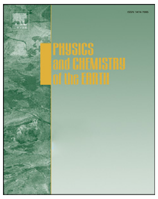
Physics and Chemistry of the Earth xxx (2016) 1–13

Contents lists available at ScienceDirect

Physics and Chemistry of the Earth

journal homepage: www.elsevier.com/locate/pce



Chitosan-based nanocomposites for de-nitrification of water

Monaheng L. Masheane [a, b], Lebea N. Nthunya [a, b], Soraya P. Malinga [a], Edward N. Nxumalo [b], Sabelo D. Mhlanga [b, *]

[a] Department of Applied Chemistry and the DST/Mintek Nanotechnology Innovation Centre - Water Research Node, University of Johannesburg, P.O. Box 17011, Doornfontein, 2028, South Africa
[b] Nanotechnology and Water Sustainability Research Unit, College of Science, Engineering and Technology, University of South Africa, Florida, 1709, Johannesburg, South Africa

ARTICLE INFO

Article history:
Received 30 May 2016
Accepted 3 October 2016
Available online xxx

Keywords:
Alumina
Carbon nanotubes
Chitosan
Nitrates
Water purification

ABSTRACT

Novel chitosan (CTs) nanocomposite beads containing alumina (Al_2O_3, denoted as Al in the nanocomposites) and functionalized multiwalled carbon nanotubes (f-MWCNTs) (CTsAl/f-MWCNTs) were prepared using an environmentally benign phase inversion method and subsequently used for the removal of nitrates (NO_3^-) in water. The ellipsoidal beads with an average size of 3 mm were readily formed at room temperature and contained a small amount of Al (20 wt%) and f-MWCNTs (5%). The beads were found to adsorb nitrates effectively over a wide range of pH (pH 2 − pH 6) and showed maximum nitrates removal of 96.8% from a 50 mg/L nitrate water solution. Pure CTs beads on the other hand removed only 23% at pH 4. Kinetic studies suggested that the particle diffusion was rate controlling step for the adsorption of nitrates on CTsAl/f-MWCNT nanocomposite beads. Langmuir-Freundlich isotherms revealed that the adsorption of nitrates was on the heterogeneous surface of CTsAl/f-MWCNT beads. The Dubinin–Radushkevich (D-R) isotherm further revealed that the adsorption of nitrates was by electrostatic interaction. Thermodynamic studies suggested that the adsorption was spontaneous and exothermic. More than 70% recovery was achieved for 5 cycles of desorption-degeneration studies. Al and f-MWCNTs have shown to improve swelling and solubility of CTs.

1. Introduction

Potable drinking water is essential for the good health of humans and a critical feedstock in a variety of industries such as electronics, pharmaceutical and food industries (EPA, 2013; Mohamed, 2013). However, less than 1% of global water available is fresh water and 2% of the fresh water is locked in sea-caps and is unavailable. The rest of the water (97%) is salty sea water (Patil et al., 2013).

Many rural communities in Africa depend on ground and surface water for drinking and other domestic activities. These water sources are often polluted with nitrates (NO_3^-) derived from agricultural activities (Schilling and Wolter, 2001). Nitrates are the end product of the oxidation of ammonia or nitrite (NO_2^-) (Wedin and Sorensen, 2013). Nitrates and nitrites are oxyanions of nitrogen (N_2) in which N is found in the +5 and + 3 oxidation state, respectively. Nitrates and nitrites occur together in the environment. Under oxidizing conditions nitrites is converted to nitrates, which is the most stable positive oxidation state of nitrogen and far most common in the aquatic environment than nitrite (WHO, 2011).

A substantial source of nitrates in natural water results from the oxidation of vegetable and animal debris from animal and human excrement. Treated sewage wastes also contain elevated concentrations of nitrates. Nitrites seem to increase in surface and ground waters sources as a result of agricultural activities and urban runoffs (Shabalala et al., 2013). In aquatic systems, high concentrations generally result to hastened growth of algae and the occurrence of algal blooms, which subsequently cause problems related with malodours and tastes in water and the possible occurrence of toxicity (Cave and Kolsky, 1999).

Nitrates in drinking water are primarily a health concern since they can be readily converted in the gastrointestinal tract to nitrites as a result of bacterial reduction. Nitrites then combine with oxygen-carrying red blood cells, haemoglobin, to form methahaemoglobin, which is incapable of carrying oxygen. This

---

* Corresponding author.
E-mail address: mhlansd@unisa.ac.za (S.D. Mhlanga).

http://dx.doi.org/10.1016/j.pce.2016.10.004
1474-7065/© 2016 Published by Elsevier Ltd.

Please cite this article in press as: Masheane, M.L., et al., Chitosan-based nanocomposites for de-nitrification of water, Physics and Chemistry of the Earth (2016), http://dx.doi.org/10.1016/j.pce.2016.10.004

phenomenon is referred to as methaemoglobinaemia or "blue baby syndrome" (Mahler et al., 2007; Shrimali and Singh, 2001). The reaction of nitrites with haemoglobin can be particularly hazardous in infants under three months of age and is compounded when the intake of Vitamin C is inadequate. Metabolically, nitrates may react with secondary and tertiary amines and amides, commonly derived from food to form nitrosamines which are also known carcinogens (Gálvez et al., 2003; Glass and Silverstein, 1999). Table 1 shows the effects of nitrates and nitrites at different dose on human beings, according to WHO (WHO, 2011).

Some conventional methods have been employed for the removal of nitrates in water. These range from chemical reduction to biological de-nitrification (Gyananath et al., 2012; Oztürk and Bektaş, 2004). However, these methods are expensive and they are not efficient at temperatures below 7 °C (An et al., 2014). Adsorption is one of the most effective and low cost methods for the removal of nitrates in water, especially using low cost biosorbents such as agricultural wastes, clays, biomass and biopolymers (Zhao et al., 2007). The use of the bead-like particles has advantages in terms of application due to a wide variety of process configurations and reusability or regeneration (Gotoh et al., 2004).

Chitosan (CTs) (poly-1,4-D-glucosamine) is a bioadsorbent derived from chitin, which is widely found in the exoskeleton of shellfish and crustacean. It is the most abundant natural polymer after cellulose (Azlan et al., 2009; Ngah and Fatinathan, 2008; Rayung et al., 2014; Wan Ngah et al., 2008; Wongpanit et al., 2005). The diverse functional groups on CTs, *i.e.* amino ($-NH_2$) and hydroxyl (-OH) groups, makes it an excellent material for the removal of pollutants including nitrates (An et al., 2014; Oztürk and Bektaş, 2004; Wongpanit et al., 2005). It offers additional advantages over other biosorbents because it is a cost effective and eco-friendly natural polymer and can be easily modified by chemical reactions (Olteanu, 2007). Nevertheless, CTs has poor stability in acidic conditions, thus limiting its applications in water treatment. Cross-linkers such as epichlorohydrin, gluteraldehyde and inorganic materials (e.g. alumina, silica and tatinia) have been used to improve its chemical stability (Mi et al., 2014).

Alumina (Al_2O_3, denoted as Al in the nanocomposites) which occurs naturally in a crystalline polymorphic phase α-Al as the mineral corundum, has well-known characteristics as an adsorbent due to its high surface area (~200 m^2/g) and its amphoteric character of hydrous aluminum hydroxide. Its acid-base dissociation leads to the positive ($-OH_2^+$) and negative ($-O^-$) charges on the surface depending on the pH (Sankar et al., 2013; Azlan et al., 2009; Khattak et al., 2000). Carbon nanotubes (CNTs) have also become ideal materials to use as inorganic fillers for reinforcing or toughening polymeric materials (Tjong, 2006).

To the best of our knowledge very few studies have been reported on the use of chitosan-alumina (CTsAl) composite beads as adsorbent for the denitrification of drinking water. The purpose of the present study was to develop novel CTs beads embedded with Al and functionalized-multiwalled carbon nanotubes (f-MWCNTs) for the denitrification of water and to investigate the interaction between the composite beads and nitrates during the adsorption process. Cross-linking of CTs with Al and f-MWCNTs has never been done before and the application for removal of nitrates from water by these nanocomposite materials is new in the field of adsorption. Al and f-MWCNTs were expected to improve the solubility, swelling and adsorption properties of CTs.

2. Experimental

2.1. Synthesis and functionalization of MWCNTs

Multi-walled carbon nanotubes (MWCNTs) were synthesized and functionalized according to a procedure reported by Mhlanga et al., 2009. Typically, acetylene (C_2H_2) was used as a source of carbon and was decomposed at 700 °C in a N_2 atmosphere on a Fe–Co/$CaCO_3$ catalyst. The obtained MWCNTs were treated with a mixture of sulphuric acid (H_2SO_4) and nitric acid (HNO_3) (3:1 composition) using microwave irradiation (Ko et al., 2004; Lee et al., 2010). The MWCNTs were characterized using a FEI Tecnai T12 transmission electron microscopy (TEM), a Perkin Elmer 100 Fourier transform infrared-attenuated total reflectance (FTIR-ATR) spectrometer, a Perkin Elmer 200 Raman microscope, an Ultima-IV X-ray diffractometer, a Micromeritics ASAP 2020 Surface Area and Porosity Analyzer and a Malvern Zetasizer Nano-ZS Nano series.

2.2. Preparation of CTsAl/f-MWCNT nanocomposite beads

A chitosan-alumna/functionalized-multiwalled carbon nanotube (CTsAl/f-MWCNT) gel was prepared by chelating Al, f-MWCNTs and CTs (in a ratio of ratio of 1:0.25:3.75) in oxalic acid using a modified procedure reported by Li et al., 2013. Firstly, Al purchased from Sigma-Aldrich was oxidized with 10% oxalic acid as a surface coating material and then was washed with deionized water to pH 7. The sludge was dried in an oven at 110 °C overnight. The oxidized Al powder and f-MWCNTs was added to 2% CTs gel as prepared by Ngah and Fatinathan (2010) and Chatterjee and Woo (2009). The mixture was stirred for 24 h and then de-gassed. The gel was added dropwise into a precipitation bath containing 2 M sodium hydroxide (NaOH) solution. The beads that formed were washed with distilled water to pH 7 and dried in an oven at 60 °C overnight and then characterized using a Perkin Elmer 100 FTIR-ATR spectrometer, a Perkin Elmer 4000 thermogravimetric analyzer (TGA), a Micromeritics ASAP 2020 Surface Area and Porosity Analyzer and a scanning electron microscope (SEM) coupled with energy dispersive spectroscopy (EDS). Pure CTs beads (without Al and f-MWCNTs) were used as control.

2.3. Adsorption studies

The adsorption of nitrates from water by the CTs-Al/f-MWCNT beads was carried out in a batch adsorption process. Exactly 50 mL nitrate solution of desired concentration (50 gm/L optimal concentration) was placed in a flask and a known amount (1 g) of CTs-Al/f-MWCNT beads was agitated at room temperature for a certain time after which the concentration of nitrates in the solutions were analyzed using Dionex ion chromatography spectroscopy 2000 (ICS).

To evaluate the effect of pH on nitrates adsorption capacity by the beads, the experiments were carried out over a pH range (pH

Table 1
Effects of nitrates and nitrites on human beings.

NO_3^-/NO_2^- range (mg/L N)	Effects
0–6	No adverse health effects.
6–10	Rare instances of methaemoglobinaemia in infants; no effects in adults. Concentrations in this range generally well tolerated.
10–20	Methaemoglobinaemia may occur in infants. No effects in adults.
>20	Methaemoglobinaemia occurs in infants. Occurrence of mucous membrane irritation in adults.

Please cite this article in press as: Masheane, M.L., et al., Chitosan-based nanocomposites for de-nitrification of water, Physics and Chemistry of the Earth (2016), http://dx.doi.org/10.1016/j.pce.2016.10.004