# Cationic Polystyrene-Based Hydrogels

Subjects: Water Resources

Contributor: Silvana Alfei, Valentina Orlandi, Federica Grasso, Raffaella Boggia, Guendalina Zuccari

Nitrites are metastable anions that are derived from the oxidation of ammonia by agricultural pollution, sewage, decaying protein, and other nitrogen sources. They are a recognized environmental issue due to their role in eutrophication, as well as in surface and groundwater contamination, being toxic to almost all living creatures. Two cationic resins (R1 and R2) forming hydrogels (R1HG and R2HG) by dispersion in water in removing anionic dyes from water by electrostatic binding.

Keywords: nitrites ; metastable ions ; environmental toxicity ; cationic polystyrene resins (R1, R2) ; cationic hydrogels (R1HG, R2HG)

## 1. Introduction

Untreated or badly treated waste released into bodies of water causes water pollution, which is one of the most widespread problems afflicting people throughout the world. Polluted waters are destructive to plants and organisms living in or around the aquatic ecosystem and can also harm the people, plants, and animals that consume these waters [1]. Water pollutants mainly include pathogens, inorganic compounds, organic material, and macroscopic pollutants.

Among inorganic pollutants, inorganic nitrogen pollution, mainly in the form of reactive ions such as ammonium ($NH_4^+$), nitrite ($NO_2^-$), and nitrate ($NO_3^-$) dissolved in water, can have detrimental ecological and toxicological effects on aquatic ecosystems [2]. In a non-altered global nitrogen cycle, ammonium, nitrite, and nitrate ions are naturally removed from water by macrophytes, algae, and bacteria, which exploit them as sources of nitrogen [3]. Facultative anaerobic bacteria including *Achromobacter, Bacillus, Micrococcus,* and *Pseudomonas* can utilize nitrites and nitrates as terminal acceptors of electrons, resulting in the ultimate formation of $N_2O$ and $N_2$ [4]. Excessively high levels of inorganic nitrogen, which the functions of ecological systems do not manage to assimilate (N-saturated ecosystems), can cause adverse effects on the least tolerant organisms and can overstimulate the growth of aquatic plants and algae. Excessive growth of these organisms can in turn clog water intake, use up dissolved oxygen as the organisms decompose, block light to deeper water, and result in killing fish due to a lack of dissolved oxygen [5].

## 2. Sources of Inorganic Nitrogen Pollutants

Agricultural pollution, including animal husbandry and $NH_3$-based fertilizer applications, sewage, decaying protein, and other nitrogen pollution sources, are suppliers of ammonia, which is oxidized (nitrified) into nitrite ($NO_2^-$) in aerobic environments. Nitrified nitrogen is in turn further oxidized into nitrate ($NO_3^-$) by bacteria that favor nitrite [6]. Conversely, nitrate can be easily reduced to nitrite in vivo. In this regard, nitrite can be produced by *Nitrosomonas, Nitrosococcus*, and *Nitrospira* bacteria in water distribution tubes where the water contains nitrate, oxygen is low, and chloramines are used to provide disinfection. In addition to existing in the environment, nitrite and nitrate exist widely in food products, mainly in the form of sodium or potassium salts. They are added to foodstuffs as preservative additives, with the principal function of inhibiting the propagation of food-poisoning microorganisms, such as *Clostridium botulinum* [7], and of improving the color and flavor of meat products [8]. Leafy vegetables and fruits are natural sources of nitrite and nitrate, but the development of modern agriculture and the abuse of inorganic fertilizers has caused a remarkable increase in nitrite and nitrate concentrations in vegetables and fruits [9]. Further, nitrite can contaminate potable water through runoff water coming into contact with fertilizer or sewage or from groundwater coming into contact with mineral deposits [10]. Additional sources of nitrites contaminating water include improperly treated sewage or septic tank effluent, or decaying plant or animal matter. Shallow wells and improperly constructed or damaged wells are extremely susceptible to nitrite contamination [10].

## 3. Toxicity of Nitrites and Nitrates

As above mentioned, nitrite and nitrate represent a recognized environmental concern due to their role in acidification, eutrophication (algal blooms in lakes and ponds), and groundwater contamination [11]. The eutrophication of freshwater, estuarine, and coastal marine ecosystems can cause ecological and toxicological effects that can be either directly or indirectly related to the hyper-proliferation of primary producers. The most dramatic event in eutrophic and hypereutrophic aquatic ecosystems with low water turnover rates is a reduction in dissolved oxygen (hypoxia or anoxia) causing the extensive death of both invertebrates and fish [4]. Additionally, the lack of oxygen can also promote the development of reduced compounds, such as hydrogen sulfide, with supplementary toxic effects on aquatic animals [4]. Moreover, cyanobacteria blooms associated with eutrophication can also produce toxic compounds that are harmful to livestock and human health [10].

Thanks to water salinity, due to the presence of sodium, chloride, calcium, and other ions, seawater animals are more tolerant to the toxicity of inorganic nitrogenous compounds than freshwater animals. Scientific reports have evidenced that when ingested, nitrites and nitrates might result in mutagenicity, teratogenicity, and birth defects. Furthermore, ingested nitrite can contribute to non-Hodgkin's lymphoma and bladder and ovarian cancers, play a role in the etiology of insulin-dependent diabetes mellitus and in the development of thyroid hypertrophy, or cause spontaneous fetal death and respiratory tract infections. A potential relationship between inorganic nitrogen pollution and human infectious diseases (malaria, cholera) has also been described. To prevent aquatic ecosystems (excluding those ecosystems with naturally high N levels) from developing acidification and eutrophication, the levels of total nitrogen (TN) should be lower than 0.5–1.0 mg/L. When present in freshwater, nitrite is known to be toxic to almost all living organisms, due to its action in decreasing the capacity of the blood to carry oxygen. In fact, nitrite can cause the irreversible conversion of hemoglobin to methemoglobin in the bloodstream, compromising the ability of hemoglobin to exchange oxygen, thus interfering with the oxygen transport system in the body [12][13]. This hazard is particularly serious for pregnant women and infants, as well as for aquatic life [14][15]. In this regard, this phenomenon is known as "blue baby syndrome" in infants, and it is referred to as "brown blood disorder" disorder in fish [16]. Infants, pregnant and nursing women, as well as elderly people should avoid consuming water with high levels of nitrite or nitrate. Moreover, nitrite can also react with secondary amines and amides in the stomach to form carcinogenic N-nitrosamines [15][17]. Due to these toxic effects, many countries have placed severe restrictions on their use in processed food products [18]. The presence of nitrite in drinking water, such as in well water, may also indicate other water quality troubles, including the presence of coliform bacteria and unsafe levels of nitrate. In good drinking water, concentrations of nitrite are usually below 0.1 mg/L [10].

## 4. Nitrite: A Water Pollutant That Needs to Be More Carefully Pondered

Nitrite is a metastable anion that tends to accept an additional oxygen ion in the presence of oxygen (as generally occurs in surface water), becoming nitrate. For this reason, ecologists, environmental scientists, analytical chemists, and catchment managers generally do not sufficiently consider its intrinsic impact on aquatic environments and species, though more attention has been paid to nitrates. An indirect consequence of this trend is that though the literature is rich in studies concerning methods to remove nitrate from wastewater, drinking water, ground water, surface water, lakes, rivers, and seas [19], studies concerning the development of new methods to remove nitrite from water are missing. In this regard, articles exist in the literature that report on nitrite removal through its oxidation into nitrates by biological treatments, hydrogen peroxide, ozone, or other costly methods that require high safety standards for the final removal of nitrates, but no method for specifically removing nitrite has been proposed recently [20][21]. Reverse osmosis, ion exchange, electrodialysis, electrocoagulation, biological denitrification, chemical denitrification, and adsorption methods are extensively described for nitrate remediation, with adsorption being the most promising method [19][22]. Concerning this, adsorption consists of the separation of compounds from the environment into the bulk or surface of a solid or liquid phase [23]. Among other separation and purification techniques such as photo-remediation, membrane technology, ion exchange, and electrochemical separation, adsorption is superior due to its unique features, such as its low cost, ease of operation, and high efficiency [23]. Zeolites, clays, biomasses, agricultural waste, activated carbons, microorganisms, nanoparticles, and metal oxides are the most widely applied, naturally available low-cost adsorbents [24].

Currently, nitrite can be removed from drinking water by reverse osmosis, distillation, or ion exchange [10], whereas boiling, carbon adsorption filters, and standard water softeners do not remove nitrite [10]. Ion exchange filters remove nitrite and other anions by adsorbing them into anion-exchange resins. Since anion-exchange resins preferentially adsorb sulfate ions, they are less effective at removing nitrite if the sulfate concentration is high [10]. Additionally, this type of filter must be replaced or regenerated before it becomes saturated, in order to avoid sulfate ions replacing nitrite ions already adsorbed by the filter, causing nitrite concentrations in the water to increase instead of decrease. In excess amounts, nitrite causes stress and diseases in fish, suffocating them, causing skin disorders, and hampering the growth rate and the development of their organs. In order to avoid this, some expedients are proposed to maintain low nitrite levels in an aquarium environment [25]. In this regard, water conditioners and nitrite removers that are able to bind to nitrite and render nitrite ions harmless to fish have been commercialized. Additionally, the use of filters with full-colonized beneficial bacteria, which are capable of converting ammonia into nitrite and then finally into nitrate, is suggested [25].

In field-based monitoring, nitrite is an effective indicator of nitrogen pollution sources, which can linger in the environment longer than sometimes assumed. As such, low-cost, up-scalable, and regenerable efficient systems that capture nitrite from the water and do not need to convert the nitrite into nitrate for nitrate removal, thus avoiding costly operations, are urgently needed.

In this regard, the adsorbent efficiency of water-insoluble polymers and copolymers (resins) in the form ammonium salts in adsorbing anionic compounds has long been studied [26][27]. These cationic macromolecules, if properly structured, may also supply hydrogels when dispersed in water. As recently reported, hydrogels are characterized by well-defined, three-dimensional (3D) porous structures, and the presence of hydrophilic functional groups, such as protonated amine groups, confers to them a high level of hydrophilicity [27]. As adsorbents, cationic hydrogels represent an important tool to remove anionic pollutants from water because of their flexible network, which allows solutes to quickly penetrate water and form stable complexes with them [27].

Additionally, hydrogels are capable of absorbing great amounts of water and of increasing to several times their original volume, thus exposing their functional groups, which become more accessible, promoting interaction with contaminants and their sorption onto polymer chains [28][29].

In this context, CMC-g-Poly (MAA-co-Aam)/Cloisite 30B (Hyd/C30B) and poly (methacrylic acid-co-acrylamide)/Cloisite 30B nanocomposite (poly (MAA-co-Aam)/Cl30B) hydrogels have demonstrated high efficiency in adsorbing methylene blue (MB) dye from wastewater samples [30][31]. Additionally, a recent paper reported the immobilization of hybrid gold–cesium nanoparticles (Au–Cs NPs) onto a magnesium ferrite ($MgFe_2O_4$) surface and detailed the behavior of the prepared composites in $N_2$ adsorption–desorption experiments [32].

The kinetics mechanisms of the adsorption processes and the possibility of regenerating R1 and R2 are also investigated. Collectively, R1HG and especially R2HG proved to be low-cost, up-scalable, and regenerable adsorbent materials that are promising for rapid nitrite remediation and drinking water decontamination through simple contact or filtration. Specifically, without using currently adopted methods that are more expensive and complicated, R1HG and R2HG could be capable of reducing nitrite concentrations under the legal limit of 0.5 mg/L (0.48 mg/L for R1HG and 0.11 mg/L for R2HG) in volumes of drinking water having the maximum contamination level registered in 2023 (1.0 mg/L), which would be 50–60 times higher than the volumes of resin used. Since there are a lack of papers in the literature concerning the development of new methods to remove nitrite from water, the present study has immense relevance and is especially novel, as there are no other previously published reports to compare it to.

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