



Removal of ortho-phosphate from aqueous solution by adsorption onto dolomite



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ABSTRACT

An experimental study on the adsorption of phosphate onto cost effective fine dolomite powder is presented. The effect of solution pH, solution ionic strength and adsorption isotherm were examined. The adsorption of phosphate was pH dependent and phosphate adsorption favoured acidic conditions. The adsorption was significantly influenced by solution ionic strength indicating outer-sphere complexation reactions. The experimental data further indicated that the removal of phosphate increased with increase in the ionic strength of solution. The experimental data were modelled with different isotherms: Langmuir, Freundlich and Redlich–Peterson isotherms. It was found that the Redlich–Peterson isotherm depicted the equilibrium data most accurately. The overall kinetic data fitted very well the pseudo-first-order rate model.

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Introduction

Phosphate is one of the most important nutrients essential for plant growth and modern agricultural methods [1]. Phosphate is discharged to water by various human activities, particularly industrial and agricultural applications. The extensive discharge of phosphate into surface water can cause eutrophication, and thus lower the water quality [2]. Therefore, effective phosphate recovery techniques will prevent the pollution of water and overcome the resource deficiency issue. The removal technologies for aqueous phosphate or phosphorous from contaminated waters include crystallization, chemical precipitation and biological removal. In phosphate removal investigations regarding crystallization [3–5], a number of materials such as sand and Ca-phosphate crystals were utilized as seeding materials to initiate and improve phosphate recycling and precipitation. However, a crystallization method requires complicated and precise control of the operating conditions [1,6]. Chemical precipitation and biological removal have other disadvantages such as the cost of chemicals, substantial additional sludge production and phosphorus release in the sludge treatment [7].

Adsorption is becoming an increasingly important process for the elimination of contaminants from wastewaters [8,9]. A detailed review of P nutrient removal and recovery technologies was given by Morse [10]. The adsorption technique offers a number of advantages

over the other techniques, for instance, it allows use of low cost materials for remediation of contaminated wastewater; the process scale-up is easy with low operational costs [11]. Several studies on the removal of phosphorus/phosphate from contaminate waters using the adsorption method have been given in literature [12–17]. Dolomite ($\text{CaMg}(\text{CO}_3)_2$), a material that is existing abundantly and cheaply worldwide [18] has been the subject of attention for more than six decades [11]. Despite a relatively low specific surface area ($1.50 \text{ m}^2/\text{g}$) [19], dolomite still shows some good adsorption properties. Karaca et al. carried out a comparison between calcinated dolomite and raw dolomite in terms of capacity of phosphate removal from aqueous solution [20]. The authors reported that the phosphate capacity increased with an increase in the solution pH at a solid–liquid ratio 2.0 g/L and adsorption temperature 20°C . The authors reported that the phosphate removal decreased with increasing temperature and slightly increased with increasing pH. It was suggested that the main mechanisms for adsorption of phosphate on dolomite could be both physical interactions and chemi-sorption.

This research was carried out to investigate the removal of phosphate from aqueous solutions by adsorption onto low cost dolomite materials, through equilibrium and kinetic studies. This research differs from the earlier studies [20,21] in a number of ways. Firstly, higher initial concentrations of phosphate solution were used to match the typical phosphate levels in slurries from anaerobic digestion plants. Unlike in the previous research reports, where coarse particles of adsorbent were used, this research used very fine raw dolomite powder as this size allows further processing of the powder after adsorption for use as soil-conditioner [22–24]. Secondly, this paper studies the effect of solution ionic strength which has not been studied before. Further insights on the mechanism and nature of the adsorption process were gained by applying appropriate equilibrium and kinetic

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models to the experimental data.

Materials and methods

Chemicals

Calcium phosphate monobasic manufactured and supplied by Aldrich – Chemical Co. Ltd., UK was used as the source of phosphate ions. The adsorbent used in this research was fine dolomite supplied by Kilwaughter Chemical Company, UK, which had a particle size between 50 and 100 μm . The fine dolomite in this study has been tested for adsorption experiments without any pre-treatment. Solutions of 1 M of HCl and NaOH were used for the manual control of pH (pH meter, Thermo, Fisher Scientific-Singapore). The electrolyte used to modify the ionic strength in the adsorption experiments was NaCl.

Equipment

A XRD analysis was performed to examine the crystalline nature of the fine dolomite sample (wide angle X-ray diffraction using a Philips PANalytical X'pert pro diffractometer). The surface structure of the fine dolomite was explored with Fourier transform infrared spectroscopy (FT-IR), to illustrate the change in the functional groups of the dolomite surface before and after adsorption. The structural ordering of the fine dolomite was analysed by scanning electron microscopic (SEM), using a JEOL-JSM 6400 scanning microscope. For batch equilibrium studies, samples have been regularly shaken (mechanical shaker, GerhardT type LS 5) for 7 days at 100 rpm and 20 °C. The initial and final concentrations of the nutrients were measured by inductive couple plasma (ICP-OES, Optima 4300 D V, 16 PerkinElmer, USA). The surface area and the cumulative pore size distribution of the dolomite powder were measured using a mercury porosimetry (PoreMaster[®], QuantaChrome Instruments).

Adsorption experiment

The influence of solution pH on adsorption capacity was investigated by adding 0.2 g of adsorbent to 250 mL bottle jars containing 50 mL solutions solution ($C_0 = 1000$ mg P/L) at room temperature (20 °C). The experiment was performed using solutions at various pH values: 2–10. The influence of ionic strength on the adsorption of phosphate onto dolomite was examined by altering the initial phosphate concentrations between 100 and 2000 mg/L in the existence of NaCl salt, at three altered concentrations 0.05, 0.1 and 0.3 M. This value was selected based on the average ionic strength values used in phosphate adsorption research paper reported in literature [25,26]. Batch equilibrium studies were performed by adding 0.2 g of adsorbent to 250 mL bottle jars containing 50 mL solutions of altered initial concentrations (100–2000 mg P/L) and agitated at 100 rpm using GerhardT type mechanical shaker. The equilibrium time for all experiments was 7 days. After the adsorption equilibrium was achieved, solutions were filtered to remove the fine dolomite, transferred into polythene tubes and diluted prior to analysis. The amount of phosphate adsorbed at equilibrium, q (mg/g), which corresponds to the difference in phosphate concentration in the solution before and after adsorption was calculated using the following equation:

$$q = \frac{V(C_0 - C_e)}{m_s} \quad (1)$$

where C_0 and C_e (mg P/L) are the concentration of nutrient at initial and equilibrium, correspondingly, V is the volume of the solution (L) and m_s is the mass of dolomite (g).

For kinetic studies, 1.0 g of the adsorbent material was contacted with 250 mL of phosphate solution with initial concentration 1000 mg P/L and stirred by a magnetic stirrer. Samples were taken at ordinary time intervals. The solution pH was not adjusted for this set of experiments; the solution had an initial pH 4. However, 100 mg/L of

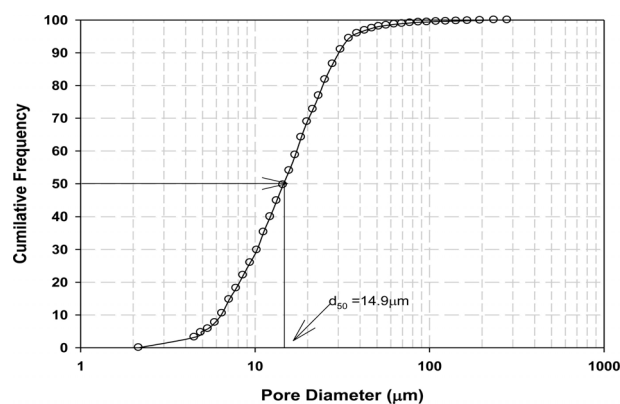


Fig. 1. Cumulative pore size distribution curves of fine dolomite based on surface area.

NaHCO_3 was added in solutions used in adsorption experiments as a pH buffer. The phosphate uptake at any time q_t (mg/g) was calculated using Eq. (1). To compare the capability of each adsorption isotherm and kinetic model to predict the experimental data, a standard deviation is calculated as follows [27–30]:

$$SD = \sqrt{\frac{\sum ((q_{t,\text{exp}} - q_{t,\text{mod}}) / q_{t,\text{exp}})^2}{N - 1}} \quad (2)$$

where N is the number of data points, $q_{t,\text{exp}}$ and $q_{t,\text{mod}}$ are the measured and calculated concentrations of adsorbate in solid phase, respectively.

Results and discussion

Characterization of adsorbent

The performance of an adsorption material is influenced by the porosity and surface area available for adsorption. Fig. 1 shows the cumulative pore size distribution of the dolomite powder. It was found that the powder median pore-diameter, d_{50} , of 15 μm . This means that pores of size of about 15 μm or less contribute to about 50% of the pore surface area; the adsorbent can therefore be described as being macroporous. The surface area of the dolomite was 0.146 m^2/g measured by the mercury porosimetry. Semi-quantitative analysis of the data given in Table 1 indicates that the main component is calcite which is about 68% of the dolomite powder. The comparison between the XRD profiles before and after adsorption with phosphate is shown in Fig. 2. The X-ray diffraction analysis undertaken on the dolomite powder presented in Fig. 2a illustrates that the main components are calcite, dolomite, quartz and periclase. It can be noted from Fig. 2b that adsorption of phosphate has the effect of shifting the peaks to the left. There is also a significant reduction in the main calcite peaks which suggests that there may be some dissolution of carbonate during the experiment. The phosphate adsorption onto dolomite results in the appearance of a sharp new peak at around 2θ of 11° and an increase in the intensity of the peak 21° (see Fig. 2b). These phenomena indicate the formation of $\text{Mg}_3(\text{PO}_4)_2$ and $\text{Ca}_3(\text{PO}_4)_2$ and the crystalline nature of these precipitates [31].

FT-IR analysis undertaken on the dolomite before and after adsorption of phosphate is presented in Fig. 3. A broad and intense band of O–H stretching vibration around 3500–3300 cm^{-1} and a band around 1700 cm^{-1} (O–H bending vibration) indicated the existence of coordinated water molecule [32]. The existence of silicate phases (Si–O vibrations) can be seen at 1040 cm^{-1} and the band at 1437.1 cm^{-1} may be assigned to CO_3^{2-} group [11]. There is a noticeable increase in the intensity of –OH group, which can be attributed to the attraction between the protonated –OH groups and phosphate ions, i.e. electrostatic attraction. The reduction of CO_3^{2-} group band may indicate the

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