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Nitrite removal from water using water-soluble polymers in conjunction with liquid-phase polymer-based retention technique

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Abstract

The retention properties of water-soluble metal polymers for nitrite anions from aqueous solution are investigated. The preparation of cationic water-soluble polymers containing $-RN^+X^-$ groups, and their nitrite retention performance was investigated using the liquid-phase polymer-based retention (LPR) technique. Poly((3-methacryloylamine)propyl)trimethyl ammonium chloride, P(ClMPTA), poly((2-acryloyloxy)ethyl)trimethyl ammonium chloride, P(ClAETA), and poly(ar-vinylbenzyl)trimethyl ammonium chloride, P(ClVBTA) were prepared by water solution radical polymerization. Structural analyses were performed using infrared (FT-IR) and nuclear magnetic resonance (NMR H^1)spectroscopy as well as thermogravimetry (TG-DSC). The LPR technique was employed in the retention assays. The studies evaluated the effect of polymer concentration and pH on retention. The change in the pH value of the aqueous solution has a great influence on nitrite retention. Specifically, P(ClVBTA) and P(ClAETA) presented higher nitrite retention at pH 6 and 8 and a lower retention capacity at pH 4. However, P(ClMPTA) behavior was virtually constant, independently of the medium's pH. The polymer:NO_2^- mole ratios of (20:1), (40:1), (60:1), (80:1), and (100:1) were essayed as washing methods at pH 8. The mole ratios (60:1) and (100:1) in basic media presented higher retention capacity for all polymers. In general, the polymer's saturation capacity was around 32–37 mg/g with the enrichment factor 4.5–5.6. The addition of monovalent and divalent anions competing for reactive sites, decreased the selectivity for NO_2^- anion in P(ClVBTA) in around 90%. Assays with drinking water for P(ClVBTA) with mole ratio polymer:NO_2^- (120:1) presented retention near to 80%.
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1. Introduction

Nitrates continue to be an important contamination problem due to their use in soil fertilizers and other applications, such as NO_x emission due to combustion processes. Ammonia, nitrites and nitrates are typical indicators for water contamination. Furthermore, nitrites and ammonia are toxic in reduced concentrations. The toxicity of nitrates is due to their reduction to nitrites and their subsequent accumulation at high levels causes cyanosis (blue baby syndrome) and carcinogenic nitrosamines [1]. Nitrates and nitrites are soluble

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compounds containing nitrogen and oxygen. Nitrate (NO_3^-) is more stable than nitrite (NO_2^-), which means that nitrite easily changes into nitrate in groundwater and nitrate-plus-nitrite test results generally indicate a predominance of nitrate. Maximum admissible concentration for nitrates in drinking water is 50 mg/L NO_3^- and 1 mg/L NO_2^- as N according to the European drinking water directive, while the World Health Organization (WHO) recommends 25 mg/L NO_3^- as acceptable level. Additionally, nitrate in drinking water is measured either in terms of the amount of nitrogen present or in terms of both nitrogen and oxygen. The federal standard for nitrate in drinking water is 10 mg/L nitrate-N, and nitrite-N is 1 mg/L when the oxygen is measured as well as the nitrogen. Nitrite levels above 0.75 mg/L in water can cause stress in fish, which present toxicity problems depending on the medium's pH, where values above 1 mg/L are completely toxic and represent an impediment to both fish life and to the establishment of a pluvial ecosystem in good conditions [2].

Conventional physicochemical methods for nitrate separation include ion-exchange, reverse osmosis, and electro dialysis [3]. The most promising techniques for their removal from wastewater include biological digestion [4] and catalytic denitrification [5–8] by using noble metal catalysis. However, these methods involve two phase systems (heterogeneous methods). On the other hand, the liquid-phase polymer-based retention technique easily allows the separation of metal ions bound to water-soluble polymers from the non-bound metal ion [9–13]. Applications of water-soluble polymers to the homogeneous enrichment or selective separation of various metal ions from dilute solutions have been reported. Ultrafiltration is considered to be the most suitable technique for LPR studies, and a vast amount of data is being published [14–18].

The aim of this study is to remove nitrite from water in one step, using different polymeric structures of water-soluble quaternary polycationic salts. Through these structures an easier anionic exchange of Cl^- with toxic NO_2^- anions in aqueous media is achieved. LPR as an alternative promising technique, carried out the separation and selection of the anions. This study will identify an optimum polymer:NO_2^- mole ratio to assure maximum exchange capacity and retention at adequate pH. Additionally, the investigation studies the effects on retention capacity of NO_2^- of those anions that might be present in drinking water. It was necessary to provide date obtained in presence of various anions (monovalent and divalent) and the potential effect of ionic strength of liquid phase on the retention progress.

2. Experimental part

2.1. Synthesis and characterization of homopolymers

Cationic homopolymers were prepared by radical polymerization using the procedure previously described [19]. Five grams of each monomer and 1 mol% of ammonium persulfate (AP) as initiator are dissolved in 100 mL of water in an inert atmosphere. The reaction is kept at 70 °C under N_2 for 24 h. The water-soluble products are lyophilized. The polymerization yields were: 99% for P(ClMPTA), P(ClAETA), and P(ClVBTA), 99% over the fraction of >100.000 D. The structural characterization was made by FT-IR and ^{1}H NMR spectroscopy. The ^{1}H NMR (250 MHz, D_2O), spectra of monomers and homopolymers were analyzed comparatively. The absence of the protons signals at 5.44 and 5.68 ppm, corresponding to double bond C=C, and the presence of signals at $\delta = 2$ ppm ($2H^1$). $\delta = 2.5$ ppm ($1H^1$) indicated that the vinyl monomer polymerization did occur. Additionally, P(ClMPTA), vinyl protons of the chain (in ppm): $\delta = 2$ (2H), side groups: $\delta = 1$ (3H), $\delta = 3.18$ (9H) quaternary ammonium group; P(ClAETA): side groups: $\delta = 3.75$ (2H); $\delta = 4.5$ (2H); $\delta = 3.18$ (9H) quaternary ammonium group; P(ClVBTA), side groups: $\delta = 4.35$ (2H) ; $\delta = 7.4$ (1H) aromatic ring. The proton signal from water HDO (D_2O) is placed at 4.8 ppm.

Characteristic absorption bands of FT-IR (in cm^{-1}): 1482 $\rho(-N^+CH_3)$, 1640 $v(C=O)$ amide group, 1733 $v(C=O)$ acryloxy group, 1641–1408 $v(C=C)$ aromatic ring are summarized in Table 1.

2.2. Measurements

The nitrite solution is 99.9% pure (Aldrich) in 1000 mg/L of nitrogen concentration. The NO_2^- content was analyzed by diazotization method, using sulfanilamide and *N*-(1-naftyl)-ethylenediamine dichloride, forming a pink-colored azo product $\lambda = 541$ nm, using a spectrometer model CADAS 100. The measurements were determined in mg/L of N.

The Fourier transformed infrared (FT-IR) were recorded with a Magna Nicolet 550 and Nexus Nic-