Removal of phosphorus from aqueous solution by Iranian natural adsorbents

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HIGHLIGHTS

- Removal of phosphorus from aqueous solution was studied using Iranian natural adsorbents.
- The adsorption process was a function of the contact time, adsorbent dosage and pH.
- The sorption isotherms of P were well described by the Freundlich and Langmuir models (except calcite).
- We used DLM model to simulate the adsorption of P onto adsorbents over a range of pH values.

ARTICLE INFO

ABSTRACT

Phosphorus (P) removal from aqueous solutions was investigated using bentonite, calcite, kaolinite and zeolite. Adsorption studied was performed to determine the optimum operation conditions such as adsorption time, pH and adsorbent dosage. Sorption isotherms was well described by the Freundlich and Langmuir models (except calcite). The maximum adsorption capacity of P was 1.82, 0.37, 0.32, and 0.28 mg g^{-1} for calcite, zeolite, kaolinite and bentonite, respectively. Desorption analysis showed that the desorption capacities were in an order of bentonite > zeolite > kaolinite > calcite. Data measured for P adsorption onto adsorbents as a function of pH were used to predict P sorption using double layer model (DLM). Results showed that DLM could be modeled P adsorption onto adsorbents over a wide range of pH. Adsorbents solution saturation indices (SIs) and P speciation were assessed using the Visual MINTEQ version 2.3 program and the probability of mineral precipitation was supported by scanning electron microscopy (SEM). According to the SEM images and SIs, high P removal by adsorbents was partly due to the P precipitation. Thermodynamic parameters confirmed the endothermic and not spontaneity nature of the P adsorption.

1. Introduction

Phosphorus (P) losses from agricultural soils to surface waters have been of recent public concern due to the negative effects of increased P concentrations on surface water quality [1]. Increasing discharge of P into natural water systems strongly contributes to eutrophication. Phosphorus removal from wastewater has received considerable attention since the late 1960s. Several methods have been used to remove P from water, including reverse osmosis, biological denitrification, electro-dialysis and adsorption [2–4]. Most of these approaches are generally more suitable for the control of high P concentration. The control of low P concentration is relatively difficult. Adsorption is recommended as one of the most effective removal processes for the low concentrations of P. The most important characteristics of

the adsorption technology that determined its high efficiency are easy handling, easy access of different adsorbents and low cost materials [5]. The success of an adsorption technology depends on the choice of an appropriate adsorbent [6]. Phosphorus sorption mechanisms include ligand exchange (adsorption), precipitation, lattice diffusion, and anion exchange, with the first two mechanisms being the most important [7]. Many natural materials possess adsorption and ion-exchange properties. The majority of natural ion-exchange materials are composed of crystalline aluminosilicates with cation exchange properties. However, some aluminosilicates can also act as anion exchangers, including zeolites [8], apatite [9], bentonite [10], and diatomite [11]. The application of efficient solid materials, involving natural materials, synthesized materials, and solid wastes, in P removal from aqueous solutions has been widely investigated in recent years. Compared with clay minerals, synthesized materials have a higher adsorption capacity due to the uniform micropore structure and high surface area [12].

In recent decades, research has considered a number of different solid adsorbents for their use in reducing P levels entering the water ways. Some of the adsorbents investigated have included clay minerals like bentonite and its pillared forms, iron oxide, red mud, fly ash, and carbonates [13,14]. In recent years, there has been increasing interest in utilizing natural clay minerals like natural bentonite, kaolinite and zeolite for the removal of P from aqueous solutions. Materials such as chitosan, zeolites, clays, or certain waste products from industrial operations are preferred to use as adsorbents due to their low cost and local availability [15].

There are some large deposits of clay minerals in Iran. At present it suggested that the country is one of the largest producers and exporters of bentonite and zeolite in the Middle East [16]. Clays play an important role in the environment by acting as a natural scavenger of pollutants by taking up cations and anions either through ion exchange or adsorption or both.

Previous studies have indicated that P adsorption is depended on the ionic strength and pH [17,18]. A number of studies have been conducted in the last years in which geochemical modeling was used as a research tool for understanding the processes and mechanisms that control adsorption of P onto adsorbents under varying pH [19–22]. Application of models can be a useful tool to predict the behavior of P in the natural environment. Surface complexation models (SCMs) have been widely used to describe adsorption of various inorganic contaminants on solids [23,24]. The SCM$_s$ can be applied to different conditions such as protonation–dissociation reactions, metal ion and inorganic anion adsorption reactions on oxides, clay minerals and soils, organic ligand and competitive adsorption reactions on oxides [25]. SCM including the constant capacitance model (CCM), double layer model (DLM) and triple layer model (TLM) have been successfully used to describe the pH, ionic strength and sorbate/sorbent ratio dependence of metal adsorption on adsorbents [22,26]. Of the most commonly used surface complexation models, the DLM is an especially attractive choice for modeling metal adsorption due to the small number of required fit parameters compared to other SCMs.

In this study, we investigated removal of P from aqueous solutions using Iranian natural bentonite, kaolinite and zeolite. Calcite was also used for comparison. Adsorption of P as a function of pH has been studied using DLM.

2. Materials and methods

2.1. Materials

The adsorbents used in the present investigation (bentonite, kaolinite and zeolite) were obtained from Iran. Calcite was purchased from Merck. The crystallinity and phase identification of the adsorbents were determined by using XRD (model: Seifert 300 diffractometer) with Cu Kα as the radiation source and Ni as the filter in the range $2\theta = 0$–70. The Scanning Electron Microscopy (SEM) measurement was carried out using SEM (model: Philips XL30).

The surface area and adsorption average pore width of the selected fraction of adsorbents was determined by the N$_2$ gas BET (Brunauer–Emmett–Teller) analysis using a Micromeritics Chemisorption ASAP 2020.

2.2. Batch experimental procedures

2.2.1. Optimum conditions

Stock solution of P (1 g l^{-1}) was prepared by dissolving appropriate amounts of KH$_2$PO$_4$ in deionized water. The uptake of P on the adsorbents was carried out using the batch method. The sorption properties of adsorbents were evaluated using different conditions such as sorption time, pH value and adsorbents dosage. Batch sorption experiments were conducted using different dose of adsorbents that ranged from 0.5 to 5 g and pH ranged from 2 to 10 with 20 ml of solution containing P with concentration (50 mg l^{-1}) at constant temperature (25 ± 0.1 °C) in 50 ml polyethylene tubes. The tubes were shaken at 150 rpm from 10 min to 72 h. At the end of experiment, the adsorbents were removed from suspension by centrifuging at 4000 rpm for 20 min and the residual total P concentration in the solutions was measured using a UV–visible spectrophotometer (Varian model).

The percentage removal (R, %) was calculated for each run using the following equation:

$$R = \frac{C_i - C_f}{C_i} \times 100 \tag{1}$$

where C_i and C_f are the concentration of P in initial and final solutions, respectively. The adsorption capacity of adsorbents was obtained from the mass balance of the sorbate in the system, where the solution volume was used to determine the experimental adsorption isotherms. The equilibrium adsorption capacity was calculated using the following equation:

$$q_e = \frac{V(C_i - C_f)}{M} \tag{2}$$

where q_e is sorption capacity (mg g^{-1}), the V is the volume of the solution (L) and M is the weight of the adsorbent (g).

The determination of the pH$_{ZPC}$ of the samples was carried out using a procedure as described previously by Rivera-Utrilla et al. [27]: 20 ml of 0.01 M NaCl solutions were placed in polyethylene tubes. The pH of each solution in each tube was adjusted to values of 2, 4, 6, 8, 10 and 12 by adding HCl 0.1 M or NaOH 0.1 M solutions. Then 0.06 g of adsorbents was added and the final pH measured after 48 h. The pH$_{ZPC}$ is the point where the curve pH$_{final}$ versus pH$_{initial}$ crosses the line equal to pH$_{final}$.

2.2.2. Sorption isotherms

The sorption isotherms of the P with bentonite, calcite, kaolinite and zeolite were determined based on batch analysis. Adsorbents were allowed to equilibrate with solutions at different initial P concentrations (0, 5, 10, 20, 40, 60, 100, 150, 200 and 250 mg l^{-1}). The pH values of the solutions were adjusted to 5.45. At the end of the equilibrium period (24 h), the pH of each suspension was measured before each sample was centrifuged for 20 min at 4000 rpm. Phosphorus concentration in the supernatant was measured using a UV–visible spectrophotometer (Varian model). The amount of P adsorbed by the adsorbents was calculated using Eq. (2).

The corresponding sorption isotherms for P has been quantitatively described by fitting the experimental data to the Freundlich and Langmuir isotherm equations using the nonlinear procedure with Sigmaplot statistical software package version 10.0, that described by following equations, respectively:

$$S = K_f C_i^{1/n} \tag{3}$$

where K_f (l kg^{-1}) is the Freundlich distribution coefficient and n is an empirical constant (unitless).

$$S = \frac{QbC_i}{(1 + bC_i)} \tag{4}$$

where b (l mg^{-1}) is a coefficient which reflects the relative rates of sorption and desorption at equilibrium and is thus bonding energy coefficient, and Q (mg kg^{-1}) is the maximum sorption.

2.2.3. Thermodynamic of sorption

Thermodynamic parameters can be determined using the equilibrium adsorption distribution coefficient (k_d) which depends on