Available online at www.sciencedirect.com
ScienceDirect
Chemosphere 69 (2007) 289–294
CHEMOSPHERE
www.elsevier.com/locate/chemosphere

Removal of phosphate from water by a highly selective La(III)-chelex resin

Rudolf S.S. Wu *, K.H. Lam, Joyce M.N. Lee, T.C. Lau *

Centre for Coastal Pollution and Conservation, Department of Biology and Chemistry, City University of Hong Kong, Tat Chee Avenue, Kowloon, Hong Kong, China

Received 3 November 2006; received in revised form 26 March 2007; accepted 2 April 2007
Available online 24 May 2007

Abstract

A new polymer ligand exchanger (PLE) has been developed for the removal of phosphate in wastewater. This PLE, consisting of lanthanum(III) bound to chelex-100 resin, was prepared by passing $LaCl_3$ solution through a column of chelex-100. Uptake of phosphate from water by this La-chelex resin was investigated in the column mode. The La-chelex resin was able to remove phosphate efficiently from water, and the uptake of phosphate was not affected by the presence of large amounts of anions (0.1 M) such as chloride and sulfate. The La-chelex resin was also able to efficiently remove phosphate from seawater to <0.1 mg-P l^{-1}, and regenerated for reuse by removing the sorbed phosphate by eluting with 6 M HCl.

Keywords: Phosphate removal; Phosphate sorption; Lanthanum(III)-chelex resin; Polymer ligand exchanger

1. Introduction

Phosphate is the major limiting nutrient in freshwater systems and excessive amounts of phosphate may cause eutrophication and pose significant environmental problems to water resources. In water bodies with poor circulation, phosphate concentrations as low as 1 mg-P l^{-1} is sufficient to stimulate algal blooms (Zhao and Sengupta, 1996). Thus, it is not surprising that extensive research effort has been devoted to the removal of phosphate in waste water in order to reduce anthropogenic input of phosphate into aquatic systems (Matejka and Weber, 1990; Ozaki et al., 1991; Urano and Tachikawa, 1991; Vural et al., 1995; Matsunaga et al., 1996; Cengeloglu et al., 1998; Strickland, 1998; Oguz et al., 2003). Approaches thus far include employment of chemical precipitation, adsorbents and biological removal (Eckenfelder and Argaman, 1991; Jenkins and Hermanowicz, 1991; Stensel, 1991; Zhao and Sengupta, 1996). Chemical precipitation and biological removal, however, are generally not able to remove phosphate to levels that can satisfy many stringent effluent standards (Zhao and Sengupta, 1998).

Recently, the use of polymeric ligand exchangers (PLEs) to remove anions in water has attracted much attention (Zhao and Sengupta, 1998; Henry et al., 2004; Zhu and Jyo, 2005). A PLE consists of a polymer with chelating functional groups that can bind tightly to a transition metal, which can remove anions from water by complex formation. For the purpose of water treatment using PLE, the following properties are desirable: (1) the polymer should have a high affinity and capacity to bind metals, (2) there should be little or no leakage of metal from the ligand during operation, (3) the metal should have a high affinity for binding the anion of target removal, (4) the PLE sorbent should be easily regenerated, and (5) the performance of the PLE should be insensitive to changes in environmental parameters such as temperature, pH and salinity. Although a number of polyvalent metal ions, including

* Corresponding authors. Tel.: +86 852 2788 7401; fax: +86 852 2788 7406 (R.S.S. Wu), Tel.: +86 852 2788 7811; fax: +86 852 2788 7406 (T.C. Lau).

E-mail addresses: bhrswu@cityu.edu.hk (R.S.S. Wu), bhtclau@cityu.edu.hk (T.C. Lau).

0045-6535/$ - see front matter © 2007 Elsevier Ltd. All rights reserved.
doi:10.1016/j.chemosphere.2007.04.022

Cu(II), Co(II), Fe(III), Al(III), Y(III), La(III), Mo(VI) and Ti(IV), have been successfully immobilized on chelating resins for anion removal (Chanda et al., 1988; Kanesato et al., 1988; Matejka and Weber, 1990; Popat et al., 1994; Haron et al., 1995; Vural et al., 1995; Matsunaga et al., 1996; Jyo et al., 1997; Zhao and Sengupta, 1998; Dambies et al., 2000; Balaji and Matsunage, 2002), the use of these PLEs has been very limited thus far because of their poor selectivity, poor regeneration and gradual loss of the sorbents' loading capacity due to fouling.

Here we report a study on sorption of phosphate from water by a novel PLE designed in our laboratory. This PLE consists of La(III) bound to chelex-100. Chelex-100 is a copolymer of styrene and divinylbenzene that contains iminodiacetate groups. It has been widely used for the removal of metal ions from water due to the strong chelating properties of its functional groups. This is the first attempt to use chelex-100 in conjunction with a metal ion for the removal of anions from wastewater. The use of La(III) for sorption of phosphate confers the following advantages: (1) La(III) has a high affinity for oxyanions such as phosphate because of its hard Lewis acidic property (Cotton et al., 1995), and it has been used successfully for removal of fluoride ions from water (Kanesato et al., 1988). (2) La(III) has a very high affinity to the iminodiacetate functional group of chelex-100 (due to the anionic nature and the presence of N, O donor atoms) and the risk of metal leakage during sorption of phosphate would be minimized. (3) The large coordination numbers of La(III) (up to 12) ensures ample labile coordination sites for binding phosphate after coordination of iminodiacetate. (4) Being substitution labile (the water exchange rate is around $10^8\ s^{-1}$ at room temperature), La(III) makes phosphate uptake very fast and equilibrium can be reached within a short period of time.

2. Materials and methods

2.1. Materials

Chelex-100 resin was purchased from Bio-Rad Laboratories, Inc. (50–100 mesh, sodium form). $LaCl_3 \cdot 7H_2O$ was purchased from International Laboratory (99%, Saint Petersburg FL, USA). Hydrochloric acid and sodium hydroxide were of analytical grade from Riedel-de Haën (RDH). Milli-Q water (18 MΩ) used in all experiments was obtained from a Milli-Q (Millipore) water purification system. Phosphate solution was prepared with analytical grade sodium dihydrogen phosphate.

All glasswares used in this study were carefully cleaned with detergent, deionized water and soaked in acid bath for at least 12 h.

2.2. Preparation of La(III)-chelex resin for phosphate sorption

Two g of sodium-form chelex-100 resin were soaked in 50 ml deionized water for 2 h before transferring to a glass column (internal diameter 1 cm). The packed column was then rinsed with 50 ml of water, and La(III)-chelex resin was prepared by passing 50 ml of 0.1 M $LaCl_3$ at a flow rate of 1 drop (~0.05 ml) s^{-1} through the column. The column was again rinsed with 50 ml of water. The total amount of La(III) bound to chelex-100 was calculated from the difference of La(III) concentration between the feed solution and the effluent, using ICP-MS (Perkin–Elmer Elan 6100 DRC). All experiments were carried out at room temperature.

2.3. Phosphate sorption by La(III)-chelex resin under different conditions

Seventy ml of phosphate solutions (sodium dihydrogen-phosphate) of different concentrations, pH, and electrolyte make up were freshly prepared and were fed at a flow rate of 1 drop s^{-1} to a glass column (diameter: 1 cm, length: 50 cm) packed with 2 g of La(III)-chelex resin. The pH values of the phosphate feed solutions were adjusted by either HCl or NaOH.

2.4. Phosphate recovery and column regeneration

Phosphate sorbed on the resin inside the glass column was eluted with either 6 M sodium hydroxide solution or 6 M HCl at a flow rate of 0.5 drop s^{-1}. The La(III)-chelex resin column was then washed with distilled water until the pH of effluent was 7. Afterwards, 50 ml of 0.1 M NaOH solution was fed to the column to regenerate the resin to the sodium form, followed by adding another 50 ml of 0.1 M $LaCl_3$ solution to replenish possible loss of La. The extent of phosphate sorption on the La(III)-chelex resin was assessed from its breakthrough curves. The breakthrough point is defined as the bed volumes of feed solution provided to the resin column when the phosphate concentration in the column effluent reaches 5% of that in the feed solution. Bed volume refers to the ratio of feed solution volume to the fixed resin bed volume (ml/ml-resin). Phosphate concentrations were measured using a flow-injection analyzer (LACHAT Instruments Quik-Chem 8000).

2.5. Effects of pH on phosphate removal

The pH is expected to affect the sorption of phosphate since the various phosphate species may have different affinities for the La(III)-chelex resin. The sorption behavior of phosphate was thus investigated in the pH range of 3–8.

2.6. Removal of phosphate from seawater

Wastewater in Hong Kong is saline (approximately 10‰) since seawater is being used in flushing toilets. Sorption of phosphate in sea water by the La(III)-chelex resin was therefore also investigated. The seawater samples were first filtered with Millipore filters (0.45 μm) and then spiked