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Removal of phosphate anions using the modified chitosan beads: Adsorption kinetic, isotherm and mechanism studies

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ABSTRACT

A new chitosan biosorbent modified with zirconium ions (ZCB) was prepared and employed for the adsorption of phosphate ions from aqueous solution. Batch of experiments were performed to investigate the effects of various conditions on the phosphate adsorption, including contact time, the initial concentration of phosphate ions, temperature and pH. The experimental data were interpreted elaborately by the different models of adsorption kinetics and isotherms. The results showed that the kinetic data were well fitted to the pseudo first-order and second-order models, indicating that the adsorption behaviors were mainly ascribed to both physic-sorption and chemic-sorption. The further analysis of kinetics indicated that the intra-particle diffusion was the rate controlling process. The equilibrium data were best described by the Langmuir isotherm model with maximum monolayer adsorption capacity of 60.6 mg g^{-1}. The values of $\triangle G°$, $\triangle S°$ and $\triangle H°$ revealed that the nature of adsorption was feasible, spontaneous and endothermic. FTIR, EDS, XPS and zeta potential studies suggested that the adsorption mechanism was possibly attributed to the electrostatic attraction and ion exchange reaction between ZCB and phosphate ions.

1. Introduction

Phosphorus (P) is one of the essential elements and important nutrients for the growth of organisms and the normal functioning of ecosystems. However, its extensive use in agriculture and industry as fertilizer and detergent inevitably poses the large quantities of P-bearing wastes and many pollution problems, notably eutrophication which can lead to algal bloom, fish death, loss of aquatic species and parasite infection [1–3]. According to the Environmental Protection Agency (EPA), the maximum permissible level and the stringent discharge limit of phosphate ions are 0.1 mg L^{-1} and less than 0.05 mg L^{-1}, respectively [1,4]. Therefore, it is necessary to develop certain efficient methods for phosphate ion removal from water and wastewater.

In last decades, there were various methods for phosphate removal from wastewater including chemical precipitation [5], ion exchange [6], biological treatment [7] and adsorption [8]. The first three methods for phosphate removal had many problems, such as instability, sophistication in operation and second-pollution. However, the adsorption method was considered to be the most promising technique due to simplicity and flexibility of design, ease of operation and cost-effectiveness [9]. Therefore, it was pressing to develop a high performance adsorbent to remove large amounts of phosphate ions from different types of wastewaters.

Chitosan, presented in crustacean shells, is the second most amount of natural polymer after cellulose [10]. Due to many advantages or unique features such as readily available, non-toxic, biocompatible,

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Abbreviations: CTS, chitosan; ZCB, zirconic chitosan beads; PCB, phosphate adsorbed zirconic chitosan beads; SEM, scanning electron microscopy; EDS, energy dispersive X-ray; XPS, X-ray photoelectron spectroscopy; FT-IR, Fourier transform infrared spectrometer; ICP-OES, inductively coupled plasma-optical emission spectrometer; q_e, amount of adsorbent in solid phase (mg g^{-1}); C_o, initial concentration of phosphate in equilibrium (mg L^{-1}); C_e, equilibrium concentration of phosphate in equilibrium (mg L^{-1}); V, volume of aqueous solution; m, mass of ZCB composite (g); t, time (min); q_t, amount of phosphate on the surface of ZCB at time t (mg g^{-1}); C_t, concentration of phosphate in aqueous solution at time t (mg L^{-1}); k_1, rate constant of pseudo-first-order adsorption (min^{-1}); k_2, second-order rate constant of pseudo-second-order adsorption (g mg^{-1} min^{-1}); k_p, equilibrium particle rate constant of particle diffusion adsorption ($min^{-1/2}$); k_i, equilibrium intra-particle rate constant of particle diffusion adsorption (mg g^{-1} $min^{-0.5}$); α, initial adsorption rate constant (mg g^{-1} min^{-1}); β, related to the extent of surface coverage and activation energy for chemic-adsorption (g mg^{-1}); k_F, Freundlich isotherm constant (L g^{-1}); $1/n$, heterogeneity factor (dimensionless); q_{max}, maximum adsorption capacity of adsorbent (mg g^{-1}); b, Langmuir adsorption constant (L mg^{-1}); R_L, equilibrium parameter; a_T, equilibrium binding constant corresponding to the maximum binding energy (L g^{-1}); b_T, Temkin constant related to the heat of adsorption (kJ mol^{-1}); k_{DR}, constant related to the mean free energy of adsorption (mol^2 kJ^{-2}); X_m, theoretical saturation capacity (mg g^{-1}); ε, Polanyi potential(kJ mol^{-1}); E, mean energy of adsorption (kJ mol^{-1}); q_m, amount of phosphate adsorbed at equilibrium (mg g^{-1}); C^*, saturation concentration (mg L^{-1}); E_s, characteristic energy of adsorption (kJ mol^{-1}); R^2, correlation coefficient; $\triangle G°$, standard free energy change (kJ mol^{-1}); $\triangle H°$, standard free enthalpy change (kJ mol^{-1}); $\triangle S°$, standard free entropy change (kJ mol^{-1} K^{-1}); R, universal gas constant (8.314 J mol^{-1} K^{-1}); T, temperature in Kelvin; K_o, thermodynamic equilibrium constant for the adsorption reaction; E_a, activation energy of adsorption (kJ mol^{-1}); S^*, sticking probability; θ, surface coverage.

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reactive as well as adsorptive [11], there is the extensive application of chitosan and its derivatives as biosorbent especially in pollutant removal from wastewater. However, some chitosan-modified adsorbents exhibited low capacity, long treatment time and inefficiency of phosphate adsorption from aqueous solutions [1,12,13]. Therefore, certain new chitosan-based adsorbents would be needed to study for treatment of phosphate-contaminated waters.

Recently, zirconium(IV) modifying composite has always been investigated for removal of pollutant from aqueous solution by many researchers, such as zirconium impregnated cashew nut shell carbon [14], granular zirconium-iron oxide [15] and chitosan supported zirconium(IV) tungstophosphate composite [16]. The main reason is that tetravalent zirconium ions are easily hydrolyzed even to form tetranuclear ions or octanuclear species, resulting in a large number of hydroxyl ions and water molecules, which can take part in the ligand exchange reaction with the target pollutant. Therefore, in this study, Zr(IV) was chosen as the cross-linking ions to synthesize Zr(IV)-chitosan beads (ZCB) and employed for phosphate adsorption from aqueous solution. The ZCB before and after phosphate adsorption were characterized by FT-IR, XPS, SEM, EDS and zeta potential. Batch experiments were also investigated for the effect of various functions on the phosphate adsorption capacity, such as contact time, initial concentration and temperature. The data of these experiments were evaluated and fitted by adsorption isotherms and kinetic models.

2. Materials and methods

2.1. Materials

All chemicals used such as hydrochloric acid, sodium hydroxide, acetic acid and anhydrous potassium dihydrogen orthophosphate were of analytical reagent grade and purchased from Sinopharm Chemical Reagent Co., Ltd. (China). Chitosan (reagent grade, 91% deacetylation, average molecular weight of 400,000 g mol^{-1}) was supplied by the Shanghai Weikang Biological Co. (China). Zirconium oxychlorideoctahydrate and glutaraldehyde were separately purchased from the Sinopharm Chemical Reagent Co., Ltd. and Merck (China). All solutions were prepared by de-ionized water.

2.2. Synthesis of ZCB

ZCB were prepared by using the precipitation and cross-linked methods. The main preparation procedure of ZCB was briefed as follows: 2.0 g chitosan powders were dissolved in a 100 mL 2% (v/v) acetic acid aqueous solution. The homogenous gel was obtained by stirring 4 h at room temperature. $ZrOCl_2 \cdot 8H_2O$ (0.1 M) was slowly added into this solution over a 5 min period and stirred at 120 rpm for 2 h. Then, under vigorous stirring condition, ZCB were formed by the drop-wise addition of the $NH_3 \cdot H_2O$ solution (v/v = 1:1) with a syringe needle, and subsequently 5 mL 5% of glutaraldehyde aqueous solution was added for another 2 h reaction. The formed beads were transferred to a refrigerator at 4 °C for 24 h to undergo complete cross-linking reaction. The prepared ZCB was washed repeatedly with de-ionized water to neutral pH followed by drying for 2 days at 40 °C. The final Zr content of ZCB was about 23.9% by the ICP-OES method. The obtained ZCB were stored in a desiccator for further phosphate adsorption studies.

2.3. Characterization of adsorbent

The surface and morphology analysis of the absorbent was carried out by a scanning electron microscopy (SEM, JSM-6360LV, JEOL, Japan). The measures of EDS of original and phosphate-loaded beads were obtained by a Falcon energy dispersive X-ray analyzer (EDS Corp., America). The XPS analysis was taken by an X-ray photoelectron spectroscopy (Escalab 250Xi, Thermo fisher Scientific Corp., America) with the monochromatic Al Kα X-ray radiation. The functional groups of absorbent without and with phosphate adsorption were analyzed by a Fourier transform infrared spectrometer (FTIR, Nicolet 6700, Thermo Electron Corp., USA). A JS94H Micro-electrophoresis meter (POWEREACH Digital Technology Equipment Co., Ltd, China) was used to perform the measures of zeta potential for the suspension solutions of ZCB and phosphate absorbed on ZCB (PCB). The pH values of solutions were determined by a precision pH meter (PHS-3D, Shanghai Precision & Scientific Instrument Co., Ltd, China).

2.4. Batch adsorption experiments

The adsorption experiments of phosphate ions were carried out by batch method. Phosphate stock solution (1.0 g L^{-1}) was prepared by dissolving 0.4390 g KH_2PO_4 in 100 mL de-ionized water. Batch adsorption experiments were conducted by placing 20 mg ZCB in 100 mL aqueous solutions with different concentrations of phosphate solutions. The pH values of all solutions were adjusted to the desired value with HCl or NaOH (0.1 M) solutions. The samples were agitated at 150 rpm using a mechanical shaker. After adsorption experiments, the concentrations of phosphate in the solutions were determined by an inductively coupled plasma-optical emission spectrometer (ICP-OES710 series, Agilent Technologies, USA). The adsorption capacities were calculated by the following expression:

$$q_e = {}^{(C_o - C_e)V}\!\Big/_{m} \tag{1}$$

The effect of pH was study with 20 mg L^{-1} initial phosphate concentration in the range of 2–10 at 15 °C. For adsorption isotherm, it was investigated by the variation of initial phosphate concentrations (5 mg L^{-1} to 50 mg L^{-1}) at 15 °C with pH 4. The kinetic experiments for ZCB were performed at initial phosphate concentrations of 10, 20 and 30 mg L^{-1} at 15 °C with pH 4. All prepared solutions were taken for analyzing the concentrations of unabsorbed phosphate at different time intervals in the range of 0–180 min.

The effect of temperature was studied by using 20 mg L^{-1} initial phosphate concentration at different temperatures such as 277, 288 and 296 K. Besides, the effect of coexisting anions was researched in the presence of chloride, nitrate and sulfate with concentrations of separately 200 and 500 mg L^{-1} by keeping the initial concentration of 20 mg L^{-1} phosphate solutions. The regeneration and reuse of ZCB after the batch of phosphate adsorption experiments were conducted by immersion in 0.5 M NaOH. After desorption, ZCB were transferred from the mixture solutions and then washed to neutral pH by de-ionized water. The beads were dried at 40 °C before reused in the next cycle. The adsorption–desorption experiments were repeated for five times for phosphate adsorption.

3. Results and discussion

3.1. Adsorption kinetics

The adsorption of phosphate on ZCB was investigated as a function of contact time at the different initial phosphate concentrations in the range of 0–180 min at room temperature (Fig. 1a). It was clear that the adsorption process for ZCB was rapid at the beginning time then increased slowly until the plateau of adsorption equilibrium was achieved. The fast adsorption rate at the incipient stage could be attributed to the increase of driving force provided by the concentration gradient of phosphate in aqueous solutions and the existence of the great number of available active sites on the surface of ZCB. In addition, the adsorption equilibrium and maximum capacity of phosphate adsorption were reached in about 50 min, which was faster than other adsorbents [12,17–19].

In order to research the adsorption mechanisms and potential rate controlling step of phosphate removal, five common kinetic models