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## Retention of phosphorous ions on natural and engineered waste pumice: Characterization, equilibrium, competing ions, regeneration, kinetic, equilibrium and thermodynamic study

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### ABSTRACT

Natural and Mg<sup>2+</sup> modified pumice were used for the removal of phosphorous. The adsorbents were characterized using XRF, XRD, SEM and FTIR instrumental techniques. In the optimal conditions, namely at equilibrium time (30 min), for a phosphorus concentration of 15 mg/L and pH 6, 69 and 97% phosphorus removals were achieved using 10 g/L of natural and modified pumice adsorbents, respectively. Maximum adsorption capacities were 11.88 and 17.71 mg/g by natural and modified pumice, respectively. Pseudo-second order kinetic model was the most relevant to describe the kinetic of phosphorus adsorption. External mass transfer coefficient decreased for increasing phosphorous concentration and film diffusion was found to be the rate-controlling step. Only a very low dissolution of the adsorbent was observed, leading to a low increase in conductivity and turbidity. Removal efficiency decreased for increasing ionic strength. It also decreased in the presence of competing ions; however modified pumice remained effective, since 67% of phosphorus was removed, versus only 17% for the natural pumice. The efficiency of the modified pumice was confirmed during the regeneration tests, since 96% regeneration yield was obtained after 510 min experiment, while only 22% was observed for the raw pumice.

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### 1. Introduction

In recent years, leakage of atmospheric precipitation in many areas leads to use of wastewater plant effluents as potential resource to recharge groundwater body and for irrigation. In that case, some elements limit the safe use of such effluents. Nitrate and phosphate are known to be the main limiting elements to the reuse of wastewater effluents [1,2]. The release of untreated wastewater containing both nitrate and phosphate leads to outbreak of eutrophication in surface water in excess of limits. Among them, phosphorous compounds known as to be the key element to outbreak of eutrophication. Naturally, phosphorous is found in some rocks and soil, it is necessary for plant growth and a macronutrient

of most of biological beings [3]. An increase in its concentration caused by higher input (wastewater, avulsion, etc.) directly results in increasing eutrophication of the water with known effects such as increased growth of algae, oxygen depletion as far as anoxia in the deeper regions, etc. [4,5]. For protection of water supply body and safe reuse of wastewater effluents containing phosphorous, the maximum discharge standards of phosphate is applied to be as low as 0.5–1 mg/L [6]. Usually, biological and physicochemical methods have been used for phosphorous removal. These techniques have some limitation such as production of excessive phosphorus-rich sludge, which consequently need to be treated for reduction of volume and stabilization for final disposal. Chemical participation by iron or aluminum salt also produce significant amounts of sludge which have to be treated to obtain a final safe product [7–9].

Adsorption is an efficient process for the removal of environmental pollutants. Usually, commercial activated carbon is used for this purpose. This product is expensive and needs to be

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regenerated continuously to reduce process cost [10]. For this reason, natural and low cost materials such as red mud, aluminum hydroxide gel, granulated coal ash and others have been recently used for adsorption process [3,4,11].

Among natural adsorbents, geomaterials has attracted more attention for the removal of various environmental pollutants. They are used both in natural and modified forms. Geomaterial adsorbent such as pumice, fired clay, bentonite, tertiary soil, kaolinite, titanium rich bauxite, surface tailored zeolites and lava, is low cost adsorbents, available in local sources and showing minimal processing requirements [12]. One of the attractive geomaterials is pumice. Pumice rocks are porous and amorphous material which consists mainly of SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub>. Traditionally, pumice has been used in construction industry [13]. In recent years, pumice has been used in the field of water and wastewater treatment both in natural and modified forms for the removal of fluoride [12], azo dyes [14], phenol and 4-chlorophenol [15], heavy metals [16], SO<sub>2</sub> [17] and water hardness [18]. For improvement of adsorption capacity of naturally occurring adsorbent, various organic and inorganic chemicals such as lanthanum salts [1], hydroxy-aluminum, hydroxy-iron salts [2], magnesium chloride and hydrogen peroxide [12] and alkali treatment [18] has been used.

In our previous work, magnesium chloride modified pumice was used for the removal of fluoride [12]. In that work, modification of natural pumice with magnesium chloride leads to an increase of the specific surface area of adsorbent and enhanced fluoride adsorption capacity. In addition, it is reported that adsorbent containing magnesium oxide (MgO) can bind with phosphorous ions allowing it recover from the considered solution [19]. Since it has been shown in our previous works [12,18] that pumice contains 1.03% (w/w) magnesium oxide, modification of natural pumice with magnesium chloride should increase its magnesium content, as well as its specific surface area leading to an improvement of the phosphorus adsorption capacity. However and to our knowledge, natural and Mg<sup>2+</sup> modified pumice have not been previously used for the adsorption of phosphorous, showing potential usefulness for researchers in the field. Therefore, the objective of this work was therefore to investigate retention of phosphorous ions by natural and Mg-modified pumice.

## 2. Materials and methods

### 2.1. Chemicals

All chemicals used in this work were obtained from Merck (Merck Co., Germany). 0.5 M H<sub>2</sub>SO<sub>4</sub> and NaOH were used for pH adjustment and control (Jenway, model 3510). K<sub>2</sub>HPO<sub>4</sub> of analytical grade (Merck) was used for the preparation of a stock solution, using deionized water. For practical use, it was further diluted to the desired concentration. The phosphorous concentration was measured by means of an UV–vis spectrophotometer at 470 nm (model 1700, Shimadzu, Japan) according to standards methods for the examination of water and wastewater section 4500-P-C, named Vanadomolybdo phosphoric Acid Colorimetric Method [20]. Natural pumice stone were obtained from Tikmeh Dash Reign (East Azerbaijan Province, Iran).

### 2.2. Preparation of the adsorbent

Natural pumice stone was thoroughly washed several times with distilled water to remove any impurities until the turbidity value became lower than 0.1 NTU. The adsorbent was then treated with 1 M HCl to complete purification and remove any acid soluble impurities. It was then washed with deionized water to remove the excess of acid (pH 7). Pumice was then dried at 55 °C for 24 h

to remove the remaining water. The dried pumice was crushed and sieved to 10–30 mesh (2000–841 μm). The prepared adsorbent (about 100 g) was then introduced into 1 L beaker which was filled with 2 M MgCl<sub>2</sub> and left for 24 h at laboratory temperature to complete the modification. The beaker containing raw adsorbent and MgCl<sub>2</sub> was stirred for 24 h at 100 rpm for more impregnation. After 24 h, the adsorbent was removed from the beaker, filtered and kept in an electric furnace at 750 °C for 6 h (Lenton, England) for more crystallization. After 6 h calcination, the adsorbent was washed several times with deionized water to remove the excess of MgCl<sub>2</sub>. The modified adsorbent was then dried at 55 °C for 24 h and used for future experiments.

### 2.3. Batch experiment

All experiments were conducted in a batch mode in 250 mL conical flasks. Various experimental parameters such as pH (3–11), temperature (10–50 °C), adsorbent mass (2–10 g/L), initial phosphorous concentration (5–20 mg/L) and contact time were investigated. For the determination of the equilibrium time and the effect of the initial phosphorous concentration on the removal efficiency, adsorption properties were first studied by varying the contact time and the phosphorous concentration. A pH of 6.5 was considered based on the zero point charge determination (see Section 2.6) and the adsorbent mass was 6 g/L based on the average adsorbent dosage. About 6 g/L of natural or modified adsorbent was introduced into each conical flask containing phosphate at a concentration in the range 5–20 mg/L and the flask was shaken at 200 rpm (Hanna-Hi 190 M, Singapore). At a pre-determined time interval, samples were taken, filtered (0.45 μm, Whatman), centrifuged (Sigma-301, Germany) and the phosphorous concentration was determined. In this section, experiments were performed at room temperature. The removal efficiency was calculated by means of the following equation (Eq. (1)):

$$RE = \frac{(C_0 - C_e) \times 100}{C_0} \quad (1)$$

where RE (%) is the percentage of chromium removed at equilibrium time; C<sub>0</sub> and C<sub>e</sub> are the initial and equilibrium concentrations of chromium (mg/L), respectively.

After determination of the equilibrium time, 250 mL phosphorous solution containing 15 mg/L solute was added to five 250 mL conical flasks and about 6 g/L of natural or modified adsorbent were introduced to each conical flask. The pH was adjusted in the range of 3–11. The conical flask was then stirred at 200 rpm until equilibrium time was reached. When the equilibrium time was reached, the suspension was filtered; centrifuged and final phosphorous concentration was measured. When the optimal pH, equilibrium time and initial phosphorous concentration were determined, a series of adsorption tests were carried out by varying the adsorbent mass in the range of 2–10 g/L. The effect of temperature was also investigated in the range of 10–50 °C at the optimal pH, adsorbent mass, initial phosphorous concentration and equilibrium time. All experiments were conducted according to the Standard Methods for the Examination of Water and Wastewater [20].

### 2.4. Adsorbent effect on conductivity (EC) and turbidity

For the EC test, 6 g/L of the natural or the modified pumice was introduced into 250 mL deionized water at pH 6.5 and shaken at 200 rpm. At predetermined time intervals, samples were taken for conductivity and turbidity measurements (Jenway, Model 4520).

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