NATURAL ZEOLITE AS A CHEMICAL SOLUTION FOR ANOXIC BASINS MANAGEMENT

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ABSTRACT

Anoxic environments' management attracted researchers' interest for decades. Mechanical ventilation or oxygenation used to restore anoxic hypolimnia in many natural and artificial lakes. These techniques improved sufficiently oxygen concentrations only in small environments, and for short time periods, since they were focused on the problems' results and not on the cause of it. The close relationship between the worldwide eutrophication increase and the rapid expansion of the hypoxic/anoxic water basins is now confirmed. In many cases anoxic ecosystems' restoration was attempted controlling the organic matter and nutrient fluxes into the water basins. However, such management efforts were quite often unsuccessful. Quickly became apparent that the failure of these management practices was due to the aquatic ecosystems' internal load that was refueling anoxia. Bottom water anoxia accelerates PO_4^{3-}, NH_4^+ and S^{2-} recycling and accumulation from organic matter decomposition. This, toxic layer is a permanent menace for the balance of the entire ecosystem, as it can supply PO_4^{3-}, NH_4^+ and S^{2-} to the surface layers altering their qualitative character and threatening the welfare of fishes and other aquatic organisms. To overcome this problem, materials with the ability to remove phosphorus and nitrogen forms from aquatic ecosystems were sought and developed. In these, activated Al_2O_3, ferrihydrite, crushed concrete, ferrous iron, titanium dioxide, calcite, natural and modified zeolites are included.

Natural zeolite is a natural inert material, particularly effective in removing ammonium from aquatic solutions, while due to its negative charge doesn't adsorb phosphate ions. However, in the presence of cations (Ca^{+2}, Na^+, K^+) it turns to an appropriate substrate for the formed phosphate salts. This study aims to demonstrate for the first time the ability of natural zeolite to remove sulfides from aqueous solutions.

The zeolitic mineral mordenite was tested under a range of physicochemical conditions. The uptake of sulfides was evaluated vs. pH in adsorption kinetics and adsorption isotherms. The effects of initial concentration, temperature and salinity on adsorption capability were also investigated. Natural zeolite can function efficiently within a wide range of pH, e.g. 5–9. Adsorption kinetics showed that the removal rate reached up to 90% after a period of 24h. Zeolite's removal capability appeared to be directly depended on the S^{2-} initial concentration. The maximum zeolite removal capacity was calculated equal to $123.1 \ 10^{-3}$ mg/g S^{2-}. Zeolite removal capacity varied by about 15% as the solution's salinity varied from 0 to 35‰. Small changes in zeolite removal capacity cause temperature variation as well. The ability of zeolite to remove from aqueous solutions forms of nitrogen, phosphorus and sulfur makes it a material that could play a key role, in eutrophic/anoxic environments restoration efforts, since PO_4^{3-}, NH_4^+ and S^{2-} constitute the three aspects of the problem called anoxic basins' internal load.

Keywords: anoxia, natural zeolite, sulfides, management, phosphate, ammonia.

1. Introduction

During the last decades, the increase of the nutrient and organic load inflows in the coastal zone increased the number of the anoxic environments. Anoxic environments' management attracted researchers' interest. Mechanical ventilation or oxygenation used to restore anoxic

hypolimnia in many natural and artificial lakes (Singleton and Little, 2006). These techniques improved sufficiently oxygen concentrations only in small environments, and for short time periods, since they were focused on the problems' results and not on the cause of it. Inputs' control constitutes one of the basic practices for the eutrophic/anoxic aquatic ecosystems management. However, such management efforts were quite often unsuccessful (Conley et al., 2009). However, the induced changes at the ecosystem characteristics resulting from the trophic state alteration, and anoxic conditions prevalence, render the ecosystem's restoration difficult if not impossible. Quickly became apparent that the failure of these management practices was due to the aquatic ecosystems' internal load that was refueling anoxia (Wang et al., 2009). Bottom water anoxia accelerates PO_4^{3-}, NH_4^+ and S^{2-} recycling and accumulation from organic matter decomposition. This, toxic layer is a permanent menace for the balance of the entire ecosystem, as it can supply PO_4^{3-}, NH_4^+ and S^{2-} to the surface layers altering their qualitative character and threatening the welfare of fishes and other aquatic organisms (Reissmann et al., 2009). To overcome this problem, materials with the ability to remove phosphorus and nitrogen forms from aquatic ecosystems were sought and developed. In these, activated Al_2O_3, ferrihydrite, crushed concrete, ferrous iron, titanium dioxide, calcite, natural and modified zeolites are included (Zamparas and Zacharias, 2014).

Having as goal the "internal load" management and based on practices that are intensively used in eutrophic environments' restoration, this study is highlighting the role of natural zeolite in the anoxic ecosystems' management. Our objective was to examine the feasibility of using natural zeolite for sulfides removal from natural waters. The zeolitic mineral mordenite was used and the sulfides uptake was evaluated vs. pH using adsorption kinetics and adsorption isotherms. The effects of temperature and salinity on sulfides removal capability were also investigated.

2. Materials and methods

The zeolitic mineral mordenite, $[(Na_2,Ca,K_2)_4 (H_2O)_{28}] [Al_8Si_{40}O_{96}]$, was used, for sulfides removal experiments. Sulfides stock solution of 1000mg/L was prepared by dissolving 0.375g $Na_2S·9H_2O$ crystals in 30ml deionized, deaerated water. Dilutions of the stock solution were used in subsequent experiments. Removal kinetic data of sulfides using natural zeolite at contact times ranging between 30min and 1440min were studied under the optimized conditions: pH 7, sulfides concentration 1mg/L, zeolite dose 1g, and 25±1 °C temperature. The removal isotherms were determined by batch equilibration of 1g of zeolite with 50mL of aqueous sulfides solutions of varied initial concentrations (ranging from 1 to 10 mg/L). The experiments were carried out, at room temperature (25±1 °C) and pH 7 for 24h. To assess the effect of different temperatures, batch experiments were conducted at 5, 15, 25 and 35°C. A temperature controlled water bath was used and the experiment lasted 24h. The effect of salinity was determined by measuring the sulfides uptake of zeolite at salinities 0, 20 and 35‰, at 25±1°C, pH 7 after 24h. For the pH-edge experiments, a buffer system of 10mM MES, HEPES acid was used in all the samples. Prior to starting the experiment, the pH was adjusted from 5 to 9, using 0.1 M HCl and NaOH solutions. The experiment was conducted at 25±1°C and its duration was 24h.

For all solutions preparation deionized, deaerated water, boiled and purged with N_2 was used. All experiments were carried out in an anaerobic chamber in triplicates. Blank samples without zeolite were perpetrated and monitored as a control. After equilibration, the suspension was separated by centrifugation and the concentration in the supernatant was measured by the methylene blue spectrophotometric method (APHA, 2005). The amount adsorbed was calculated from the difference in concentration between the initial and the equilibrium concentrations.

In order to approach and modeling isotherms data from the sulfides removal experiments using natural zeolite in aqueous solutions, the Langmuir equation was used. This equation is the result of kinetic and thermodynamic considerations and has the following form:

$$q_e = \frac{b \cdot q_m \cdot c_e}{1 + bc_e}$$

(1)

Where: c_e (mg/L) and q_e (mg/g) denote the equilibrium adsorbate concentrations in the aqueous and solid phases, respectively. q_m (mg/g) is the maximum removal capacity and b is the Langmuir adsorption equilibrium constant.

3. Results

Sulfides removal kinetics: Removal kinetic data of sulfides on zeolite in contact times ranging between 30min and 1440min are presented in Figure 1A. As resulted from the removal kinetics experiments during the first hour, about 36% of the total S^{2-} were removed from the solution, while after the second hour the 56% of the initial concentration was removed. For the next three hours the removal rate was almost zero, while it increased again during the 5th and 12th experiment's hour where about the 85% of the initial S^{2-} removed from the solution. In the next 12h an additional 7% of the initial sulfides' concentration was removed.

Sulfides removal isotherms: In order to simulate removal isotherms and establish the relationship between the amounts of sulfides removed using the natural zeolite and the concentration of sulfides remaining in the solution, the Langmuir model was used. Figure 1B shows the equilibrium removal capacities of sulfides as a function of initial concentrations. The isotherm data showed a rapid rise in the removal capacity with an increase in the equilibrium solution concentration, followed by a plateau at equilibrium, demonstrating typical Langmuir isotherm characteristics. The experimental isotherm data can be described satisfactory by the typical Langmuir-curve (R^2 = 0,998). The maximum removal capacity (q_m) calculated from the Langmuir model was 123.1 10^{-3} mg/g. In this type of isotherm, the initial slope does not significantly change with the increase of the solute concentration. The sulfides uptake increases dramatically with the equilibrium concentration increasing from 0 to 2 mg/L. With further increase of the equilibrium concentration, the increase of sulfides uptake is less significant.

Influence of initial pH in sulfides removal: pH is considered as one of the most important parameters controlling the removal process at water-zeolite interfaces. The amount of sulfides removed as a function of the pH is illustrated in Figure 1C. As the initial pH increased in the range of 5–7, the removal efficiency of zeolite increased gradually reached a maximum value of 91.7%, for pH value equal to 7. When the pH increased to 9, the removal efficiency was declined to 65.7%.

Effect of temperature and salinity: The ability of the natural zeolite to remove sulfides from an aqueous solution was studied in three different salinity values, 0‰ (fresh water), 20‰ (brackish water) and 35‰ (seawater). As shown in Figure 2A, zeolite's removal capacity exceeds the 90% in fresh water and brackish water. But even in salinity value equal to 35 ‰ zeolite succeeds to remove 80% of the initial sulfides' concentration after a period of 24h. As shown in Figure 2B, temperature increase from 5 to 35°C results in an increase of zeolite removal capacity of 12%. High temperature is advantageous for sulfides removal, and this indicates that the removal reaction is of endothermic nature.
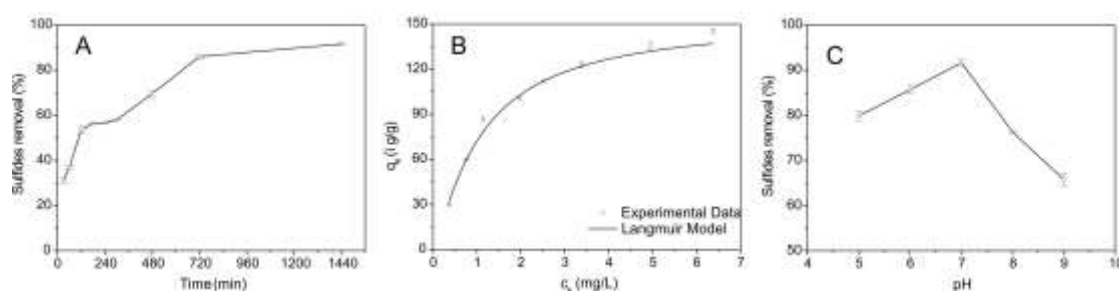
Figure 1: (A) Kinetics of sulfides-uptake by natural zeolite. (B) Isotherms and Langmuir, model fitting for sulfides-uptake by natural zeolite. (C) Effect of pH on sulfides uptake by natural zeolite.
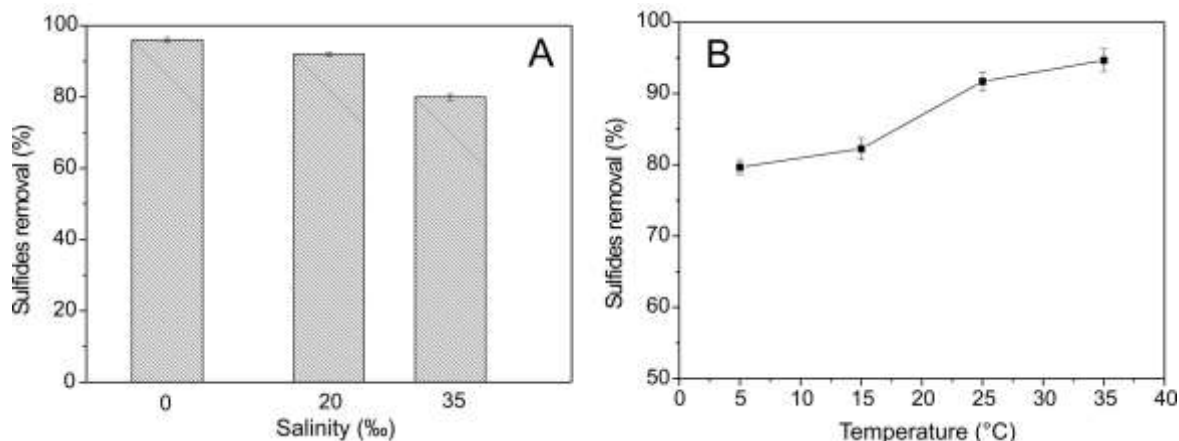
Figure 2: Effect of salinity (A) and temperature (B) on sulfides uptake by natural zeolite.

4. Discussion / conclusions

The current knowledge about the phosphorus and nitrogen removal methods from the natural aquatic ecosystems resulted from the need to reduce eutrophication levels in them. The initial laboratory approaches revealed several methodologies and materials mainly for phosphorus control. Complexation/precipitation of P using salts of Fe, Ca and Al was in many cases effective in reducing the internal load of phosphorus as well as water column P of several lakes (Cooke *et al.*, 2005). The use of aluminium sulphate (Alum) was a preferable solution since the resulting complex is chemically stable even under anoxic conditions. Its toxicity was the reason of its replacement of environmental friendly materials, such as calcite (Berg *et al.*, 2004) and natural or modified clays (Robb *et al.*, 2003). During environmental applications, these materials are dropped into the aquatic ecosystem and basin's bottom is covered with them, in order to remove water column P during their precipitation and control P release from sediments under anoxic conditions. However, such management efforts were quite often unsuccessful (Robb *et al.,* 2003; Berg *et al.*, 2004). The integrated management of a eutrophic environment requires both the combinatorial control of external and internal nutrient load as well as combined phosphorus and nitrogen management. Especially in anoxic environments, sulfides management is equally important.

Natural zeolite is particularly effective in removing ammonium (Cincoti *et al.*, 2001) but due to its negative charge, it cannot adsorb phosphate ions. However, the presence of cations in the solution (Ca^+, Na^+, K^+) makes it an appropriate substrate which can bind the formed phosphates (Karapinar, 2009). In the present study some initial experimental results are presented, intended to enhance the ability of the natural zeolite to remove dissolved sulfides from aqueous solutions. The removal capability of the natural material appeared to depend directly on the initial sulphides concentration. For initial concentration of 1mg/l, the zeolite's removal capability reached up to 90% after 24h. The maximum removal capacity of the zeolite was calculated equal to $123.1 \cdot 10^{-3}$mg/g. Natural zeolite is more effective for sulfides removal from waters at pH values between 5 and 7, while its capability decrease in alkaline environments. Salinity and temperature variations affect zeolite efficiency by only about 15% and 12% respectively.

The ability of zeolite to remove from aqueous solutions forms of nitrogen, phosphorus and sulfur makes it a material that could play a key role, in eutrophic/anoxic environments restoration efforts, since PO_4^{3-}, NH_4^+ and S^{2-} and constitute the three aspects of the problem called anoxic basins' internal load.

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