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A novel quaternized resin with acrylonitrile/divinylbenzene/vinylbenzyl chloride skeleton for the removal of nitrate and phosphate

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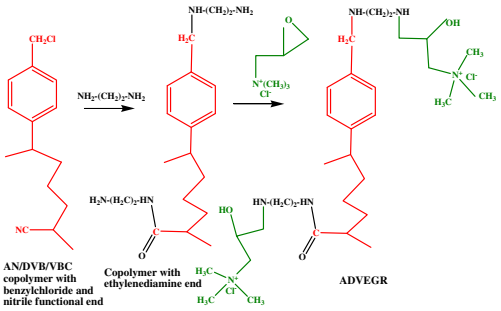
HIGHLIGHTS

- A novel quaternary resin namely ADVEGR has been synthesized.
- The nitrate and phosphate adsorption efficiency of the resin is laudable.
- The resin has been found to be selective towards nitrate.

GRAPHICAL ABSTRACT

A novel nitrate selective quaternized resin namely ADVEGR has been synthesized. The resin has excellent nitrate and phosphate removal efficiency and it has retained its 100% efficiency even after 10 regeneration cycles.



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ABSTRACT

A copolymer with acrylonitrile/divinylbenzene/vinylbenzyl chloride (AN/DVB/VBC) matrix was prepared and quaternary ammonium chloride functional group was introduced in it using ethylenediamine and glycidyl trimethyl ammonium chloride (GTMAC) to utilize it for the removal of nitrate and phosphate. The physico-chemical properties of this quaternized resin named as ADVEGR was analyzed using the techniques like FTIR, SEM, EDAX, XRD, TGA, DTA, BET surface area and water regain property. Batch studies were carried out to optimize the conditions for adsorption. ADVEGR was found to be selective towards nitrate. The nitrate and phosphate removal capacity of resin from 1000 mg/L of respective aqueous solutions were 167.54 and 183.18 mg/g respectively. Langmuir, Freundlich and Dubinin-Radushkevich adsorption isotherms were used to fit the equilibrium data. Effect of Cl^-, HCO_3^- and SO_4^{2-} on the adsorption capacity of the resin towards nitrate and phosphate was analyzed in batch and column mode. The order of selectivity of ADVEGR towards various anions was as follows: $NO_3^- > SO_4^{2-} > H_2PO_4^- > Cl^- > HCO_3^-$. The resin has been applied for the real water sample treatment and the values obtained after treatment showed that the adsorbent had a total anion removal efficiency of 100% which validates the method. The resin regained its 100% efficiency even after 10th regeneration cycle.

1. Introduction

Nitrate and phosphate are essential nutrients for living organisms. It comes under the category of water pollutants if they present in excess than the necessary amount. Presence of these anions especially phosphate in water bodies induces eutrophication which makes the water bodies breathless [1,2]. Eutrophication affects human through food chain. Nitrate causes methemoglobi-

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nemia in infants [3,4]. According to World Health Organization (WHO) [5], most chemicals found in drinking water cause health concern only after extended exposure of years, rather than months. The principal exception is nitrate. Also it is one of the key chemicals that cause large scale health effects through drinking water exposure. WHO declared the drinking water limit of nitrate as 50 mg/L. According to Environmental Protection Agency (EPA) and Indian Standard (IS 10500) specifications for drinking water, the drinking water limit of nitrate is 45 mg/L [6,7]. Phosphate is not directly regulated by WHO, EPA and IS. Phosphate is not toxic to people or animals unless they are present in very high levels. Digestive problems happen from extremely high levels of phosphate. The eutrophication inducing limit of phosphate is 0.1 mg/L but long term eutrophication can usually be prevented if total phosphorus levels are below 0.5 mg/L [8,9]. Hence there is a need for the removal of these anions.

Among the methods developed for the removal of nitrate and phosphate, adsorption by ion exchange is the best method since it is simple, easy to operate and regenerable [10]. Synthetic resins are very potential and well established ion-exchange materials because of their high physical and chemical stability. The stability of the resins enables them to use, regenerate and reuse for years without losing its capacities [11]. More and more research is going on in this field in search of an efficient and selective material.

In the adsorptive removal of nitrate and phosphate, effect of sulphate is an issue of interest because, sulphate adsorbs preferentially due to its bivalency. The selectivity of nitrate and phosphate even in the presence of sulphate is a compulsory fact for the development of treatment technology. To make a polymeric resin selective towards phosphate, impregnation of metals and metal oxides/hydroxides on it was one of the practises. Hybrid resins loaded with ferric hydroxide, hydrated ferric oxide, La(III), Cu(II), Zr(IV), Fe^{2+} and Fe^{3+} were reported as selective towards phosphate [12–18]. Phosphate forms inner sphere complex with the metal sites but the simple anions like chloride, sulphate and nitrate couldn't able to form inner sphere complex [19].

The problem of selective adsorption of nitrate is important since nitrate toxicity has direct health impact. Considerable amount of studies have been reported with a focus on the preferential adsorption of nitrate in the presence of sulphate. It was proved that the preference of an anion exchange resin for nitrate over sulphate increases as the resin becomes more hydrophobic. Jackson and Bolto reported that nature of the polymer backbone or the nature of substituents at the nitrogen render hydrophobicity to a resin [20]. They have also reported that, the increase in cross-linking would affect the flexibility of the chain and hence reduce its ability to reorient to enable two positive sites to satisfy the divalent sulphate ions. Imac HP555 [21], Purolite A-520E [22], NDP-2 [23] and NDP-5 [24] are some of the nitrate selective resins which possess triethyl groups at the quaternary nitrogen. Soldatov et al. [25] observed that, presence of higher percent of cross-linkers like divinylbenzene also makes the resin as nitrate selective.

In this study, co-polymer with long chain matrix, AN/DVB/VBC was synthesized and ethylenediamine was introduced in it (AN/DVB/VBC-ED) as reported by Bartkowiak et al. [26]. Then AN/DVB/VBC-ED was quaternized with GTMAC to get ADVEGR. The importance of AN/DVB/VBC skeleton is that, ethylenediamine could add at the benzyl chloride end as well as at the nitrile end. This facilitates the availability of more amino groups for quaternization. GTMAC readily reacts with the primary amino groups through the opening of epoxide bond. The resin was used for the removal of nitrate and phosphate. The nitrate selectivity of this resin was investigated. Since eutrophication is a phenomenon associated with both nitrate and phosphate, the combined removal of nitrate and phosphate was also focused in this study. The equilibrium data were fitted well with the isotherms namely Freundlich, Langmuir and D-R. Thermodynamic parameters viz., ΔG°, ΔH° and ΔS° were calculated to recognize the nature of adsorption.

2. Materials and methods

2.1. Materials

Divinylbenzene (DVB) and polyvinyl alcohol (PVA) were purchased from Fluka. Vinylbenzyl chloride (VBC) and glycidyl trimethyl ammonium chloride (GTMAC) were purchased from Sigma–Aldrich. Acrylonitrile (AN), benzoyl peroxide, ethylenediamine (ED), 1,2-dimethylformamide (DMF), calcium chloride, toluene and acetone were purchased from Merck. KNO_3 and KH_2PO_4 (Analytical grade) were used as the source of nitrate and phosphate anions respectively. The other reagents used in the study viz., $CaCl_2$, NaOH, HCl, Na_2SO_4, NaCl, $NaHCO_3$ also of analytical grade.

2.2. Preparation of ADVEGR

The quaternized resin named as ADVEGR has been prepared by suspension polymerisation method. The copolymer resin skeleton (AN/DVB/VBC-ED) was prepared as reported by Bartkowiak et al. [26]. The polymeric matrix AN/DVB/VBC containing 2 wt.% of cross-linker (DVB) and 20 mol% of acrylonitrile was obtained by suspension polymerization method using 0.5 wt.% of benzoyl peroxide as the initiator. Polymerization was carried out in the presence of toluene (50 wt.% with respect to the monomers mixture) in order to obtain a polymeric material with an expanded gel structure. The mixture of monomers and diluent were suspended in aqueous phase (7 wt.% solution of $CaCl_2$, containing 1.5 wt.% in respect to organic phase) of PVA. The temperature was kept at 60 °C for 1 h, at 70 °C for 1 h, at 85 °C for 2 h and finally at 95 °C for 6 h. After polymerization, the polymeric beads were washed with hot water, acetone and then dried. Then the AN/DVB/VBC copolymeric beads were swollen in DMF for 24 h and aminolysed with ethylenediamine [27]. The reaction mixture was kept at room temperature and stirred for 19 days. Finally the ethylenediamine modified beads (AN/DVB/VBC-ED) were filtered and washed with 1 M HCl, 1 M NaOH and double distilled water. The gel beads were immersed in 20% of GTMAC solution at 60 °C for 24 h and was washed with double distilled water to remove excess GTMAC and dried in room temperature to get ADVEGR. The preparation route is schematically represented in Scheme 1.

2.3. Instrumental techniques

The analysis of nitrate and phosphate was carried out using UV/VIS spectrophotometer (Spectroquant Pharo 300, Merck). The analysis of nitrate and phosphate was also carried out using Ion-Chromatogram, 883 Basic IC Plus provided by Metrohm. The anionic column namely MetroSep A Supp 4 – 250/4.0 with a size of 250 mmL X 4.0 mmID was used. The eluent consists of the mixture of 1.8 mM Na_2CO_3 and 1.7 mM $NaHCO_3$. The chloride and sulphate ions were also measured using the same column. The pH of the samples was determined using expandable ion analyzer (Orion EA 940 USA) with pH electrode. pH_{zpc} of adsorbent was measured using the pH drift method [28]. SEM and EDAX for the materials were obtained with VEGA3TESCAN fitted with Bruker Nano GmbH, Germany. FTIR spectra were collected on FTIR spectrometer (JASCO-460 plus model) using KBr pellets prepared by mixing the material with KBr. TGA/DTA was carried out using Universal V4.7A TA instruments in the N_2 atmosphere. X-ray diffraction (XRD) measurements were obtained using Rigaku Ultima III X-ray diffractometer. The surface area of the material was analyzed by BET isotherm method with NOVA 1000 model.