



Preparation and characterization of zirconia-loaded lignocellulosic butanol residue as a biosorbent for phosphate removal from aqueous solution



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ABSTRACT

Zirconium(IV) loaded lignocellulosic butanol residue (LBR-Zr) used for the adsorption of phosphate (P) ions from aqueous solution was synthesized and evaluated. The adsorption isotherms were fitted well with the Freundlich and Temkin modes. Thermodynamic analyses indicated that phosphate adsorption on the LBR-Zr increased with increasing temperature from 298 to 338 K. The kinetic datas were described better by the pseudo-second-order adsorption kinetic rate model. Increasing pH suppressed phosphate adsorption. Coexisting anions study exhibited that the incorporation of CO_3^{2-} anion had the largest influence on the phosphate adsorption capacity. The mechanism of adsorption process on LBR-Zr was analyzed by FTIR (Fourier transform infrared spectroscopy), scanning electron microscope (SEM) with an EDX (energy dispersive X-ray) and X-ray photoelectron spectroscopy (XPS) technologies, respectively. The above results confirmed that surface hydroxyl groups on biosorbent LBR-Zr were replaced by phosphate. The LBR-Zr with good specific affinity towards phosphate was a promising biosorbent for phosphate removal from aqueous solution. The research would be beneficial for developing a promising, eco-friendly phosphate biosorbent from plentiful lignocellulosic butanol residue.

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1. Introduction

Phosphorus (P) is a very important limiting nutrient for growth of organisms [1]. It plays a major role in the development of animals, plants and the industrial manufacture [2]. However, the extensively application of phosphate has caused serious environmental issues. Particularly, the residue of phosphates in water with a large amount may cause eutrophication leading to excessive growth of algal called algal blooms [3]. Furthermore, it is recommended that a criterion maximum contaminant level for phosphate ions is less than 0.05 mg L^{-1} by the United States Environmental Protection Agency (USEPA) [4]. As a consequence, it is necessary to develop certain efficient methods to remove phosphate ions from water. Presently, the methods used for the removal of phosphate from water were summarized as chemical precipitation, ion exchange, crystallization, biological treatment, and adsorption methods [1,5–9]. Among

these methods, the adsorption method is usually considered to be superior to other techniques when being applied in the remove of pollutants from aqueous solutions because of its simpleness, effectivity, and low cost [10]. There has been growing interest in developing novel, low-cost and sustainable biosorbents for phosphate removal using renewable agricultural by-products such as apple peels [11], okara [12], soybean milk [13], aspen wood fiber [14], eggshell [15], wood particles [16], coir pith [17], orange waste gel [1].

The lignocellulosic butanol residue is a byproduct obtained from industrial of bio-butanol, a superior liquid fuel with a potential to substitute for fossil fuel. The bio-butanol was produced by the method of biorefinery processes based on agricultural biomass such as wheat straw and corn, and meanwhile, and generated a larger quantity of lignocellulosic butanol residue (LBR) as a by-product [18]. As expected, the further utilization of LBR therefore can reduce the cost of production of bio-butanol [19]. Lignin is the main component of LBR, in which the content of lignin is higher than eighty percent. It was acknowledged that lignin exhibited high capture abilities to various heavy metals [20–23]. To the best of our

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Table 1
Composition and functional group content of LBR (wt.%).^a

Sample	Ash	Lignin	Holocellulose	Polysaccharide	Total hydroxyl	Phenolic hydroxyl	Aliphatic hydroxyl	Methoxyl
LBR	3.9	81.0	11.9	1.5	20.9	3.3	17.6	2.7

^a The data was from Zhang et al. [18].

knowledge, it has not been reported the utilization of LBR for removal phosphate.

Generally, cationic binding sites were usually introduced into sorbent by metal impregnation to improve their uptake capacity of phosphate. As a consequence, cationization of agricultural by-product is widely used for activating its phosphate sorption ability using metal salts. Many studies have been reported, which confirm the enhanced phosphate removal of metals loaded biosorbents [2,12,16,24].

For LBR, apart from the function groups (e.g. –OH) derived from lignin, it also reported to have –CHO and –COOH, which allows LBR to be facily chemical modification. For example, the introduction of alkoxyamine ligands can afford LBR with anion exchange abilities. Therefore, these unique properties of LBR enable LBR to be a promising substrate for developing phosphate biosorbents [25–29].

During the last decades, several different metallic oxides including Fe(III), La(III), Zn(IV), and Ce(III) oxides used as cationic binding site, have been developed as phosphate adsorbents [14,17,30,31]. Among of these metal oxides, hydrous Zr(IV) oxide has been receiving lots of in eliminating phosphate because of its high binding affinity for phosphate and high physicochemical stability over the whole pH range [32]. Furtherly, our previous studies also demonstrated that incorporating hydrous zirconium could dramatically improve phosphate sorption abilities of nano-paricles [32,33].

Herein, in this context, we immobilized zirconium oxide (ZrO₂) to LBR by post-grafting method, which can be used as a novel biosorbent (LBR-Zr) for removing phosphate ions from water. To the best of our knowledge, our research is the first report to load zirconium on LBR as adsorbent for phosphate removal from aqueous solution.

In this work, the feasibility of using ZrO₂-loading LBR biosorbent (LBR-Zr) as an adsorbent for phosphate removal from aqueous solutions was evaluated in batch experiments. The absorption isotherms, kinetics involved in the adsorption process were discussed. Meanwhile, several factors affecting the phosphate adsorption such as pH value, initiate phosphate concentration, temperature and the incorporation of foreign anions were also investigated. In addition, the underlying mechanism for phosphate adsorption was fully studied by SEM-EDX, FTIR and XPS technologies. This study could provide a new pathway for phosphate adsorption based on by-products of the bio-butanol industries (lignocellulosic butanol residue).

2. Materials and methods

2.1. Materials

The lignocellulosic butanol residue (LBR) used in the present study was a byproduct of a biobutanol industrials supplied by songyuan bairui bio-polyos Co., Ltd. (China) and used without further purification. The LBR mainly contained 81.0 wt.% lignin, 11.9 wt.% Holocellulose, 3.9 wt.% Ash and so on [18], and the results are shown in Table 1. Zirconium isopropoxide (Zr(OC₃H₇)₄) solution in propanol was purchased from Aldrich Chemical Co., Ltd. and used as received without further purification. All the other chemical reagents such as KH₂PO₄, KCl, KNO₃, K₂SO₄, KHCO₃, K₂CO₃, NaF, NaOH and HCl were of analytical grade and used as obtained.

2.2. Preparation of lignocellulosic butanol residue loading Zr(IV) (LBR-Zr)

The reaction was carried out in a dry 50 mL schlenk flask equipped with a magnetic stirrer. A 1.0 g of LBR was dissolved in 20 mL DMSO with stirring until the reaction mixture became homogeneous. The schlenk flask was immersed in a silicone oil bath set at 110 °C. 1.5 mL of 70% zirconium isopropoxide (Zr(OC₃H₇)₄) solution in propanol was gradually added into the above mixture and the reaction was run for 3 h with stirring. The resulting product was finally precipitated with *n*-hexane, collected and washed successively by anhydrous ethanol and deionized water in sequence. The precipitation was dried under vacuum until a constant weight was reached, and the resulting material was denoted as LBR-Zr. The obtained LBR-Zr was stored in a desiccator for further use.

2.3. Adsorption studies

The adsorption experiments were conducted in batch method at 298 K. Appropriate amount of anhydrous KH₂PO₄ was dissolved in distilled water as a phosphate ion stock solution (1000 mg PL⁻¹) and then further diluted to desired concentration. Each experiment was conducted at the pH of the stock solution (6.0 ± 0.2), which was adjusted to desired value with 0.1 mol L⁻¹ HCl or 0.1 mol L⁻¹ NaOH solution. At the end of adsorption process, all samples containing phosphate were filtered through a 0.45-μm membrane filter and then the concentrations of phosphate ions were determined by molybdate blue spectrophotometric method. All the sorption experiments were performed in duplicate, and the experimental details were given in the related figures and tables. The equilibrium sorption capacity was calculated from:

$$q_e = \frac{(C_0 - C_e)V}{m} \quad (1)$$

where q_e (mg g⁻¹) is the equilibrium adsorption amount, C_0 (mg L⁻¹) is the initial phosphate concentration, C_e (mg L⁻¹) is the equilibrium concentration, V (mL) is the solution volume, and m (g) is the adsorbent mass.

The adsorption kinetic experiments for LBR-Zr were carried out at 298 K, and initial concentrations were 5, 10 and 20 mg PL⁻¹ with pH 6.0 ± 0.2 respectively. After a specific time interval, about 1.0–2.0 mL aliquots were withdrawn from the suspensions for the analysis of phosphate concentrations. The study of the pH (2–8) dependency of phosphate onto LBR-Zr was carried out with 40 mg L⁻¹ initial phosphate concentration at 298 K. The effect of temperature was studied by using 20 mg L⁻¹ initial phosphate concentration at three temperatures (298, 318 and 338 K). The effect of foreign anions (Cl⁻, NO₃⁻, F⁻, SO₄²⁻, CO₃²⁻ and HCO₃⁻) with concentrations of 300 mg L⁻¹ separately was also investigated at 298 K under a fixed initial concentration of 40 mg L⁻¹ phosphate solutions, and initial solution pH of 6.0 ± 0.2.

2.4. Adsorbent characterization

2.4.1. X-ray photoelectron spectroscopy (XPS) analysis

The chemical composition of LBR, LBR-Zr and LBR-Zr-P (after phosphate adsorption) samples were carried out to investigate using a PHI 5000 Versa Probe XPS spectrometer (ESCALAB 250 US Thermo Electron Co.), and the experimental data were fitted with

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