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Kinetics and thermodynamic study of phosphate adsorption on iron hydroxide-eggshell waste

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ABSTRACT

This study explored the feasibility of using waste iron hydroxide-eggshell as adsorbent for the removal of phosphate under different experimental conditions. In our experiments, the batch sorption is studied with respect to solute concentration (2.8–110 mg/L), contact time, adsorbent dose (2.5–20 g/L) and solution temperature (20–45 °C). The Langmuir, Freundlich, and Langmuir–Freundlich adsorption models were applied to experimental equilibrium data at different solution temperatures and the isotherm constants were calculated using linear regression analysis. A comparison of kinetic models applied to the adsorption of phosphate onto iron hydroxide-eggshell was evaluated for the pseudo-second-order, Elovich, intra-particle diffusion and Bangham's kinetics models. The experimental data fitted very well the pseudo-second-order kinetic model and also followed by intra-particle diffusion model up to 5 min, whereas diffusion is not only the rate-controlling step. The results show that the sorption capacity increases with an increase in solution temperature from 20 to 45 °C at the initial phosphate solution concentration of 27 mg/L. The thermodynamics parameters were evaluated. The positive value of ΔH° (81.84 kJ/mol) indicated that the adsorption of phosphate onto iron hydroxide-eggshell was endothermic, which result was supported by the increasing adsorption of phosphate with temperature. The positive value of ΔS° (0.282 kJ/mol) reflects good affinity of phosphate ions towards the waste iron hydroxide-eggshell. The results have established good potentiality for the waste iron hydroxide-eggshell particles to be used as a sorbent for the removal of phosphorus from wastewater.

1. Introduction

Phosphorus exists in natural waters in particulate and dissolved form. It is known that phosphorus is essential to the growth of algal and other biological organisms. Because of algal blooms that occur in surface waters, the amount of phosphorus compounds in domestic and industrial discharges must be controlled using either chemical or biological techniques. The usual forms of phosphorus found in aqueous solutions include orthophosphates, polyphosphates and organic phosphates [1]. The principal phosphorus compounds in wastewater are generally orthophosphates [2]. Municipal wastewater may contain from 4 to 15 mg/L phosphorus as PO_4^{3-}. However, industrial wastewaters (such as detergent manufacturing and metal coating processes) may contain phosphate levels well in excess of 10 mg/L [3]. Chemical treatment is widely used for phosphate removal. Chemicals such as lime, alum, and Ferric chloride are the common precipitants used for phosphate removal [4] but their cost and sludge production make chemical treatment an unattractive option for wastewater treatments. Sorption method can remove phosphate steadily. In recent years, considerable attention has been paid on economic and environmental concerns to the study of using different types of low-cost sorbents such as alum sludge [5] red mud [6], fly ash [7], blast furnace slag [8], spent alum sludge [9], aluminium and iron-rich residues [10], synthetic boehmites [11] and calcite [12].

The objective of this work was to study the feasibility of using hydroxide-eggshell as an adsorbent for phosphorus removal from wastewater. It is well known that calcite [12] and iron oxides are the important phosphorus adsorbent [13]. Eggshell is composed mainly of calcium carbonate which should behave as known sorbents that contain this compound, i.e. calcite [14] calcareous soil [15].

The objective of this work was to study the feasibility of using iron hydroxide-eggshell as an adsorbent for phosphate species removal from wastewater. In doing so, the adsorption of phosphate on this waste material from aqueous solutions was evaluated in batch experiments. The adsorption isotherms, kinetics and temperature effect were studied.

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Table 1
Chemical components of eggshell

Component	%
Na_2O	0.489
MgO	0.845
Al_2O_3	0.055
SiO_2	0.010
P_2O_5	0.181
SO_3	0.747
K_2O	0.050
$CaCO_3$	97.015
Fe_2O_3	0.029
SrO	0.140
Cl	0.138
Volatile matter	0.300

2. Experimental

2.1. Materials and methods

2.1.1. Adsorbent

Our previous study [16] explored the feasibility of utilizing waste eggshell as adsorbent for iron removal from aqueous solution, then, the waste (iron hydroxide-eggshell) derived from adsorption process of iron into eggshell was used for adsorption of phosphate species in this work. The chemical composition of eggshell is summarized in Table 1; values are expressed as % (w/w).

For the preparation of iron hydroxide-eggshell, solution of 5 mg/L Fe (III) was prepared by dissolving ($FeCl_3$, $2H_2O$) in distilled water. 0.25 g sample of eggshell were added to each 100 mL of 5 mg/L Fe (III) (several samples were prepared). The mixture was agitated on shaker at a constant temperature at equilibrium. Then, the samples were centrifuged and the adsorption amount on eggshell was calculated indirectly from the difference of iron concentration in solution before and after the experiment [16]. Waste (iron hydroxide-eggshell) resulting in each sample contain 1.99 mgFe (III) adsorbed per unit mass of eggshell (∼2 mgFe (III)/g). The sorbent was dried, screened through a set of sieves to get a geometrical size of 50–315 μm and used for phosphate removal.

2.1.2. Absorbate

Stock solutions were prepared by dissolving accurately weighed samples of anhydrous potassium phosphate (KH_2PO_4) in distilled water to give a concentration of 1000 mg/L and diluted with distilled water when necessary.

2.2. Kinetic studies

The iron hydroxide-eggshell mass (7.5 g/L), except for the studies of adsorbent concentration effect, was mixed with 1000 mL of the desired phosphate concentration and temperature in conical flasks. Initial pH of each solution was adjusted to the required value (pH 7) with diluted NaOH solutions before mixing the adsorbent solution. The flasks were agitated on a shaker at constant temperature. Samples were withdrawn at suitable intervals and were separated from the sorbent by centrifugation for 20 min. The phosphate concentration was determined by measuring the absorbance of the solution using UV visible at 880 nm wavelength after the samples were pre-treated using the ascorbic acid method [17]. Experiments were repeated for different initial phosphate concentration (2.8, 14, 53 and 110 mg/L) and temperature (20, 25, 35 and 45 °C) values.

2.3. Equilibrium studies

2.3.1. Effect of adsorbent dose

Adsorption equilibrium studies were conducted at initial phosphate solution pH of 7. Equilibrium data were obtained by adding 0.25–2.0 g of iron hydroxide-eggshell into a series of conical flasks each filled with 100 mL of phosphate solution. The initial phosphate concentration ranges from 14 to 53 mg/L. The conical flasks then covered with aluminium foil and were then placed in a thermostatic shaker for 4 h. During the adsorption the temperature of system was kept constant at 45 °C.

2.3.2. Sorption isotherms

Adsorption experiments were carried out by adding a fixed amount of adsorbent (0.75 g) to a series of conical flasks filled with 100 mL diluted solutions (7–140 mg/L). The conical flasks were placed in a thermostatic shaker at 20, 25, 35 and 45 °C at pH 7.

The removal efficiency (E) of phosphate on iron hydroxide-eggshell, the sorption capacity, (q) and distribution ratio (K_d) were calculated from Eqs. (1)–(3):

$$E\,(\%) = \frac{C_i - C_f}{C_i} \times 100 \quad (1)$$

$$q = \frac{V(C_i - C_f)}{m} \quad (2)$$

$$K_d = \frac{\text{amount of phosphate in adsorbent}}{\text{amount of phosphate in solution}} \times \frac{V}{m}\,(\text{L/g}) \quad (3)$$

where C_i and C_f are the initial and final concentrations of phosphate (mg/L) in aqueous solution, respectively, V is the volume of the solution (L) and m represents the weight of the adsorbent (g).

3. Results and discussion

3.1. Effect of initial phosphate concentration and contact time

Experiments were undertaken to study the effect of varying initial concentration (2.8–110 mg/L) at 30 °C on phosphate removal by iron hydroxide-eggshell. Fig. 1 indicates a rapid initial uptake rate of phosphate at the beginning and, thereafter, the adsorption rate decreased gradually. The adsorption of phosphate reached

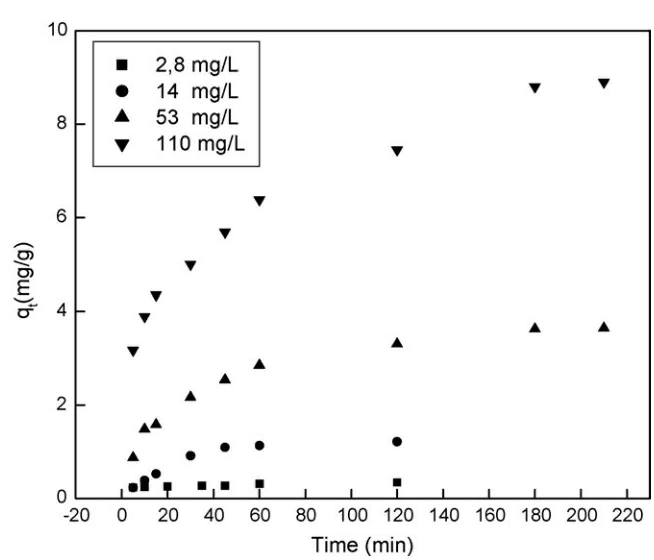

Fig. 1. Effect of contact time at several initial phosphate concentration on sorption kinetics (30 °C, pH 7, C_s = 7.5 g/L).