Contact time optimization of two-stage batch adsorber design using second-order kinetic model for the adsorption of phosphate onto alunite

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Abstract

The adsorption of phosphate onto alunite in a batch adsorber has been studied. Four kinetic models including pseudo first- and second-order equation, intraparticle diffusion equation and the Elovich equation were selected to follow the adsorption process. Kinetic parameters, rate constants, equilibrium adsorption capacities and related correlation coefficients, for each kinetic model were calculated and discussed. It was shown that the adsorption of phosphate onto alunite could be described by the pseudo second-order equation. Adsorption of phosphate onto alunite followed the Langmuir isotherm. A model has been used for the design of a two-stage batch adsorber based on pseudo second-order adsorption kinetics. The model has been optimized with respect to operating time in order to minimize total operating time to achieve a specified amount of phosphate removal using a fixed mass of adsorbent. The results of two-stage batch adsorber design studies showed that the required times for specified amounts of phosphate removal significantly decreased. It is particularly suitable for low-cost adsorbents/adsorption systems when minimising operating time is a major operational and design criterion, such as, for highly congested industrial sites in which significant volume of effluent need to be treated in the minimum amount of time.
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1. Introduction

Phosphates are used in many consumer products and industrial processes that involve particles of a colloidal nature. Examples of such applications are as diverse as fertilizers, detergents, pigment formulation, water treatment and mineral processing [1]. Phosphate discharged into the surface waters stimulates the growth of aquatic micro- and macro-organisms in nuisance quantities, which in excess can cause eutrophication in stagnant water bodies [2]. Therefore, removal of phosphate from the wastewaters can be an effective method for the control of eutrophication in lakes and similar stagnant water bodies [3].

The adsorption process is one of the efficient methods to remove phosphate from effluent. Phosphate is adsorbed onto a solid adsorbent surface from the amount of the phosphate removed depending on the adsorption capacity of adsorbent [4]. Activated alumina and zeolites are the most widely used adsor-

bents for this aim because of their extended surface areas, microporous structures, high adsorption capacities and high degree of surface reactivities. However commercially available activated alumina and zeolites are very expensive [5,6]. This has led to the search for low-cost materials as alternative adsorbents. In recent years, a number of low-cost, easily available adsorbents have been tried for phosphate removal. These include fly ash, blast furnace slag, different soils including metal oxides, goethite, pumice, titanium dioxide and alunite [2,4,6,7–12]. However these studies have not been directed towards the design of phosphate adsorption systems such as batch adsorber design. Also, only limited application of such data has been directed towards the batch adsorber design for the pollutant adsorption processes [13–18]. Most previous optimization models for batch adsorbers [13,14,18] are based on minimizing the mass of adsorbent required to remove a certain amount of pollutant from a fixed volume of wastewater. This optimised parameter is a critical factor when using expensive adsorbents, such as activated carbons, activated alumina, zeolites, silica and resins, because it makes maximum use of the adsorbent but gives little consideration to operating time.

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In many countries, however, industries find that space management a major challenge and optimising the rate of treatment of a fixed volume of wastewater is crucial. Therefore using cheaper adsorbents and minimizing the operating time to achieve a desired percentage of pollutant removal, with a fixed mass of adsorbent will enable the treatment of more batches of polluted wastewater per day. Thus, the process plant equipment items can be reduced in size, with a decrease in the plant capital costs.

This paper describes studies of the adsorption of phosphate onto alunite and develops a two-stage batch adsorber design model. A design analysis method has been used to predict the percentage of phosphate removal at various operating times for a fixed mass of adsorbent. The model proposed by Ho and McKay [16,17] is based on predicting the minimum operating time required to remove a fixed percentage of phosphate from a given volume of wastewater effluent of specified phosphate concentration, using a fixed mass of alunite. This minimum operating time enables the minimum size of the batch adsorption equipment to be specified and therefore minimize capital investment costs.

2. Theory

2.1. Kinetic and equilibrium models of adsorption

In order to examine the mechanism of adsorption process such as chemical reaction, diffusion control and mass transfer, several kinetic models are used to test experimental data. From a system design viewpoint, a lumped analysis of kinetic data is hence sufficient for practical operation [7,19,20].

2.1.1. Pseudo first-order equation

The pseudo first-order equation is generally expressed as follows [7,19,21]:

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \tag{1}$$

Integrating Eq. (1) and applying the boundary conditions $q_t = 0$ at $t = 0$ and $q_t = q_t$ at $t = t$, gives:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303}t \tag{2}$$

where q_e and q_t are the amounts of phosphate adsorbed at equilibrium and at time t (mg/g), respectively, and k_1 is the rate constant of pseudo first-order adsorption (1/min).

2.1.2. Pseudo second-order equation

If the rate of adsorption is a second-order mechanism, the pseudo second-order chemisorption kinetic rate equation is expressed as [7,16,17,19]:

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \tag{3}$$

After define integration by applying the boundary conditions, Eq. (3) becomes:

$$\frac{1}{q_e - q_t} = \frac{1}{q_e} + k_2t \tag{4}$$

Eq. (4) can be rearranged to obtain a linear form:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}t \tag{5}$$

where k_2 is the equilibrium rate constant of pseudo second-order adsorption (g/mg min).

2.1.3. Intraparticle diffusion equation

The fraction of phosphate adsorbed $((C_0 - C_t)/C_0)$ changes according to a function of $(Dt/r^2)^{1/2}$, where r is the particle radius and D the diffusivity of solute within the particle. The rate parameter (k_{int}) for intraparticle diffusion can be defined as [7,20,22]:

$$q_t = k_{int}t^{1/2} \tag{6}$$

where k_{int} is the intraparticle diffusion rate constant (mg/g min$^{1/2}$).

2.1.4. The Elovich equation

The Elovic equation is given as follows [21,23]:

$$\frac{dq_t}{dt} = \alpha e^{-\beta q_t} \tag{7}$$

The integration of the rate equation with the same boundary conditions as the pseudo first- and second-order equations becomes the Elovich equation.

$$q_t = \frac{1}{\beta}\ln(\alpha\beta) + \frac{1}{\beta}\ln t \tag{8}$$

where α is the initial adsorption rate (mg/g min), and the parameter β is related to the extent of surface coverage and activation energy for chemisorption (g/mg).

2.1.5. The Langmuir isotherm

The widely used Langmuir isotherm [4,7,8,13,19,24] has found successful application in many real adsorption processes and is expressed as:

$$q_e = \frac{K_L C_e}{1 + a_L C_e} \tag{9}$$

A linear form of this expression is:

$$\frac{C_e}{q_e} = \frac{1}{K_L} + \frac{a_L}{K_L}C_e \tag{10}$$

where q_e (mg/g) and C_e (mg/L) are the amount of adsorbed phosphate per unit weight of adsorbent and unadsorbed phosphate concentration in solution at equilibrium, respectively. The constant K_L is the Langmuir equilibrium constant and the K_L/a_L gives the theoretical monolayer saturation capacity, Q. Therefore a plot of C_e/q_e versus C_e gives a straight line of slope a_L/K_L and intercept $1/K_L$.

2.2. Batch adsorber design analysis

Kinetic equations can be used to predict the design of two-stage batch adsorption systems [16,17]. A schematic diagram for a two-stage adsorption system is shown in Fig. 1. The solution to
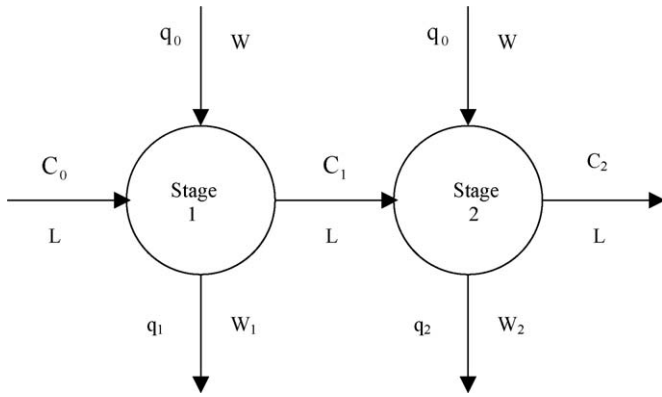
Fig. 1. Schematic for a two-stage crosscurrent batch adsorption process.

be treated contains V (L) solution and the phosphate concentration is reduced for each stage from C_0 to C_n (mg/L). The amount of adsorbent added is W (g) with solid phase phosphate concentration on the alunite q_0 (mg/g). The phosphate concentration on the adsorbent increases from q_0 to q_n (mg/g) adsorbent. The mass balance equation gives:

$$V(C_{n-1} - C_n) = W(q_{t,n} - q_0) \tag{11}$$

When fresh adsorbents are used at each stage and the pseudo second-order equation employed to describe equilibrium in a multi-stage adsorption system, then the mass balance equation may be obtained by combining Eqs. (5) and (11):

$$C_n = C_{n-1} - \frac{Wkq_{e,n}^2 t}{V(1 + kq_{e,n}t)} \tag{12}$$

The total amount of phosphate removal can be calculated analytically as follows:

$$\sum_{n=1}^{m} C_{n-1} - C_n = \sum_{n=1}^{m} \frac{Wkq_{e,n}^2 t}{V(1 + kq_{e,n}t)} \tag{13}$$

where n is the adsorption system number ($n = 1, 2, 3, \ldots, m$). The phosphate removal, R_n, in each stage can be evaluated from the equation as follows:

$$R_n = \frac{100(C_{n-1} - C_n)}{C_0} = \frac{100Wkq_{e,n}^2 t}{VC_0(1 + kq_{e,n}t)} \tag{14}$$

The total removal of phosphate can be determined analytically:

$$\sum_{n=1}^{m} R_n = \frac{100W}{VC_0} \sum_{n=1}^{m} \frac{kq_{e,n}^2 t}{1 + kq_{e,n}t} \tag{15}$$

It is further considered that k and q_e can be expressed as a function of C_0 for phosphate as follows:

$$k = X_k C_0^{Y_k} \tag{16}$$

$$q_e = X_q C_0^{Y_q} \tag{17}$$

Substituting the values of k and q_e from Eqs. (16) and (17) into Eqs. (14) and (15) allows these two latter equations to be represented as follows:

$$R_n = \frac{100W(X_k C_{n-1}^{Y_k})(X_q C_{n-1}^{Y_q})^2 t}{VC_0[1 + (X_k C_{n-1}^{Y_k})(X_q C_{n-1}^{Y_q})t]} \tag{18}$$

$$\sum_{n=1}^{m} R_n = \frac{100W}{VC_0} \sum_{n=1}^{m} \frac{(X_k C_{n-1}^{Y_k})(X_q C_{n-1}^{Y_q})^2 t}{[1 + (X_k C_{n-1}^{Y_k})(X_q C_{n-1}^{Y_q})t]} \tag{19}$$

Eqs. (18) and (19) can be used for predicting the removal of phosphate at any given initial phosphate concentration and the reaction time for multi-stage systems can be determined.

3. Materials and methods

Alunite, $KAl_3(SO_4)_2(OH)_6$, is a mineral not soluble in water in its original form. It is formed by hydrothermal alteration of tuff. Therefore it contains approximately 50% SiO_2. Alunite used in this study was obtained from Kütahya–Şaphane, Türkiye. The composition of alunite, used in these studies, prior to and after calcination process is given in Table 1. The alunite samples were treated before using in the experiments as follows [24]. Alunite was prepared by grinding it in a laboratory type ball-mill. The alunite samples were calcined in muffle furnace at 1073 K for 30 min. This calcination temperature and time were found to be the optimum for phosphate adsorption in our previous studies [4,7,8]. Then it was sieved to give different particle size fractions using ASTM standard sieves, and 90–150 μm particle size was used in the experiments. The BET specific surface area was measured to be 133.3 m²/g from N_2-adsorption isotherms with a sorptiometer (Porous Materials Inc., model BET-202A).

Standard phosphate solutions were prepared by dissolving the anhydrous K_2HPO_4 (Merck) in appropriate amounts in distilled water. The adsorption experiments were carried out by agitating 1 g of the calcined alunite with 1 L of phosphate solutions of desired concentration, and at 298 ± 2 K temperature in a magnetic stirrer operating at 500 rpm. The experiments were performed at the initial pH 5. This pH was found to be the optimum for phosphate adsorption onto calcined alunite in the previous experiments [4,7,8]. The pH of the solutions was adjusted with HCl or NaOH solution by using a pH meter. At the end of the adsorption period, the samples were taken and filtered through a 0.45-μm Milipore filter paper and then the concentration of

Table 1
The chemical composition of original and calcined alunite ores in weight percentage

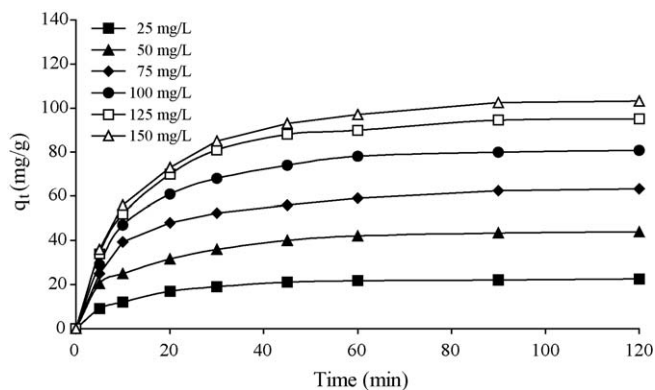|	Al₂O₃	SiO₂	SO₃	Fe₂O₃	TiO₂	CaO	MgO	K₂O	Na₂O	H₂O
Original	20.85	48.19	17.91	0.07	0.17	0.17	0.10	4.59	0.06	7.89
Calcined	26.22	60.61	6.68	0.09	0.21	0.21	0.13	5.77	0.08	–

Fig. 2. Adsorption kinetics of phosphate on calcined alunite at different initial concentration. Conditions: 90–150 μm particle size, 1073 K and 30 min calcination, 1 g/L dose, 298 K temperature and pH 5.

the residual phosphate, C_t, was determined by the stannous chloride method described in Standard Methods [25] with the aid of a spectrophotometer (Shimadzu UV-150-02). The measurements were made at the wavelength $\lambda = 690$ nm, which corresponds to maximum absorbance. The amount of phosphate adsorbed onto calcined alunite, q_t (mg/g), was calculated as follows:

$$q_t = \frac{(C_0 - C_t)V}{W} \tag{20}$$

where C_0 and C_t are the initial and time t solution concentrations of phosphate (mg/L), respectively, V the volume of the solution (L) and W the weight of calcined alunite used (g).

4. Results and discussion

4.1. Kinetic and equilibrium analysis

Fig. 2 shows that the amount of phosphate adsorption increases with time and it remains constant after a operating time of 60 min (i.e. the equilibrium time). The equilibrium time is independent of initial phosphate concentration.

The kinetics of phosphate adsorption onto alunite have been studied using four models: pseudo first- and second-order kinetics, intraparticle diffusion and the Elovich equation. Fig. 3 shows a plot of Eq. (5) for the adsorption of phosphate onto alunite.
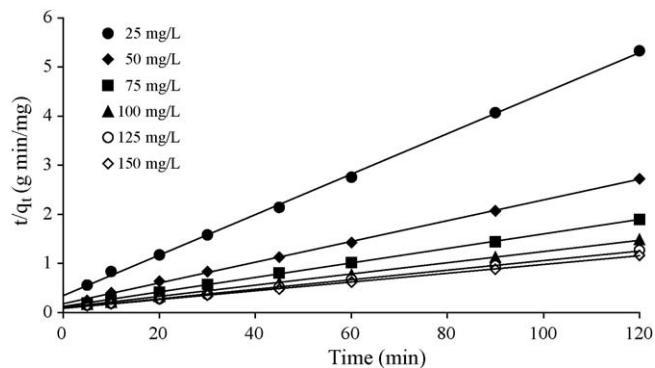

Fig. 3. Plot of the pseudo second-order adsorption kinetics of phosphate on calcined alunite at different initial concentration. Conditions: 90–150 μm particle size, 1073 K and 30 min calcination, 1 g/L dose, 298 K temperature and pH 5.

Table 2
Comparison of kinetic parameters for the adsorption of phosphate onto alunite

| C_0 (mg/L)	$q_{e,exp}$ (mg/g)	First-order kinetic equation				Second-order kinetic equation				The Elovich equation				Intraparticle diffusion equation		
		q_1 (mg/g)	k_1 (1/min) $\times 10^2$	r_1^2	S.D.	q_2 (mg/g)	k_2 [g/(mg min)] $\times 10^3$	r_2^2	S.D.	α	β	r_E^2	S.D.	k_{int} [mg/(g min$^{1/2}$)]	r_{int}^2	S.D.
25	22.5	13.8	4.35	0.961	0.537	24.3	4.88	0.999	0.039	6.03	0.203	0.975	0.061	3.19	0.976	0.298
50	44.0	30.6	4.56	0.999	0.464	47.2	2.52	0.999	0.058	12.8	0.108	0.979	0.061	5.84	0.956	0.275
75	63.3	41.1	4.17	0.982	0.518	67.6	1.78	0.999	0.026	18.2	0.075	0.975	0.065	8.52	0.936	0.277
100	80.7	58.5	5.00	0.997	0.406	87.7	1.31	0.999	0.041	21.4	0.056	0.976	0.071	11.4	0.963	0.279
125	95.0	77.5	5.34	0.982	0.301	103	1.06	0.999	0.034	24.2	0.048	0.978	0.065	13.6	0.977	0.280
150	103	90.3	5.21	0.978	0.246	112	0.88	0.999	0.017	25.2	0.044	0.986	0.055	14.3	0.977	0.258
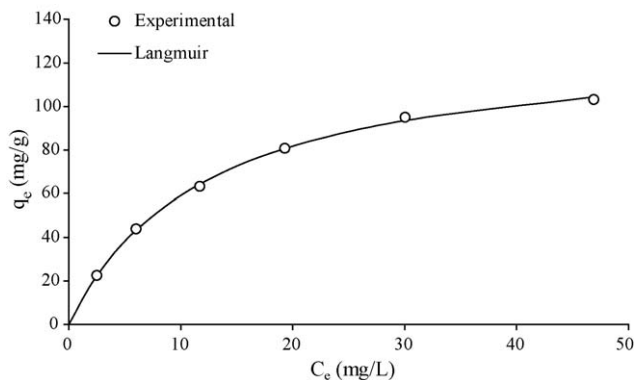
Fig. 4. Equilibrium isotherms of phosphate on calcined alunite. Conditions: 90–150 μm particle size, 1073 K and 30 min calcination, 1 g/L dose, 298 K temperature and pH 5.

The results demonstrate a highly significant linear relationship between adsorbed phosphate, t/q_t, and t in these studies with high correlation coefficients and least standard deviations. The kinetic parameters for the pseudo first- and second-order equations, intraparticle diffusion and the Elovich equation and correlation coefficients are tabulated in Table 2.

In order to quantitatively compare the applicability of each kinetic model, a standard deviation (S.D.) is calculated as follows [26]:

$$\text{S.D.} = \sqrt{\frac{\sum \left[(q_{t,\exp} - q_{t,\text{cal}})/q_{t,\exp}\right]^2}{n-1}} \qquad (21)$$

where n is the number of data points. Table 2 lists the calculated results for each kinetic equation. Four different kinetic models were used to fit the experimental data. The comparison of the standard deviation of the kinetic models should assist in identifying the best fit equation. Since the S.D. method represents the agreement between the experimental data points and models, the S.D. value provides a numerical value to interpret the goodness of fit of a given mathematical model to the data. Table 2 shows that the least values of S.D. are given by pseudo second-order equation. The Elovich equation follows the pseudo second-order one and also provides a good fitting to the experimental data points.

The model providing the best correlation with experimental data was the pseudo second-order model and this has been used to analyse the experimental batch adsorber operating time data in the present paper.

An isotherm study is significant in obtaining the equilibrium adsorption capacity as the maximum capacity. The Langmuir isotherm for the adsorption of phosphate onto alunite is shown in Fig. 4. The maximum adsorption capacity of phosphate, Q, calculated from the intercept and slope of the linear Langmuir equation and was found to be 132.4 mg/g.

The calcined alunite has high phosphate adsorption capacity as compared to original alunite. Because the structure of aluminum in the alunite is in the form of $Al(OH)_3$ and $Al_2(SO_4)_3$, it does not have good adsorbent properties. The aluminum in the alunite is converted to the Al_2O_3 releasing H_2O and SO_3 during the calcination process. Thus the calcined alunite shows a good

adsorbent property as it forms Al_2O_3. We observed in one of our previous study related with the adsorption of reactive dyes onto calcined alunite [19] that the original alunite does not have good adsorbent properties.
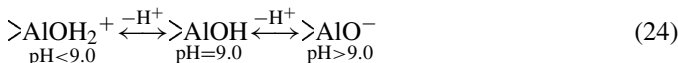
4.2. Adsorption mechanism

The major components of alunite are metal oxides mainly of Al and Si (Table 1). These metal oxides form metal-hydroxide complexes in solution and the subsequent acidic or basic dissociation of these complexes at the solid-solution interface leads to the development of a positive or negative charge on the surface. The pH of the phosphate solution plays an important role in the whole adsorption process and particularly on the adsorption capacity. The adsorption capacity is strongly pH dependent, i.e. capacity increases for decreasing pH. However, below a pH value of about 4–4.5 the adsorption capacity decreases due to a higher solubility of alumina [4,27]. At the acidic pH values, activated alumina in the alunite in solution tends to form an aqua complex to yield a positively charged surface [13,24,28].

$$> \text{AlOH} + \text{H}^+ \rightarrow > \text{AlOH}_2^+ \qquad (22)$$

At alkaline pH values, the surface of alumina tends to become negatively charged.

$$> \text{AlOH} + \text{OH}^- \rightarrow > \text{AlO}^- + \text{H}_2\text{O} \qquad (23)$$
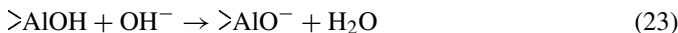
The pH at zero point of charge (pH_{ZPC}) is reported as 9.0 for alumina [28,29]. For this reason, the pH of the aqueous suspension of alumina is changed from acidic to alkaline pH range; equilibrium is reached as follows:

$$\underset{\text{pH}<9.0}{>\text{AlOH}_2^+} \overset{-\text{H}^+}{\underset{}{\longleftrightarrow}} \underset{\text{pH}=9.0}{>\text{AlOH}} \overset{-\text{H}^+}{\underset{}{\longleftrightarrow}} \underset{\text{pH}>9.0}{>\text{AlO}^-} \qquad (24)$$

The pH dependency is both related to the amphoteric properties of the alumina surface and to the polyprotic nature of phosphate, however, several explanations to these phenomena are proposed in literature [4,30]. The following type of interactions between phosphate ion and alumina surfaces are possible: (i) the increase in the density of the positive charges for pH values is lower than the pH_{ZPC} resulting from the protonation of Al–OH surface groups in Al–OH_2^+ and (ii) at this pH values, practically two phosphate species (H_2PO_4^- and HPO_4^{2-}) exist in the solution. Phosphate adsorption on oxide surface was shown to be chemical in nature. Specifically, a strong contribution to the phosphate binding comes from a complexation or ion exchange process on the Al–OH_2^+ and Al–OH sites. Phosphate adsorption as a function of pH is more likely to be determined by the stability of phosphate surface complexes (Al $-$ $\text{OPO}_3\text{H}_x^{x-2}$, where x is 1, 2 or 3) than the electrostatic attraction/repulsion from the surface charge.

If it is to consider that 1 g of alunite, the chemical composition shown in Table 1, it has 2.571 mmol Al_2O_3 having the structure of $>\text{AlOH}_2^+$ in the solution medium, then this amount of alunite has theoretically the anion exchange capacity of 2.571 meq/g alunite. The phosphate adsorption capacity of alunite has been found to be 132.4 mg/g from the Langmuir

equation. This amount is equal to 1.394 mmol phosphate. Phosphate is hydrolyzed in the water as HPO_4^{2-} and $H_2PO_4^-$ anions in the studied pH range. If we assume that there is only HPO_4^{2-} or $H_2PO_4^-$ anions in the solution then the required anion exchange capacity should be 1.379 meq and 2.730 meq, respectively. But phosphate is predominantly present as the $H_2PO_4^-$ species with a minor fraction present as the HPO_4^{2-} species in solution at pH 5. From the theoretical calculations the anion exchange capacity of alunite is more than the required level for the phosphate adsorption.

It can be shown from Table 1 that alunite contains higher amount of SiO_2 than Al_2O_3. Therefore, it is considered that phosphate is also adsorbed on SiO_2 surface. But the structure of SiO_2 found together with alunite is in quartz form and is not in activated SiO_2 form. Küçük and Gülapoğlu [31] showed that even though the alunite was calcined over 1273 K temperature, SiO_2 has the structure of quartz, and this structure does not contribute the adsorption of phosphate.

4.3. Batch adsorber design analysis

Batch type processes are usually limited to the treatment of small volumes of wastewaters. The efficiency of solute removal can be improved if the solution is treated using a number of batch stages rather than a single stage batch process. In a batch adsorption process, adsorbent is contacted with the solution in a tank for a period of time at fixed operating conditions. The adsorbent is separated from the mixture by settling, filtration or centrifugation, and then regenerated or discharged.

The application of the operating time model to the design and time optimization of batch adsorbers is undertaken. The corresponding linear plots of the values of k and q_e against initial phosphate concentration (from Eqs. (16) and (17)), were regressed to obtain expression for these values in terms of the initial phosphate concentration. High correlation coefficients were obtained as shown in Table 3.

The S.D. values were also calculated for Eqs. (16) and (17), and given in Table 3. Table 3 shows that the S.D. values for Eqs. (16) and (17) were considerably low. Therefore, these equations can be successfully used for the batch adsorber design, and the results obtained from batch adsorber design model provide good fitting to experimental data.

A typical example is considered for the case of a two-stage crosscurrent batch adsorption, when the solution to be treated 10,000 L solution, the amount of alunite added is 10 kg in each of the two-stages and the initial phosphate concentration is

Table 3
Empirical parameters for predicted k and q_e from C_0

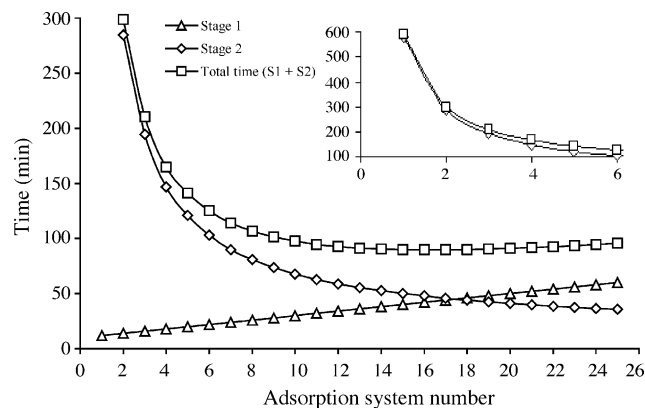|	
X_k	0.106
Y_k	−0.953
r^2	0.999
S.D.	0.016
X_q	1.521
Y_q	0.872
r^2	0.995
S.D.	0.047

Fig. 5. Comparison of 95% phosphate removal time of each stage in two-stage phosphate/alunite process. Conditions: 90–150 μm particle size, 1073 K and 30 min calcination, 1 g/L dose, 298 K temperature and pH 5.

100 mg/L in the first stage. A series of operating times from 12 min up to 60 min in 2 min increments has been considered in Stage 1 of a two-stage batch adsorber system, that is twenty-four 2 min increments. Therefore, in Figs. 5 and 6 each system number (1–25) is based on a 2 min operating time interval in Stage 1 of two-stage system. In the first adsorber for example, system number 10 implies that the first adsorber operating time is 12 min + (10 − 1) × 2 min = 30 min, because system number 1 represents 12 min operating time in adsorber number 1. Therefore the operating time in the second adsorber, t_2, is the time required, T (min), to achieve a fixed total percentage phosphate removal minus the operating time in the first adsorber stage t_1, therefore:

$$T = t_1 + t_2 \tag{25}$$

For N system, t_1, becomes:

$$t_1 = 12 + (N - 1) \times 2 \text{ min} \tag{26}$$

And the total batch operating time, T, is:

$$T = 12 + (N - 1) \times 2 \text{ min} + t_2 \tag{27}$$

The total operating time is calculated for each system number, $N = 1$–25 (based on the fixed t_1 values), for a fixed percentage
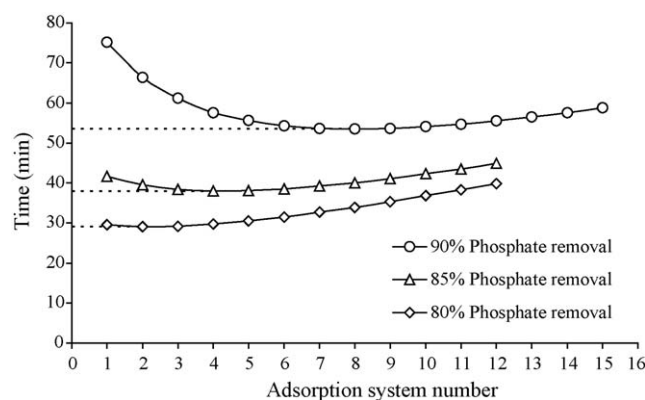

Fig. 6. Minimum contact time for various percentage phosphate removal in a two-stage phosphate/alunite process. Conditions: 90–150 μm particle size, 1073 K and 30 min calcination, 1 g/L dose, 298 K temperature and pH 5.

Table 4
Minimum adsorption times (min) to achieve various percentage phosphate removal for a series of two-stage and a single-stage adsorption systems

	Two-stage adsorber				Single stage adsorber
	System number	Stage 1 (min)	Stage 2 (min)	Total time (min)	Time (min)
95% removal time	17	44	45.7	89.7	No removal over 83%
90% removal time	10	30	24.1	54.1	
85% removal time	4	18	20	38	600 (83% removal)
80% removal time	2	14	15.1	29.1	170

phosphate removal. The T values are plotted against the system number, N, as shown in Figs. 5 and 6, and the minimum operating time can be determined.

Fig. 5 shows a comparison of the time for 95% phosphate removal for each stage and the total reaction time of the two-stage crosscurrent batch adsorption process. Table 4 shows the reaction time for each individual stage and the minimum total operating time for various percentage phosphate removals in the two-stage process can be evaluated from Eq. (18) for each system. From the design criteria, the percentage phosphate removal by the adsorber system is defined. In the two-stage system in Table 4, four examples have been shown, namely, 95, 90, 85 and 80% phosphate removal. The total operating time, T, to achieve this fixed percentage phosphate removal can be determined based on the fixed operating time assigned to Stage 1, t_1. The data can then be plotted for the 25 systems at a fixed percentage phosphate removal for Stage 1, Stage 2 and Stage 1 + Stage 2 as shown by the three curves in Fig. 5. The minimum operating time for 95% phosphate removal can be found, using Eq. (18) or by plotting graphs analogous to Fig. 5. The data for Stage 1 + Stage 2 at three percentage phosphate removal are presented in Fig. 6. The minimum total operating time to achieve each percentage phosphate removal is shown by the dashed line.

To compare with two-stage process, the times needed by a single stage process resulting the same removal have been determined and are given in Table 4. As can be seen from Table 4, to obtain same removal in a single stage process needs more time than two-stage process.

The average total phosphorus concentration in domestic wastewater is found to be about 10 mg/L expressed as elemental phosphorus [32]. This value is equal to 30.65 mg/L PO_4^{3-} concentration, and this concentration is about 30% of used concentration (100 mg/L) in this modeled study. If the suggested two-stage batch adsorption system in the present study is applied in the case of real world, the required time for the 95% phosphate removal is about 30 min. Since the required time for the 95% phosphate removal from aqueous solution containing 100 mg/L phosphate is 90 min. The suggested model will provide more effective phosphate removal in the case of real world, because the phosphate concentration of real wastewater is lower than the studied concentration.

5. Conclusion

Kinetic studies were made for the adsorption of phosphate from aqueous solutions onto alunite in the concentration range 25–150 mg/L at initial pH 5 and 298 ± 2 K temperature. The

kinetic data have been analyzed using pseudo first- and second-order equations, intraparticle diffusion equation and the Elovich equation. The characteristic parameters for each kinetic equation and related correlation coefficients have been determined. It was clear that the sorption kinetics of phosphate to alunite obeyed second-order adsorption kinetics. The equilibrium data fit well in the Langmuir isotherm.

The design model presented is based on a pseudo second-order equation and this has been used for minimizing the reaction time used in a two-stage crosscurrent system. The minimum operating time to achieve a fixed percentage of phosphate removal from aqueous solutions by adsorption using a fixed mass of adsorbent can be readily predicted. It is particularly suitable for low-cost adsorbents/adsorption systems, when minimizing operating time is a major operational and design criterion. To obtain same removal, in single stage process, is required more time for phosphate with respect to removal in two-stage process. Also, phosphate cannot be removed over 83% in single stage process.

It is concluded that alunite can be used as a low-cost, natural and abundant source for the removal of phosphate and it may be alternative to more costly materials. Assuming the batch adsorption to be two-staged kinetic and equilibrium operation, the separation process can be defined mathematically using this adsorber design model to estimate the minimum operating time for desired purification.

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