



## Enhanced phosphate selectivity from wastewater using copper-loaded chelating resin functionalized with polyethylenimine

Byungryul An<sup>a</sup>, Juhee Nam<sup>a</sup>, Jae-Woo Choi<sup>a</sup>, Seok-Won Hong<sup>a</sup>, Sang-Hyup Lee<sup>a,b,\*</sup>

<sup>a</sup> Center for Water Resource Cycle Research, Korea Institute of Science and Technology, Hwarangno 14-gil 5, Seongbuk-gu, Seoul 136-791, Republic of Korea

<sup>b</sup> Graduate School of Convergence Green Technology and Policy, Korea University, Anam-ro, Seongbuk-gu, Seoul 136-701, Republic of Korea

### ARTICLE INFO

#### Article history:

Received 20 May 2013

Accepted 17 July 2013

Available online 29 July 2013

#### Keywords:

Phosphate  
Ion exchanger  
Selectivity  
Regeneration

### ABSTRACT

In water and wastewater, phosphate is considered a critical contaminant due to cause algae blooms and eutrophication. To meet the stringent regulation of phosphate in water, a new commercial chelating resin functionalized with polyethylenimine was tested for phosphate removal by loading  $\text{Cu}^{2+}$  and  $\text{Fe}^{2+}/\text{Fe}^{3+}$  to enhance selectivity for phosphate. Batch and column experiments showed that CR20-Cu exhibited high selectivity for phosphate over other strong anions such as sulfate. The average binary phosphate/nitrate and phosphate/sulfate factors for CR20-Cu were calculated to be 7.3 and 4.8, respectively, which were more than 0.97 and 0.22 for a commercial anion exchanger (AMP16). The optimal pH for the phosphate removal efficiency was determined to be 7. According to the fixed-bed column test, the breakthrough sequence for multiple ions was  $\text{HPO}_4^{2-} > \text{SO}_4^{2-} > \text{NO}_3^- > \text{Cl}^-$ . Saturated CR20-Cu can be regenerated using 4% NaCl at pH 7. More than 95% of the phosphate from CR20-Cu was recovered, and the phosphate uptake capacity for CR20-Cu was not reduced after 7 regeneration cycles.

© 2013 Elsevier Inc. All rights reserved.

### 1. Introduction

The discharge of phosphorus as a nutrient in wastewater enters the environment from municipal, industrial, human, detergent, and natural sources. It leads to serious environmental problems, such as algae blooms and eutrophication. Moreover, it has been reported that the concentration of phosphorus has significantly increased [1] and continues to increase in Europe [2]. Although concentrations of phosphorus are currently unregulated in drinking water, phosphate ranging from 0.03 to 0.1 mg/L is associated with algae blooms [3,4]. To prevent algal growth, the USEPA has recommended that the total phosphates which comprise the phosphorus concentration in water should not exceed 25  $\mu\text{g}/\text{L}$  in a lake or reservoir [3].

In general, phosphorus is present in various forms of phosphate in solution, including organic phosphate, metaphosphates, orthophosphate, and polyphosphate. Among these four forms, the most predominant species of phosphate in treated municipal and industrial wastewater is orthophosphate which has three acid ionization constant ( $\text{p}K_{\text{a}1} = 2.1$ ,  $\text{p}K_{\text{a}2} = 7.2$ , and  $\text{p}K_{\text{a}3} = 12.3$ ), indicating that at above pH 7.2, the primary species that exists in the aqueous phase is  $\text{HPO}_4^{2-}$  [5].

There are a variety of conventional and advanced technologies used in the treatment of phosphate from wastewater. Biological treatment, chemical precipitation, and adsorption are some of the existing technologies used to remove phosphate. Biological treatment does not require the addition of chemical reagents for high removal efficiency. However, biological treatment processes are sensitive to seasonal and diurnal variations in temperature and to changes in feed composition, which are needed to maintain high-efficiency removal [6]. Chemical precipitation, which involves adding calcium, aluminum and iron, is a traditional and effective method that has long been used as a way to regulate phosphate concentrations. Nevertheless, both chemical and biological treatment methods have difficulty removing phosphorus below 0.1 mg/L [7–9] and require further treatment to dispose of the large amount of sludge that is produced.

To overcome these drawbacks, adsorption using ion exchanger (IX) was considered to be an alternative method to effectively remove phosphate from water and wastewater. According to prior research [10], the use of IX in the field of water treatment has proven operational simplicity, adaptability to change flow rates and input compositions, and reusability. With these advantages, IX is currently one of the EPA-identified best available technologies (BAT) for the removal of arsenate [11], which is characterized by similar behavior to phosphate in water. However, the target contaminants can be significantly less efficient when current commercial strong base anion (SBA) resins are used. Clifford [10] and Zhao and SenGupta [12] reported that in using IX for arsenate removal,

\* Corresponding author at: Center for Water Resource Cycle Research, Korea Institute of Science and Technology, Hwarangno 14-gil 5, Seongbuk-gu, Seoul 136-791, Republic of Korea. Fax: +82 2 958 5839.

E-mail address: yisanghyup@kist.re.kr (S.-H. Lee).

the removal capacity was highly dependent on the presence of other dissolved anions, such as sulfate, which is commonly present in wastewater at much higher concentrations than phosphate due to the strong competition between phosphate and sulfate on the active sites.

The concept of ligand exchange based on organic ion exchanger was first introduced by Helfferich [13] to separate and isolate ammonia and diamine, which can form complexes or adducts with transition metal ions ( $\text{Cu}^{2+}$  and  $\text{Ni}^{2+}$ ). Later, a new ligand exchanger was prepared and used to remove arsenate by loading ferric ions onto a weak base chelating resin [14]. Due to the low amount of  $\text{Fe}^{3+}$  loaded onto the chelating resin, Ramana and SenGupta [15] and Zhao and SenGupta [12] tried to replace  $\text{Fe}^{3+}$  with  $\text{Cu}^{2+}$  on the same chelating resins (known as DOW 2N and 3N) with 2-picolylamine and di(2-picolyl)amine groups, respectively. Using a ligand exchanger loaded with  $\text{Cu}^{2+}$  resulted in the higher selectivity of phosphate over sulfate and increased the removal efficiency of phosphate despite high concentrations of sulfate. In this paper, organic-based chelating resin functionalized with polyethylenimine was used as the parent resin, and copper and iron were loaded onto the surface of this parent resin as functional groups.

The overall goal of this study was to explore new ways to achieve the selective separation of strong ligands such as phosphate. The specific objectives were to (1) prepare a new Polymeric Ligand Exchanger (PLE) using CR20 chelating resin, (2) determine and characterize the phosphate adsorption capacity for the new PLE, (3) perform column tests to obtain breakthrough behavior, and (4) investigate the availability of regeneration for a saturated PLE.

## 2. Materials and methods

### 2.1. Materials

In this study, two ion exchanger resins were used to investigate phosphate removal. A commercial chelating resin (CR20, Mitsubishi Chemical, Japan) with polyethylenimine groups as the parent resin was compared with a commercial anion exchanger resin (AMP16, Samyang Chemicals, Ulsan, Korea). Three different copper salts, i.e.,  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ ,  $\text{CuSO}_4 \cdot 2\text{H}_2\text{O}$ ,  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  and NaOH and HCl were used, and all were ACS grade. All solutions were prepared with ultrapure, deionized (DI, 18.2 M  $\Omega$ ) water.

### 2.2. Synthesis of modified ion exchanger

The procedure for loading the copper onto CR20 followed that of An et al. [16], except for the initial copper solution concentration. Both the CR20 and AMP16 resins were first conditioned using 1 M HCl, DI water, and 1 M NaOH for 3 h, sequentially. After rinsing with DI water until the pH reached 7.0, AMP16 resin was dried in air and then tested. For CR20 chelating resin, the process was as follows. First 10 g of  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  was dissolved in 500 mL DI in three round-bottom flasks, and then, 100 g of CR20 was added to the 2% copper solution. During the day, the mixed copper solution was kept at 70 °C, which can enhance the copper loading kinetics and stability by swelling the resin, and it was then brought down to ambient temperature at night ( $\sim 21$  °C). The solution took two weeks to reach copper equilibrium. During preparation, the pH was kept at  $4.0 \pm 0.2$  with dilute NaOH and HCl, and nitrogen gas was fed into the solution at regular intervals. After two weeks, the resin was rinsed with DI several times and air-dried. The CR20 loaded with Cu was referred to as CR20-Cu. This same procedure was used to prepare CR20-Cu from solutions of  $\text{CuSO}_4$  and  $\text{Cu}(\text{NO}_3)_2$ .

### 2.3. Batch adsorption test

Isotherm tests for both resins in 55 mL tubes were conducted by adding different initial concentrations of phosphate ranging from 0 mg/L to 100 mg/L at 0.05 mg of each resin. The mixture was then gently rotated at 30 rpm for 48 h, which is enough time to reach equilibrium, as confirmed by kinetic tests for both resins. After 48 h, 5 mL samples from each tube were taken out, filtered with a 0.2  $\mu\text{m}$  filter, and then analyzed for  $\text{PO}_4^{2-}$ ,  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$  and  $\text{Cl}^-$ . According to the preliminary tests, the additional process of filtration using syringes did not affect the concentrations of phosphate or other anions. The pH of the solution was initially 7.5–8.0 and was maintained using dilute HCl and NaOH. The amount of uptake for each anion was calculated using the following equation based on mass balance:

$$q_e = \frac{V(C_o - C_e)}{M} \quad (1)$$

where  $q_e$  is the equilibrium mass uptake of phosphate by a sorbent (mg/g),  $V$  is the solution volume (L),  $C_o$  and  $C_e$  are the initial and final concentrations of phosphate in solution, respectively (mg/L), and  $M$  is the mass of a sorbent added (g).

Another batch experiments were conducted to determine the removal efficiency of phosphate with competing ions. 250 mL solution containing 100 mg/L of nitrate, phosphate, and sulfate was prepared at 0.25 g of each resin. The mixture samples were shook at 150 rpm on a platform shaker (JSSI-100C) under the same experiment condition of isotherm tests.

### 2.4. Fixed-bed column test

Fixed-bed column tests were performed to test the phosphate breakthrough profiles of both anion exchangers. The column test setup included an acrylic column (10 mm in diameter and 150 mm in length), MasterFlex L/S pump, and GILSON FC203B collector. For each column test, 1.5 g of each resin was packed into column with a 0.45  $\mu\text{m}$  filter at the bottom of column to protect against the loss of resin beads. The influent passed in the down-flow mode contained phosphate and other competing ions, such as nitrate, and sulfate, and the pH was initially fixed at 7.5. The physical operating conditions for the flow rate and superficial liquid velocity (SLV) were 1.0 mL/min and 0.76 m/h, respectively. The effluent was automatically collected in 8.5 mL glass tubes and was stored in a refrigerator until analysis.

### 2.5. Regeneration and reuse

Regeneration of saturated CR20-Cu was carried out in the batch test with 4% and 8% NaCl for 6 h. During regeneration, the solution pH was kept at 7.0. After regeneration of CR20-Cu, the regenerated resin was reused with the same batch conditions described in Section 2.3. All batch experiments were duplicated.

### 2.6. Chemical analyses

Phosphate, sulfate, nitrate, and chloride were analyzed by Dionex Ion Chromatography (Model: ICS-1000, USA), and Inductively Coupled Plasma (ICP) (model: Agilent 700 series, USA) was used for copper and iron analyses. Fourier transform infrared spectroscopy (FTIR) was used to determine the formation of copper and iron (model: spotlight 200, PerkinElmer, USA). The solution pH was measured using an ORION Star A211 (Thermo scientific, USA).

Download English Version:

<https://daneshyari.com/en/article/6998925>

Download Persian Version:

<https://daneshyari.com/article/6998925>

[Daneshyari.com](https://daneshyari.com)