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Nitrate decontamination through functionalized chitosan in brackish water

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ABSTRACT

N, *N*, *N*-Triethyl ammonium functionalized cross-linked chitosan beads (TEACCB) was prepared by alkylation of glutaraldehyde cross-linked chitosan beads to remove nitrate from brackish water. Physico-chemical characteristics of TEACCB were analyzed using FTIR, SEM, EDAX, TGA, DTA, BET surface area, swelling ratio and pH_{zpc}. The maximum nitrate removal capacity of TEACCB was 2.26 meq/g and is higher than other reported chitosan based adsorbents. Nitrate removal ratio in the presence and absence of common anions like chloride and sulphate demonstrated the selectively of TEACCB towards nitrate. The kinetic data of nitrate removal fitted well with the pseudo-second-order kinetic model. The thermodynamic parameters indicated that nitrate removal could be spontaneous and exothermic in nature. TEACCB was reused with 100% efficiency after regenerating with 0.05 N HCl. Column study was carried out to remove nitrate from brackish water. These results are very significant to develop TEACCB based nitrate removal technology with great efficiency.

1. Introduction

Nitrate, the nutrient turned pollutant, is one of the key chemicals that cause large scale health effects through drinking water exposure. Nitrate pollution in drinking water is a global issue. According to World Health Organization (WHO) (WHO, 2006), nitrate is among the few chemicals found in drinking water which cause very quick health concern. The major health hazards from drinking water with nitrate occur when nitrate is transformed to nitrite in the digestive system. Methemoglobin is formed when nitrite oxidises the ferrous iron in haemoglobin to the ferric form and it cannot bind oxygen which leads to the condition known as methemoglobinemia or blue baby syndrome (WHO, 1985). WHO declared the drinking water limit of nitrate as 50 mg/L (WHO, 2004). According to Environmental Protection Agency (EPA) and Bureau of Indian Standards (BIS) specifications for drinking water, the drinking water limit of nitrate is 45 mg/L (USEPA, 2012; BIS, 2012). According to a study on Indian scenario of nitrate pollution in groundwater, various parts of 170 districts from 13 states are found to have nitrate concentration >45 mg/L (Khandare, 2013). Sustainable technology for the selective removal of nitrate from drinking water is a need of the time.

Adsorption through ion exchange mechanism is an efficient method for the removal of nitrate since the adsorbent can be regenerated and reused (Sowmya & Meenakshi, 2013a). Polymeric resins with polystyrene-divinylbenzene matrix and quaternary ammonium chloride functional groups are extensively used for the removal of nitrate (Chabani, Amrane, & Bensmaili, 2007; Milmile et al., 2011; Dron & Dodi, 2011; Sowmya & Meenakshi, 2013b). Selective removal of nitrate in the presence of common anions viz., sulphate and chloride is a major concern (Sowmya & Meenakshi, 2014a). Considerable amount of studies were reported with a focus on the preferential adsorption of nitrate in the presence of sulphate. According to previous reports, hydrophobic nature of an ion exchange resin renders it nitrate selectivity. Nature of the polymer backbone or the nature of substituent at the nitrogen is the factor behind the hydrophobic nature (Jackson & Bolto, 1990). Polymers with triethyl groups at the quaternary nitrogen viz., Purolite A-520E (Samatya, Kabay, Yuksel, Arda, & Yuksel, 2006), NDP-2 (Song, Zhou, Li, & Mueller, 2012a) and NDP-5 (Song, Zhou, Li, & Mueller, 2012b) are reported as nitrate selective.

Strong base anion exchange resin from abundantly available biomaterials is always a better option since it could act as an eco-friendly approach for the environmental sustenance. Chitosan is an abundantly available and biodegradable biopolymer which has primary amine in its structure. Chitosan based ion exchange resins for nitrate removal is few. Cross-linked chitosan based anion exchangers namely QCB (Sowmya & Meenakshi, 2013a) and

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QCMGR (Sowmya & Meenakshi, 2014b) are reported for nitrate removal. In both the cases, quaternary ammonium chloride group was introduced on the modified beads using glycidyl trimethyl ammonium chloride (GTMAC) which is comparatively expensive than the method followed in the present study. Different modifications of cross-linked chitosan beads were also carried out with sodium bisulphate conditioning (Chatterjee, Lee, Lee, & Woo, 2009), protonation (Sowmya & Menakshi, 2014c) carboxylation (Sowmya & Menakshi, 2014c), Zr(IV) loading (Sowmya & Meenakshi, 2015) and Zn(II) loading (Sowmya & Meenakshi, 2014d) to remove nitrate. But, chitosan based anion exchangers retained its maximum nitrate removal efficiency even after several regeneration cycles.

Quaternary ammonium derivatives of chitosan are water soluble and are widely used for biological, pharmaceutical and catalytic applications (Martins et al., 2015; Patrulea, Applegate, Ostafe, Jordan, & Borchard, 2015; Caiqin, Ling, Yumin, Xiaowen, & Jiawei, 2002). Among them, N-methyl and N-benzyl derivatives of chitosan are most studied (Jayakumar et al., 2010; Badawy, Rabea, & Taktak, 2014). Cross-linking of chitosan facilitates the preparation of water insoluble quaternized chitosan for water purification application. In this study, chitosan was cross-linked with glutaraldehyde to certain limit and the free amines were ethylated to produce $-N^+(C_2H_5)_3$. In general, synthesis of N-alkyl derivative of chitosan follows the formation of a Schiff base with an aldehyde and reduction of the Schiff base to amine (Badawy, Rabea, & Taktak, 2014; Sajomsang, Tantayanon, Tangpasuthadol, Thatte, & Daly, 2006). For our case, the Schiff base formed by glutaraldehyde cross-linking should not get reduced. The physico-chemical nature of prepared *N*, *N*, *N*-triethyl ammonium functionalized cross-linked chitosan beads (TEACCB) was characterized by various instrumental techniques. Effects of various parameters such as contact time, concentration, pH of the nitrate solution and temperature on the nitrate removal capacity of TEACCB were optimized by batch method. TEACCB was powdered and used for nitrate removal to prove its ion exchange behaviour. Nitrate selectivity of TEACCB was evaluated in the presence of sulphate and chloride anions. Nitrate removal studies from brackish water were carried out in batch and column mode. The fitness of reaction based kinetic models was investigated. Thermodynamic parameters viz., ΔG°, ΔH° and ΔS° were calculated to identify the nature of reaction.

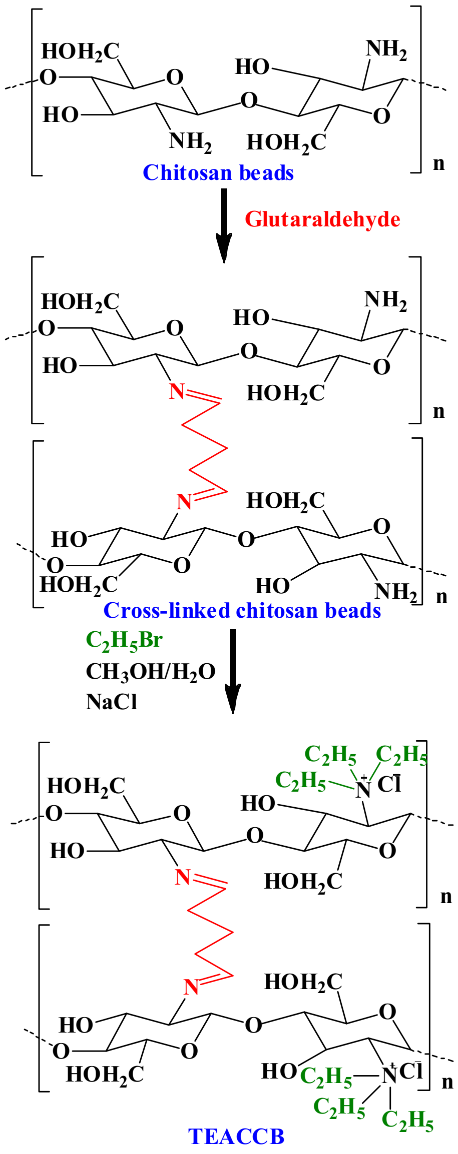
2. Materials and methods

2.1. Materials

85% Deacetylated chitosan flakes were supplied by Pelican Biotech and Chemical Labs, India and the flakes were fully soluble in mild acids. KNO_3 (Analytical grade) was used as the source of nitrate ion. The other reagents used in the study viz., ethyl bromide, methanol, NaCl, $CaCl_2$, Na_2SO_4, NaOH, HCl also of analytical grade. Double distilled water was used throughout the study.

2.2. Preparation of TEACCB

Cross-linking of chitosan was carried out using glutaraldehyde (Jeon & Holl, 2003). 20 g of chitosan was dissolved in 1000 mL of 2% glacial acetic acid solution. Uniform chitosan gel beads were obtained by dropping chitosan solution in 1 M NaOH. After gelling for a minimum of 16 h in 1 M NaOH solution, the beads were neutralised with distilled water. The wet beads were reacted with glutaraldehyde (5% wt) for 48 h and then cross-linked beads were washed with distilled water to remove any free glutaraldehyde. The wet cross-linked chitosan beads (35 g) were thoroughly mixed in 30% methanol/water (100 mL) and ethyl bromide was added drop wise with constant stirring. To ensure the availability of ethyl bromide for the complete quaternization of cross-linked chitosan beads, different reactions with 2.5, 5, 7.5 and 10% of ethyl bromide were carried out. The reaction mixture was refluxed at 70–80 °C for 12 h and continued for another 3 h at 90 °C after the addition of 5% NaCl (Badawy, Rabea, & Taktak, 2014). The quaternized beads were washed well with double distilled water to remove excess of unreacted reagents and dried at room temperature to have TEACCB. The preparation route of TEACCB is schematically represented in Scheme 1.



Scheme 1. Preparation route of TEACCB.

2.3. Nitrate removal by batch and column methods

Batch adsorption studies have been conducted to optimize the conditions for maximum nitrate removal. 50 mL of nitrate solution was taken in an iodine flask and 0.1 g of TEACCB was added into it. The system was agitated in mechanical shaker (120 rpm) at room temperature for a fixed time followed by filtration. The concentration of nitrate after removal process was analyzed using UV/Visible spectrophotometer (Cary 60 UV–vis, Agilent technologies) (Eaton, Clesceri, Rice, & Greenberg, 2005). The effect of contact time (15–150 min) on the removal process was analyzed and the