficiency of the zeolite filter for nitrogenous pollutants (nitrates and ammonium) was determined using the following equation [29]:

\[
\text{Filter efficiency} (\%) = \frac{A_1 - A_2}{A_1} \times 100
\]

where \(A_1\) and \(A_2\) are the primary and final contaminant concentrations, respectively.

3. Results and discussion

3.1. Influence of pH level
The influence of pH level on the removal efficiency of nitrogenous pollutants was investigated by treating 500 ml water with 3 g/l of zeolite filter for 30 minutes at a range of pH levels, with values from 3 to 10.

Figure 1 provides a graphic representation on the impact of pH on the removal efficacy of nitrogenous pollutants. The removal efficiency for both pollutants increased with the decrease in wastewater acidity. The best removal efficiency was reached at a neutral pH level (from 5 to 7), as when the wastewater became alkaline (pH higher than 7), the removal efficiency decreased with the increase in pH level. This variation in elimination efficiency occurs due to the impact of pH on the charge of the filter. Researchers have highlighted that the surface of zeolite became negative at high pH values, which in turn prevents the adsorption of the negatively charged nitrates and ammonium [13]. However, as the isoelectric point for the natural zeolite filter is about 3 [45], the surface of the filter media (zeolite) encompasses more protons at very low pH levels, which in turn minimizes the removal efficiency of the filter media [46]. At moderate pH levels (between 5 and 7), the filter media is positively charged, however, which attracts the negatively charged nitrogenous pollutants [46]. Accordingly, a pH level of 6.5 was selected for experiments to identify the impact of initial pollutant concentration, zeolite dose, and contact time.
Figure 1. Impact of pH on the removal of nitrogenous pollutants (nitrates and ammonium).

3.2. The impact of initial pollutant concentrations
The influence of initial pollutant concentrations for nitrates and ammonium on the removal performance of the zeolite was analysed by treating 500 ml water at a pH level of 6.5 with 3 g/L of zeolite for 30 minutes with pollutant concentrations of 10, 30, and 50 mg/l. As illustrated in figure 2, the removal of both pollutants declined with the increase in their initial concentrations, most likely due to the ions of the pollutants contesting with each other for available adsorption sites [46]. With higher initial concentration and a constant zeolite dose, the availability of sites on the filter media is significantly lower than the negative ions available to be absorbed, leading to untreated pollutants remaining.

Figure 2. The impact of initial concentration on the removal of pollutants.

3.3. The influence of the zeolite dose
The dosage of media adsorbent strongly influences the removal of both nitrates and ammonium, as this is the main factor affecting the superficial area available for adsorption. Accordingly, the impacts of zeolite filter on the removal of both pollutants from the water were considered by treating the same sample size (500 ml) of water for the same duration (30 minutes) at the optimum pH level of 6.5. The pollutants’ initial concentration was 50 mg/L, while the doses of zeolite were 1, 3 and 5 g/L, allowing examination of the impact of the zeolite quantity on pollutant treatment. Figure 3 highlights that the increase in the zeolite dose significantly increased the removal of both nitrogenous pollutants. This confirms that the higher the zeolite dose, the more space is available to adsorb pollutants which significantly enhances the removal of both nitrates and ammonium.
3.4. The influence of contact time

Time plays a vital role in any water treatment activity, particularly filtration. Extended time in treatment allows longer contact between the nitrates and the ammonium ions and the adsorbent. Thus, the influence of treatment duration on the removal of both pollutants was analysed by treating samples of size of 500 ml with initial pollutant concentrations of 50 mg/l and a pH level of 6.5 for 120 minutes with a zeolite dose of 5 g/l. The outcomes, shown in Figure 4, highlight that the removal efficiency of the nitrogenous contamination improved to reach over 93% for both contaminants (nitrates and ammonium) by the end of 120 minutes.

4. Conclusions

This study investigated the use of a natural zeolite, clinoptilolite, for the treatment of nitrogenous pollutants (the nitrates and the ammonium) in water and wastewater. Based on the experimental study, the natural zeolite is a suitable option for the removal of both nitrates and the ammonium ions from water or wastewater. Higher zeolite doses and longer contact times provide better removal of nitrogenous contaminants from water and wastewater, although the removal effectiveness of the zeolite filter is affected by the pH value of the treated wastewater. A neutral pH is the most favourable for using clinoptilolite for the treatment of nitrogenous pollutants.

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