

## NUTRIENTS REMOVAL FROM WASTEWATER USING MODIFIED ZEOLITE



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**Summary:** Natural and modified (with  $Fe^{2+}$ ,  $Na^+$  and  $Mg^{2+}$ ) zeolite-clinoptilolite, has been studied in respect of its ability to immobilize ammonium and phosphate ions from wastewater. Data are presented on the process kinetics, and the impact of the initial pollutants' concentrations and pH of the wastewater on the uptake effectiveness.

**Key words:** natural zeolite clinoptilolite, modified zeolite, nutrients, wastewater

Природен и модифициран (с  $Fe^{2+}$ ,  $Na^+$  и  $Mg^{2+}$ ) зеолит-клиноптилолит е изследван по отношение на способността му да имобилизира амониеви и фосфатни йони от отпадъчни води. Представени са данни за кинетиката на процеса, въздействието на първоначалните концентрации на замърсителите и началното рН на отпадъчните води върху ефективността на процеса.

**Ключови думи:** естествен зеолит-клиноптилолит, модифициран зеолит, отпадъчна вода

**Introduction.** Nitrogen- and phosphor-bearing pollutants usually enter the surface water bodies through diffuse (e. g. agricultural runoff) and point (e.g. discharge of industrial wastewater from different industries, landfill leachates) sources. An idea for their quantities can be obtained by looking at the maximum allowable concentrations (MAC) in wastewater released by different industries – Table 1 [1].

Municipal wastewater, when discharged untreated to surface water bodies, “contributes” significantly to their pollution. Table 2 summarizes data on the content of nutrients in municipal wastewater [2]. As it can be seen from the Table, the major polluting species are ammonium nitrogen and inorganic phosphates.

Both nitrogen and phosphorus are essential nutrients for growth. When discharged to the aquatic environment, these nutrients can lead to the growth of undesirable algal. Algal growth adds to the sediment load on a river, lake, or estuary. The excess algae production leads to serious oxygen depletion in water body. Nitrogen in the form of ammonia is oxidized by the dissolved oxygen and causes a depletion of oxygen that leads to the fish killing.

Polluted surface water may cause ground and drinking water pollution, when hydraulic connection is available.

Residual amounts of N- and P-bearing compounds also impede water reuse in the technological cycle.

**Table 1.**  
The MAC of N and P in wastewater released by different industries

Industry	N total <sup>1</sup> , mg/L	P total, mg/L
Petrochemicals industries	10	-
Manufacture of electrical and electronic products	10	5
Production of nitrogen fertilizers	10 ( $NH_4^+$ )	-
Production of phosphate fertilizers	-	5
Production, processing and canning of meat and meat products, fruit and vegetable; Production and refining of vegetable oils	10	5
Production of dairy; Production of sugar	10	2
Production of beer and malt	10	5
Treatment of leather	10	2

Above-mentioned negative impacts require removal of ammonium and phosphates.

<sup>1</sup> – If not denoted by NH<sub>4</sub><sup>+</sup>, i.e. ammonia N, total nitrogen means the sum of total Kjeldahl nitrogen (organic and ammonia nitrogen), nitrate nitrogen and nitrite nitrogen; “-“ means – not MAC defined for the corresponding industry.

Treatment technologies presently available include:

**Table 2.**

**Typical contents of nutrients in raw municipal wastewater with minor contributions of industrial wastewater, in mg/L**

Parameter	High value	Medium value	Low value
N total:	100	60	30
Ammonium N	75	45	20
Nitrate+Nitrite N	0.5	0.2	0.1
Organic N	25	15	10
P total:	25	15	6
Ortho-P	15	10	4
Organic P	10	5	2

- Physical: application of membrane technologies, filtration for particulate matter bearing phosphorus and nitrogen. There are several drawbacks of utilization of membrane technologies: high initial investments, expensive membrane replacement, higher energy consumption in comparison to other methods, relatively big amounts of sludge produced by the concentrate treatment.

- Biological:

Biological Nitrogen Removal (BNR) is a combination of nitrification and denitrification, occurring as sequential processes. Biological Phosphorus Removal (BPR) is process, where conditions are created that encourage certain types of bacteria to uptake excessive amounts of phosphorus. The bacteria are then removed from the treatment process before they have time to release back this phosphorus.

A combination of micro-algae (*Chlorella vulgaris* or *C. sorokiniana*) and a micro-algae growth-promoting bacterium (*Azospirillum brasi-lense strain Cd*), co-immobilized in small alginate beads, was developed to remove P and N from municipal wastewater [3].

- Chemical and physical-chemical: adsorption, precipitation, ion exchange (using a combination of a cation and an anion exchanger).

Ammonium (NH<sub>4</sub><sup>+</sup>) and phosphate (PO<sub>4</sub><sup>3-</sup>) ions were simultaneously removed from wastewaters through precipitation with

magnesium sulfate [4]. The resulting precipitate (magnesium ammonium phosphate) is in fact an useful product. However, the method is feasible at relatively high concentrations of pollutants (PO<sub>4</sub><sup>3-</sup> of 2 g/L and NH<sub>4</sub><sup>+</sup> of 0.4 g/L).

Activated carbon is widely applied sorbent for removing pollutants from wastewater. Different activated carbons showed different ability to immobilize NH<sub>4</sub><sup>+</sup> and PO<sub>4</sub><sup>3-</sup>. For example, Fisher activated carbon was better than Aldrich activated carbon in phosphate removal (and removed appr. 18 % of PO<sub>4</sub><sup>3-</sup> from grey water), while the Aldrich was better in ammonium removal (and removed appr. 18 % of NH<sub>4</sub><sup>+</sup> from grey water). Biochar showed around 50% removal for both pollutants [5]. It has been found that biochar, derived from phyto-remediation plants, with the high Mg content showed relatively high sorption capacity for phosphate and ammonium [6].

Recently, the research has been pointed at using abundant naturally occurring low-cost materials in the wastewater treatment, such as natural and modified zeolites and bentonites, as well as zeolites synthesized from waste materials.

The feasibility of using natural and Fe-modified bentonites as adsorbents for phosphate removal from natural waters was studied [7]. The results showed that the adsorption capacities of Fe-modified bentonites were close to the capacity of the Phoslock (a commercial bentonite product coated with lanthanum) and much higher compared to unmodified bentonite. More than 75% were removed (at initial PO<sub>4</sub><sup>3-</sup> concentration of 50 mg/L) within one hour.

The removal of ammonium by natural and modified zeolitic materials has been widely investigated recently since use of zeolites would contribute to developing an environmentally friendly and sustainable technology for pollutants removal.

Clinoptilolite and mordenite were found as the most effective natural zeolites for NH<sub>4</sub><sup>+</sup>, due to their high selectivity for ammonium ion in the presence of competing cations (such as K<sup>+</sup>, Ca<sup>2+</sup> and Mg<sup>2+</sup>), across a wide range of NH<sub>4</sub><sup>+</sup> concentrations [8]. It was found that Australian natural zeolite - clinoptilolite, may be successfully employed in a fixed-bed ion-exchange process to achieve high ammonia removal efficiencies from aqueous solutions at

rates commensurable with sand filtration [9]. A combined system with zeolite and lime was proposed for removal of nutrients from wastewater. Removals of 98 %  $\text{NH}_4^+$  and 100 % total phosphorus were achieved [10]. Zeolite synthesized from fly ash and modified by acid treatment (with 0.01 mol/L  $\text{H}_2\text{SO}_4$ ) showed promising removal efficiency for both  $\text{NH}_4^+$  and  $\text{PO}_4^{3-}$  at low concentrations [11].

Bulgaria, in the Eastern Rhodopes area, is rich in zeolite-clinoptilolite. All described above, suggests the need to study the ability of Bulgarian zeolite to remove nitrogen (as ammonium ions) and phosphorus (as phosphates) from wastewater.

**Methods and materials.** Bulgarian natural zeolite (with clinoptilolite as predominating mineral) from Kardhzali region was used. It had the following chemical compositions, in mass %:  $\text{SiO}_2 = 68.70$ ,  $\text{Fe}_2\text{O}_3 = 2.28$ ,  $\text{TiO} = 0.15$ ,  $\text{Al}_2\text{O}_3 = 11.83$ ,  $\text{CaO} = 2.66$ ,  $\text{MgO} = 0.76$ ,  $\text{MnO} = 0.04$ ,  $\text{Na}_2\text{O} = 1.60$ ,  $\text{K}_2\text{O} = 4.01$ ,  $\text{P}_2\text{O}_3 = 0.14$ ,  $\text{SO}_3 = 0.225$ , ignition loss = 7.62, totalling – 100.02. Its cation exchange capacity was 134.3 meq/100 g. Zeolite was modified by placing it in contact for 7 days (at room temperature and solution to mass of zeolite ratio equal to 1 L : 100 g) with corresponding chemicals (2 M solutions of  $\text{NaCl}$ ,  $\text{FeCl}_2$  and  $\text{MgCl}_2$ ). Then zeolite was washed with distilled water until negative reaction for chlorides and air-dried at 90 °C.

Experiments were conducted batchwise: 1.0 g of zeolite, contacting with solutions, was shaken with an ESZTERGOM (Hungary) shaker (20 strokes/min, throw of 6 cm). Experiments were conducted at room temperature. Materials' particles sizes were between 0.09 and 0.325 mm. Experiments were carried out with model wastewater, prepared by dissolving in distilled water the corresponding amounts of  $(\text{NH}_4)_2\text{HPO}_4$  and  $\text{NH}_4\text{NO}_3$ . Water pH values were measured with WTW Multi 3400i-meter. Concentrations of ammonium N and ortho-P were determined photometrically correspondingly with Nessler reagent [12] and molybdenum blue method [13].

Solution to zeolite mass ratio of 100 : 1 was found to be the optimum one by means of preliminary experiments made at solution to material ratios of 20:1, 50:1, 100:1, 200:1. This ratio was further used in experiments. The

influence of a specific process parameter was determined by calculating the pollutants' uptake by zeolite and changing that parameter at keeping other parameters constant.

Desorption experiments were made in order to check how strongly  $\text{NH}_4^+$  ions were immobilized by zeolite. One gram of dry loaded modified zeolite that showed the highest uptake was placed in contact for 24 hrs with 100 mL of 2 % solution of  $\text{CH}_3\text{COOH}$ .

Each experimental result presented was obtained by averaging the data from two parallel experiments.

Removal efficiency was calculated using the equation:

$$\text{Removal, \%} = [(C_o - C_t) / C_o] \cdot 100 \quad (1),$$

where  $C_o$  and  $C_t$  are pollutant liquid-phase concentration (mg/L) - in the beginning and at time t.

The amount of immobilized pollutant (mg/g) at time t was calculated using equation:

$$q_t = (C_o - C_t) \cdot V / W \quad (2),$$

where  $C_o$  and  $C_t$  have the above-described meaning, V is the volume of the solution (L) and W is the mass of dry adsorbent used (g).

The amount of adsorption at equilibrium,  $q_e$  (mg/g), was calculated by equation:

$$q_e = (C_o - C_e) \cdot V / W \quad (3),$$

where  $C_e$  is the equilibrium pollutant liquid-phase concentration (mg/L) and all other designations are as described above.

**Results and discussion.** The kinetics of ammonium and phosphate removal by natural and modified zeolite is presented in Figures 1 - 4. Data are for initial concentrations of 64 mg/L  $\text{NH}_4^+$  and 75 mg/L  $\text{PO}_4^{3-}$ , corresponding to five times the corresponding MAC for nitrogen and phosphorus (see Table 1), and denoted as 5 MAC; as well as for 38.5 mg/L  $\text{NH}_4^+$  and 45 mg/L  $\text{PO}_4^{3-}$  - denoted as 3 MAC and room temperature.

Two-stage process can be clearly distinguished in all cases – with a fast first stage and second stage with significantly lower speed.

The data on kinetics show that over 50% of the pollutants' removal occurred in 30 min. That is why a contact time of 30 min was chosen for the experiments aimed at revealing possible differences, due to the influence of initial pH value of polluted water.

The effect of initial pollutant concentration on the removal also can be seen in Figures 1 - 4.

In all cases higher removal percent is observed for lower pollutant initial concentrations.

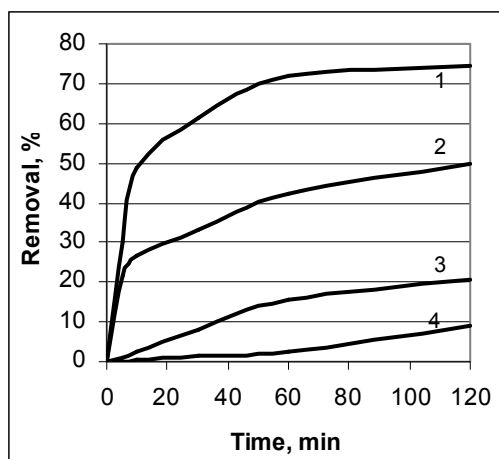


Figure 1. Kinetics of  $\text{NH}_4^+$  (1 - 3 MAC; 2 - 5 MAC) and  $\text{PO}_4^{3-}$  (3 - 3 MAC; 4 - 5 MAC) uptake by natural zeolite

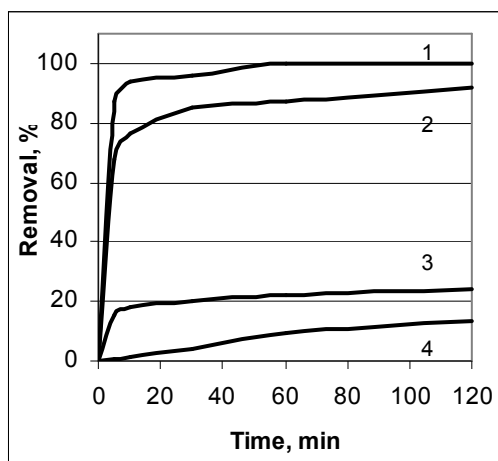


Figure 2. Kinetics of  $\text{NH}_4^+$  (1 - 3 MAC; 2 - 5 MAC) and  $\text{PO}_4^{3-}$  (3 - 3 MAC; 4 - 5 MAC) uptake by  $\text{Na}^+$  modified zeolite

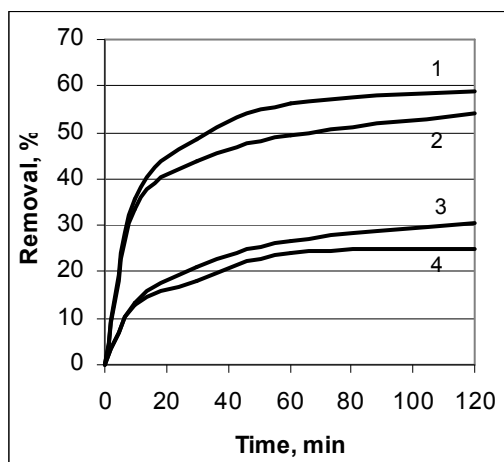


Figure 3. Kinetics of  $\text{NH}_4^+$  (1 - 3 MAC; 2 - 5 MAC) and  $\text{PO}_4^{3-}$  (3 - 3 MAC; 4 - 5 MAC) uptake by  $\text{Fe}^{2+}$  modified zeolite

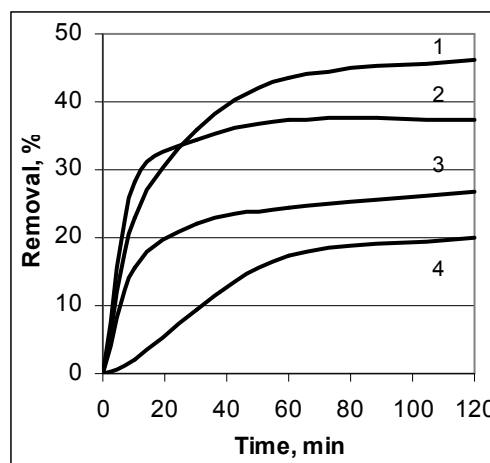


Figure 4. Kinetics of  $\text{NH}_4^+$  (1 - 3 MAC; 2 - 5 MAC) and  $\text{PO}_4^{3-}$  (3 - 3 MAC; 4 - 5 MAC) uptake by  $\text{Mg}^{2+}$  modified zeolite

However, in absolute values of removed pollutant (in mg per g of zeolite) an increase in the ammonium initial concentration increases the removal. Similar behavior was observed for Turkish zeolite, where increasing the initial ammonium nitrogen concentration from 5.0 to 12.0 mg/L, increased the exchange capacity of zeolite from 0.70 to 1.08 mg  $\text{NH}_4^+\text{-N}$  / g zeolite [14]. Since it is widely accepted that the uptake process is controlled by heterogeneous diffusion, the higher difference in concentration of  $\text{NH}_4^+$  in the solution and at zeolite surface is most probably the reason for the higher  $\text{NH}_4^+$  availability at the boundary layer and hence - for the higher uptake by ion exchange surface sorption at higher initial concentration. This idea is confirmed also by results found by processing the experimental data according to the Weber's intraparticle diffusion equation:

$$q_t = k_{id}t^{1/2} + C \quad (4)$$

where  $C$  is the intercept and  $k_{id}$  is the intraparticle diffusion rate constant ( $\text{mg/g h}^{1/2}$ ), which can be evaluated from the slope of the linear plot of  $q_t$  versus  $t^{1/2}$  [15]. If the dependence of  $q_t$  on  $t^{1/2}$  is linear and passes through the origin of the coordinate system, then intraparticle diffusion is the sole rate-limiting step. When the linear plots do not pass through the origin this shows that the intraparticle diffusion is not the only rate controlling step [16]. Then, the larger is the intercept, the greater is the contribution of the surface sorption (in the boundary layer) in the rate. In our case, the larger intercepts were found for all modified zeolites for the case of 5

MAC and only for the natural zeolite - for the case of 3 MAC. Additional experiments are needed to explain findings on the impact of the initial PO<sub>4</sub><sup>3-</sup> concentration on the pollutant removal.

The effect of zeolite modification on the pollutants removal also can be seen when comparing Figures 1 - 4.

Zeolite modification with Na<sup>+</sup> ions significantly improved the ability of the natural zeolite to remove NH<sub>4</sub><sup>+</sup>. Findings for the removal efficiency and process rate with respect to ammonium are in line with findings of other authors [17]. A small increase in NH<sub>4</sub><sup>+</sup> uptake was observed for Fe<sup>2+</sup> modified zeolite - in the case of initial pollutant concentration of 5 MAC. Increased PO<sub>4</sub><sup>3-</sup> uptake, compared to natural zeolite, was observed when iron- and magnesium-modified zeolite was used - bigger in the case of Fe<sup>2+</sup> modified zeolite. This finding could be related to formation of small amounts of insoluble in water iron(II) phosphate. Significant increase in NH<sub>4</sub><sup>+</sup> and PO<sub>4</sub><sup>3-</sup> uptake by different zeolites, modified with iron, was observed also by other authors [18].

Practically, in respect of NH<sub>4</sub><sup>+</sup> removal, the best results were obtained for sodium modified zeolite. Only in one hour and in one step, by using Na-modified zeolite, the ammonium concentration was decreased from 5 times MAC to the level required by the standard. The result could be explained by the availability of higher amount of Na<sup>+</sup> ions exchangeable for NH<sub>4</sub><sup>+</sup> and by the fact that clinoptilolite has the higher affinity to NH<sub>4</sub><sup>+</sup>, compared to Na<sup>+</sup> [19].

Desorption experiments showed that NH<sub>4</sub><sup>+</sup> ions were strongly immobilized by Na<sup>+</sup>-modified zeolite - only 1-2 % of the bound NH<sub>4</sub><sup>+</sup> were released by 24 hours contact of loaded zeolite with the acidic solution.

The uptake of pollutants by zeolite was studied with respect to the kinetic model which is obeyed.

A linear form of pseudo-first-order kinetic model can be presented with the equation [16]:

$$\log(q_e - q_t) = \frac{\log q_e - k_1 t}{2.303} \quad (5)$$

A linear plot of log(q<sub>e</sub> - q<sub>t</sub>) against time, with good correlation coefficient, indicates that the pollutant immobilization process can be described as a pseudo-first-order process.

The pseudo-second-order kinetics may be expressed in a linear form with the equation [16]:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e t} \quad (6)$$

A linear plot of t/q<sub>t</sub> versus t, with good correlation coefficient, indicates that the pollutant immobilization process can be described as a pseudo-second-order process.

Since the ions' uptake by zeolites is often considered to be a result of ion exchange adsorption, the equation describing adsorption was also checked:

$$\ln(dw/d\tau) = \ln a - \alpha \cdot w \quad (7),$$

where w is the amount of substance adsorbed for time τ, a and α are constants which depend on the adsorbent / adsorbate system and on the temperature. A linear plot of ln(dw / dτ) versus w, with good correlation coefficient, indicates that the pollutant immobilization process can be described as typical adsorption process [20].

It has been found that the uptake of NH<sub>4</sub><sup>+</sup> follows the pseudo-second-order kinetic model, with the coefficient of determination r<sup>2</sup> correspondingly: 0.999 and 0.989 - for natural zeolite for 3MAC and 5MAC; and 0.999 - for all modified zeolites - both for 3MAC and 5MAC.

The influence of initial pH value of polluted water on removal of NH<sub>4</sub><sup>+</sup> and PO<sub>4</sub><sup>3-</sup> was studied at pH = 5.5; 7.5 and 9.0 and 3MAC. Results are presented in Table 3.

**Table 3.**

**Impact of initial pH value of polluted water on removal of NH<sub>4</sub><sup>+</sup> and PO<sub>4</sub><sup>3-</sup>**

Material Initial pH	Natural	Na <sup>+</sup> -modified	Fe <sup>2+</sup> -modified	Mg <sup>2+</sup> -modified
NH <sub>4</sub> <sup>+</sup> removal				
5.5	48.7	96	43.6	34.5
7.5	61.5	96.2	48.7	35.9
9.0	48.9	96.4	53.4	36
PO <sub>4</sub> <sup>3-</sup> removal				
5.5	3	16.6	23.6	25.1
7.5	7.8	20	21	22.2
9.0	16.6	33	50	40

As it can be seen from Table 3, the initial pH value of water to be treated practically do not impact significantly the removal of NH<sub>4</sub><sup>+</sup> for



modified zeolites. An increase in  $\text{PO}_4^{3-}$  removal was observed with increasing the pH, more pronounced for  $\text{Fe}^{2+}$ - and  $\text{Mg}^{2+}$ -modified zeolite. Most probably, this fact may be connected with an enhanced sorption of  $\text{PO}_4^{3-}$  on formed iron and (probably partially) magnesium oxides-hydroxides. Similar effect was observed by other authors [21, 22].

**Conclusions.** Natural Bulgarian zeolite (clinoptilolite) shows relatively good removal efficiency with respect to  $\text{NH}_4^+$  from wastewater. It exhibits low capacity to remove  $\text{PO}_4^{3-}$  from wastewater.

Zeolite modification with  $\text{Na}^+$  significantly improves its uptake efficiency with respect to

$\text{NH}_4^+$ . Only in one hour and in one step, by using Na-modified zeolite, the ammonium concentration was decreased from 5 times MAC to the level required by the standard.

The uptake of  $\text{NH}_4^+$  follows the pseudo-second-order kinetic model.

Zeolite modification with  $\text{Mg}^{2+}$  and especially with  $\text{Fe}^{2+}$  improves its ability to uptake  $\text{PO}_4^{3-}$  from wastewater, at practically keeping the ability exhibited by natural zeolite with respect to  $\text{NH}_4^+$  immobilization.

Use of naturally occurring, inexpensive materials, such as zeolites for treating waste effluents will contribute to the sustainable development of our society.

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