

# Phosphorus Adsorption–Desorption on a Surfactant-Modified Natural Zeolite: A Laboratory Study

Nina S. Dionisiou · Theodora Matsi ·  
Nikolaos D. Misopolinos

Received: 18 May 2012 / Accepted: 7 November 2012 / Published online: 28 November 2012  
© Springer Science+Business Media Dordrecht 2012

**Abstract** Phosphorus adsorption–desorption on a surfactant-modified zeolite (SMZ) was studied with laboratory experiments, in the perspective of using the SMZ for P removal from waters enriched with P. The effects of temperature, pH, and  $\text{NO}_3^-$  concentrations on P adsorption on the SMZ were assessed. In addition, P desorption from the SMZ spiked with P at two concentrations (50 and 200  $\text{mg kg}^{-1}$ ) was investigated. Adsorption data indicated that the SMZ has a high adsorption capacity for P and conformed satisfactorily to the nonlinear forms of Freundlich and Langmuir equations, the latter being slightly superior. Phosphorus adsorption on the SMZ was a fast, exothermic reaction. As the pH of the equilibrium solution increased from the acidic to alkaline range, P adsorption was also increased. In the presence of  $\text{NO}_3^-$  in the external solution, P adsorption was reduced only at the highest  $\text{NO}_3^-$  concentration studied (50  $\text{mg L}^{-1}$ ). In both cases of the P-spiked SMZ, P desorption was not affected by P initial concentration and the overall amount of desorbed P reached only the 7.5  $\text{mg kg}^{-1}$ .

Results showed that SMZ can be an effective adsorbent for P and could be used for P removal from waters enriched with P; however, the latter has to be confirmed by large-scale experiments.

**Keywords** Surfactant-modified zeolite · Phosphorus adsorption · Phosphorus desorption · Water quality

## 1 Introduction

Excessive application of fertilisers and chemicals in arable soils, intensive livestock operations and disposal of high volumes of untreated wastewater and solids have resulted in an increasing number of surface water, groundwater and soil contamination problems (Dou et al. 2009; Shin et al. 2004; Valsami-Jones 2001). High levels of P, along with N, due to farm effluents and fertilisers application to soils, pose a significant threat to many water bodies because of the eutrophication risk (Daniel et al. 1998). Although P is an essential element for plant growth and necessary to maintain profitable crop yield, it also increases the biological productivity and thus it can cause adverse environmental effects on surface waters (Correll 1998). Water-quality criteria for P have been established and translated to legislated limits, below which environmental risks are unlikely or risk is within an acceptable range (Council Directive 91/271/EC 1991; USEPA 1986).

---

N. S. Dionisiou (✉) · N. D. Misopolinos  
Laboratory of Applied Soil Science, School of Agriculture,  
Aristotle University of Thessaloniki,  
54124 Thessaloniki, Greece  
e-mail: odionyisi@agro.auth.gr

T. Matsi  
Soil Science Laboratory, School of Agriculture, Aristotle  
University of Thessaloniki,  
54124 Thessaloniki, Greece

Based on the above, the removal of P from waters is of prime importance, especially for aqua sources near urban and agricultural areas. Various P removal methods from contaminated water resources have been reported in the literature, including physical such as membrane technologies, biological such as P bacterial removal or plant and algae uptake (Drizo et al. 1999) and chemical methods, such as precipitation and adsorption. Each of the above methods has advantages and disadvantages; however, chemical adsorption techniques, due to their simplicity and low cost, are attracting more attention. Different materials can be used for removing P from waters, including fly ash (Agyei et al. 2002; Drizo et al. 1999; Grubb et al. 2000), slag (Agyei et al. 2002), gas concrete (Oguz et al. 2003), Fe and Al oxides, gibbsite, dolomite (Hesterberg and Beauchemin 2000), aluminium oxide-hydroxide (Tanada et al. 2002), calcined layered double hydroxides (Hosni and Srasra 2010), hematite and bentonite (Dimirkou et al. 2002), calcium-modified bentonite (Khadhraoui et al. 2002), bauxite, shale, limestone and clay aggregates (Drizo et al. 1999). However, many of these materials exhibited insufficient adsorption and regeneration capacities as well as poor selectivity and limited surface area (Saad et al. 2008). Therefore, it is worthy studying other materials, with high surface area, open pore structure and high adsorption capacity, as adsorbents for P.

Zeolite is a porous alumino-silicate mineral, with high adsorption capacity for cations because of its high negative charge (Bowman et al. 2000). Zeolites have been widely used to improve the quality of water systems through removing inorganic cations, trace and radioactive elements (Faghihian et al. 1999; Mercer and Ames 1978; Misaelides et al. 1995; Rajec et al. 1998). Surfactant-modified zeolite (SMZ), i.e. zeolite with positive surface charge, because of its surface modification with a cationic surfactant substance, may be useful in removing P anionic species from water through adsorption. The fact that zeolite is highly available from natural sources at low cost, in certain countries, combined with the simple techniques that can be used for its surface modification, suggests that this material could be an alternative to other adsorbents for remediating P enriched waters. Several studies have indicated that SMZ is an effective adsorbent for many anions, such as  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$  (Li et al. 1998),  $\text{CrO}_4^{2-}$  (Haggerty and Bowman 1994; Li 2004),  $\text{H}_2\text{AsO}_4^-$  and  $\text{HAsO}_4^{2-}$  (Li et al. 2007),  $\text{ClO}_4^-$  (Zhang et al.

2007),  $\text{HSeO}_3^-$  and  $\text{SeO}_4^{2-}$  (Frenay et al. 2000). There are few studies, however, that have investigated P adsorption on SMZ (Allred 2010; Dao 2003; Vujakovic et al. 2000, 2003; Widiastuti et al. 2008).

The objectives of this study were to further evaluate certain factors that could affect P adsorption on a SMZ, in the perspective of using the SMZ for P removal from waters enriched with P. Specifically, the effect of: (a) temperature (exothermic or endothermic character of adsorption reaction), (b) pH (as a factor controlling P speciation) and (c)  $\text{NO}_3^-$  (as competing anion, present at two concentrations typical for agricultural subsurface drainage systems), on P adsorption on the SMZ were studied. In addition, the desorbability of externally added P from the SMZ was investigated.

## 2 Materials and Methods

### 2.1 Surface Modification of the Zeolite

The natural zeolite used was clinoptilolite with the chemical formula  $(\text{Ca}_{1.5}\text{K}_{1.4}\text{Mg}_{0.6}\text{Na}_{0.5}) (\text{Al}_{6.2}\text{Si}_{29.8}\text{O}_{72}) \cdot 20\text{H}_2\text{O}$  and its chemical composition, as it was determined by the Department of Mineralogy-Petrology-Economic Geology of the Aristotle University of Thessaloniki using TXRD analysis (Denaix et al. 1999), is presented in Table 1. The zeolite was sieved through a 2 mm stainless steel screen

**Table 1** Certain chemical properties of the natural zeolite

Cation exchange capacity ( $\text{cmol}_c\text{kg}^{-1}$ )	226
External cation exchange capacity ( $\text{cmol}_c\text{kg}^{-1}$ )	10
$\text{SiO}_2$ ( $\text{gkg}^{-1}$ ) <sup>a</sup>	679
$\text{H}_2\text{O}$ ( $\text{gkg}^{-1}$ ) <sup>a</sup>	131
$\text{Al}_2\text{O}_3$ ( $\text{gkg}^{-1}$ ) <sup>a</sup>	120
$\text{CaO}$ ( $\text{gkg}^{-1}$ ) <sup>a</sup>	31
$\text{K}_2\text{O}$ ( $\text{gkg}^{-1}$ ) <sup>a</sup>	25
$\text{MgO}$ ( $\text{gkg}^{-1}$ ) <sup>a</sup>	8.9
$\text{Na}_2\text{O}$ ( $\text{gkg}^{-1}$ ) <sup>a</sup>	5.1
$\text{TiO}_2$ ( $\text{gkg}^{-1}$ ) <sup>a</sup>	<0.1
$\text{Fe}_2\text{O}_3$ ( $\text{gkg}^{-1}$ ) <sup>a</sup>	<0.1
$\text{MnO}$ ( $\text{gkg}^{-1}$ ) <sup>a</sup>	<0.1
$\text{Si}/\text{Al}$ <sup>a</sup>	4.8

<sup>a</sup> The determination of the chemical property was performed by the Department of Mineralogy-Petrology-Economic Geology of the Aristotle University of Thessaloniki (TXRD method)

sieve, and this material was used for all analyses and P adsorption-desorption experiments, after the modification of its surface charge. The total and the external cation exchange capacity of the zeolite determined using the method of Ming and Dixon (1987) and found to be 226 and 10  $\text{cmol}_c\text{kg}^{-1}$ , respectively (Table 1).

Modification of the zeolite's surface charge was accomplished using hexadecyltrimethylammonium bromide ( $\text{C}_{19}\text{H}_{42}\text{BrN}$  or HDTA-Br), according to Bowman et al. (2000). Specifically, a quantity of zeolite sufficient to conduct all the experiments was equilibrated with 0.05 M HDTMA-Br, for 24 h, at  $25\pm 1$  °C, with intermittent shaking. The solution of 0.05 M HDTMA-Br was added to the zeolite at a ratio 4/1 (v/w) and contained an amount of HDTMA-Br equivalent to the double external cation exchange capacity of the zeolite. At the end of the equilibration period, the suspension of the SMZ and HDTMA-Br was centrifuged (at 7,000 rpm, for 5 min) washed three times with distilled water and air-dried. This material was used to all subsequent experiments.

## 2.2 Phosphorus Adsorption Experiments

To establish the optimum equilibration solution/adsorbent ratio and time for P adsorption on the SMZ, two preliminary batch adsorption experiments were conducted (data not shown). For the first parameter, a tentative equilibration time of 24 h was used, the solution/adsorbent ratios tested were 5/1, 10/1, 20/1 and 50/1 (v/w). From the four ratios, the highest percentages of P adsorbed on the SMZ were obtained for the ratios 5/1 and 10/1 (v/w) and finally the ratio 10/1 (v/w) was selected for practical reasons, in respect to laboratory work mainly. Using the solution/adsorbent ratio of 10/1 (v/w), the equilibration time was selected by testing different periods of equilibration time (1, 2, 4, 6, 8, 10 and 24 h) and found to be 1 h, as it was found also by Vujakovic et al. (2000, 2003). Consequently, the equilibration solution/adsorbent ratio and time used in all subsequent P adsorption experiments on the SMZ were 10/1 (v/w) and 1 h, respectively.

Phosphorus adsorption data were obtained by a slight modification of the technique used by Li et al. (2007). Four grammes sub-samples of the SMZ, in three replicates, were placed in 50 mL polypropylene centrifuge tubes with 40 mL of deionized water, containing varying concentrations of P (0, 0.5, 1, 2, 5, 8, 10, 12, 15, 20, 30, 40 and 50  $\text{mgL}^{-1}$ ) as  $\text{KH}_2\text{PO}_4$ . The

suspensions were equilibrated for 1 h at  $25\pm 1$  °C with intermittent shaking. After equilibration the tubes were centrifuged and the supernatant liquid was filtered and analysed for P, employing the ascorbic acid method (Murphy and Riley 1962), using a UV-vis Spectrophotometer (Lambda 5, Perkin-Elmer). The amount of adsorbed P was calculated by the difference between the amount added and that found in solution at equilibrium. Phosphorus adsorption data were obtained at: (a) three temperatures, namely,  $25\pm 1$  °C,  $35\pm 1$  °C (data not shown) and  $65\pm 1$  °C, (b) two pH values of the external solution, namely,  $4.2\pm 0.1$  (adjusted by 0.5 M HCl) and  $10.4\pm 0.1$  (adjusted by 0.5 M NaOH), at  $25\pm 1$  °C and (c) two  $\text{NO}_3^-$  concentrations in the external solution, namely 25 and 50  $\text{mg NO}_3^- \text{L}^{-1}$ , as  $\text{KNO}_3$ , at  $25\pm 1$  °C. In all cases, pH in the equilibrium solution was determined.

The following nonlinear equations were fitted to P adsorption data by nonlinear regression, using the Levenberg-Marquardt algorithm and the statistical package SPSS, version 19:

$$\text{Langmuir equation : } x = \text{KMC}/(1 + \text{KC}) \quad (1)$$

$$\text{Freundlich equation : } x = \text{kC}^n \quad (2)$$

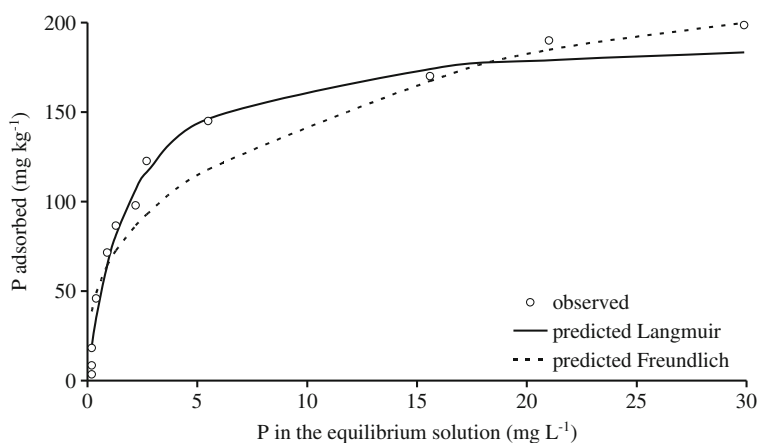
where  $x$  is the amount of P adsorbed (in milligrammes per kilogramme),  $C$  is P concentration in the equilibrium solution (in milligrammes per litre),  $K$  is a parameter related to the affinity of the adsorbent to adsorbate (in litres per milligramme),  $M$  is the maximum P adsorption capacity (in milligrammes per kilogramme),  $n$  is a parameter that can be considered as a measure of adsorption intensity and  $k$  is a parameter corresponding to the amount of P adsorbed when  $C$  is equal to 1.

To evaluate the goodness of fit of each equation, the standard errors (SE) of the estimate were used along with  $F$  tests. In addition, the standard errors of the estimated parameters along with  $t$  tests were used. Appropriate comparisons among the estimated parameters were performed using  $t$  test.

## 2.3 Phosphorus Desorption Experiments

Sub-samples of the SMZ were spiked with P in the form of a solution of  $\text{K}_2\text{HPO}_4$ , at rates equal to 200 and 50  $\text{mg Pkg}^{-1}$  of the substance; these concentrations were equal to the maximum and a quarter of the maximum P adsorption capacity, respectively,

**Fig. 1** Isotherms (experimental, Langmuir and Freundlich) of P adsorption on the SMZ, at  $25\pm 1$  °C



according to the Langmuir equation (see next section). After P addition, the samples were left to equilibrate for 10 days with periodical wetting and drying, then air-dried and used to the two following (one short-term and the other long-term) batch desorption experiments. In both experiments, a slight modification of the technique reported by Li (2003) was used.

For the short-term desorption experiment of P from the SMZ, 4 g of the P-spiked sub-samples of the SMZ, in three replications, were placed in 50 mL polypropylene centrifuge tubes with 40 mL of deionised water and equilibrated for different periods, namely, 0.25, 0.5, 1, 2, 4, 6, 8, 10 and 12 h, at  $25\pm 1$  °C, by intermittent shaking. At the end of each equilibration period, three tubes were centrifuged and the supernatant liquid was filtered and analysed for P, employing the ascorbic acid method. The same desorption experiment was conducted with 0.01 M KCl as external solution instead of deionised water (data not shown). For the long-term desorption experiment of P from the SMZ, 4 g of the P-spiked sub-samples of the SMZ, in three replications, were placed in 50 mL polypropylene centrifuge tubes with 40 mL of deionised water and equilibrated for 24 h, at  $25\pm 1$  °C, by intermittent shaking. After equilibration the tubes were centrifuged, 25-mL aliquot of the supernatant solution

was removed and analysed for P, employing the ascorbic acid method. The 25-mL aliquot removed was replaced with 25 mL of deionised water; the mixtures were re-suspended and equilibrated for 24 h, at  $25\pm 1$  °C. This procedure was repeated until P concentration in the supernatant liquid reached undetectable levels ( $< 0.1$  mgL<sup>-1</sup>), resulting in a total of four desorption steps, i.e. a maximum of 96 h desorption time. The amount of P desorbed at each step was corrected for the amount of P transferred from the previous step.

Multway factorial analysis of variance was performed to the desorption data to evaluate main effects and interactions and Duncan's multiple range test was used for mean comparisons, using the statistical package SPSS, version 19.

### 3 Results and Discussion

#### 3.1 Phosphorus Adsorption on the SMZ

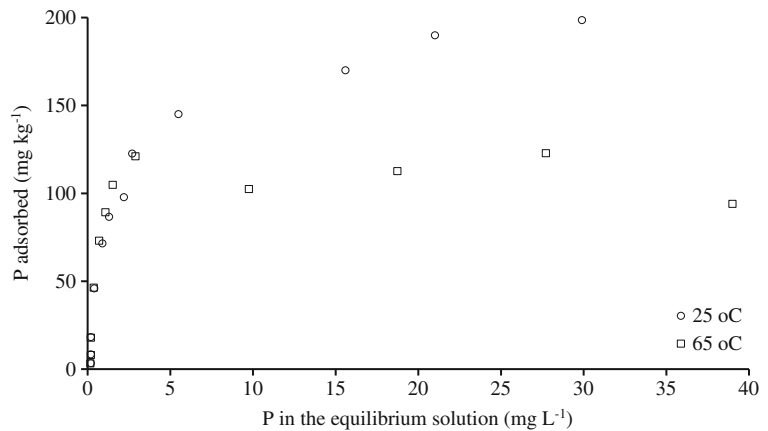
Phosphorus adsorption isotherm obtained at  $25\pm 1$  °C was L-shaped (Fig. 1) and according to Sparks (1984), such adsorption behaviour, could be explained by the strong affinity of the SMZ for P, at low P concentrations,

**Table 2** The standard errors of the estimate (SE), the values of the *F* test and the respective *p* values of the equations Langmuir and Freundlich and their estimated parameters, at  $25\pm 1$  °C

Equation	SE	<i>F</i> test	<i>p</i>	Estimated parameters			
				<i>M</i> (mean±SE mg kg <sup>-1</sup> )	<i>k</i> (mean±SE)	<i>K</i> (mean±SE L mg <sup>-1</sup> )	<i>n</i> (mean±SE)
Langmuir	14.0	396	<0.001	194±10		0.55±0.10	
Freundlich	22.5	152	<0.001		67±8		0.34±0.05

SE standard error

**Fig. 2** Isotherms of P adsorption on the SMZ, at the two temperatures



which then decreases as P concentration increases. Adsorption data conformed satisfactorily to the nonlinear forms of both the Langmuir and Freundlich equations (Fig. 1). However, the Langmuir equation was slightly superior as judged by data fit (presented in Fig. 1), but also by the lower SE of the estimate and the higher value of the  $F$  test which were used as the criteria of goodness of fit (Table 2). Consequently, the Langmuir equation was selected to evaluate adsorption data obtained from all adsorption experiments. In both cases, the estimated values of the parameters,  $K$  and  $M$  of the Langmuir equation but also of the parameters  $k$  and  $n$  of the Freundlich equation, were significant, as evidenced by their low standard errors (Table 2) but also by the  $p$  values of the  $t$  tests, which were  $<0.001$ . According to literature, the nonlinear Langmuir equation satisfactorily described the adsorption of different anions onto SMZs, such as  $\text{CrO}_4^{2-}$  (Bowman et al. 2000; Li et al. 1998),  $\text{NO}_3^-$  (Li 2003),  $\text{H}_2\text{AsO}_4^-$ ,  $\text{HAsO}_4^{2-}$  (Li et al. 2007) and  $\text{ClO}_4^-$  (Zhang et al. 2007). In all cases of this and also in the rest of the adsorption experiments where un-buffered external solutions were used, pH of the equilibrium solution was  $6.9 \pm 0.3$ .

Comparing the SMZs P adsorption Langmuir  $M$  to other adsorbents, certain other materials exhibited comparable adsorbing capacity, such as kaolinite–goethite systems (Ioannou et al. 2001) and some kaolinite clays (Sei et al. 2002). However, other showed higher adsorbing capacity, such as fly ash, synthetic zeolite by-product (Dao 2003), ammonium-functionalised mesoporous silica materials (Saad et al. 2008), natural and synthetic palygorskite (Hengpeng et al. 2006) and calcined-layered double hydroxides (Hosni and Srasra 2010).

Conducting the adsorption experiments at  $25 \pm 1$  and  $35 \pm 1$  °C, it was revealed that no safe conclusions concerning the exothermic or endothermic character of the adsorption reaction could be drawn. For this reason, data obtained at  $35 \pm 1$  °C are not shown and P adsorption on the SMZ at  $65 \pm 1$  °C was also studied. Phosphorus adsorption data at the two temperatures ( $25 \pm 1$  and  $65 \pm 1$  °C) showed that the SMZ removed more than 80 % of the added P, when P concentration in the external solution was less than  $20 \text{ mg L}^{-1}$ . The Langmuir equation was adequately fitted to the adsorption data obtained at  $65 \pm 1$  °C ( $\text{SE}=17$ ,  $F=42$ ,  $p<0.001$ ;  $p$  values of the  $t$  tests were  $<0.001$  for  $M$  and  $<0.01$  for  $K$ ). Plotting P adsorption isotherms at  $25 \pm 1$  and  $65 \pm 1$  °C revealed the exothermic character of the reaction since the isotherm at the lower temperature was located above the isotherm at the higher temperature; this trend was more pronounced at higher P concentrations in the equilibrium solution (Fig. 2). The exothermic character of the reaction was reflected in the estimated Langmuir adsorption  $M$  which was significantly higher at  $25 \pm 1$  than  $65 \pm 1$  °C (Table 3). Reported studies relevant to the endothermic or exothermic nature of adsorption of different anions on SMZs are rare. However, Sullivan et al. (2003) reported that As

**Table 3** Parameters of the Langmuir equation, at the two temperatures

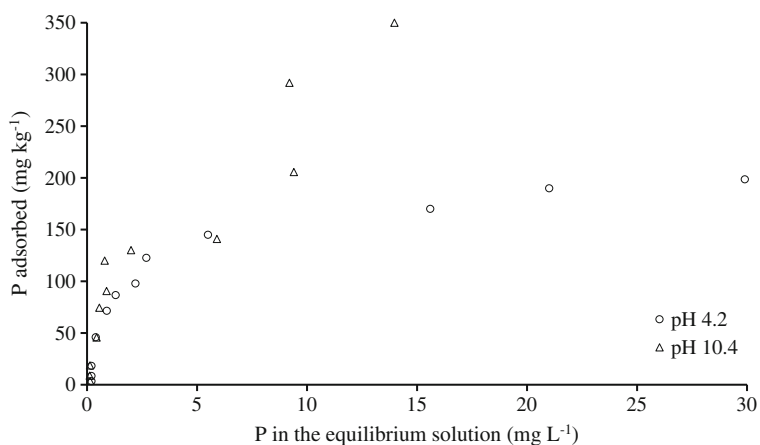
Temperature (°C)	$M$ (mean $\pm$ SE $\text{mg kg}^{-1}$ )	$K$ (mean $\pm$ SE $\text{L mg}^{-1}$ )
25 $\pm$ 1	194 $\pm$ 10 a	0.55 $\pm$ 0.10 a
65 $\pm$ 1	127 $\pm$ 10 b	1.46 $\pm$ 0.44 a

Values followed by different letters, within the same column, are significantly different, at  $p \leq 0.05$ , using  $t$  test

SE standard error



**Fig. 3** Isotherms of P adsorption on the SMZ, at the two pH values of the equilibrium solution



adsorption on a SMZ was an endothermic reaction since maximum As adsorption declined when temperature decreased from 25 to 15 °C.

The SMZ removed P effectively regardless of the pH of the equilibrium solution ( $4.2 \pm 0.1$  and  $10.4 \pm 0.1$ ) (Fig. 3). More than 70 and 40 % of the added P was removed when P concentrations in the external solution exceeded 15 and 20 mgL<sup>-1</sup>, respectively, and more than 80 % of the added P was removed when P concentrations in the external solution was 1–5 mgL<sup>-1</sup>. Adsorption data obtained at both pH values conformed satisfactorily to the Langmuir equation (for pH=4.2±0.1 SE=9.5,  $F=677$ ,  $p<0.001$  and for pH=10.4±0.1 SE=25,  $F=123$ ,  $p<0.001$ ;  $p$  values of the  $t$  tests were <0.001 for  $M$  in both cases and for  $K$  at pH=4.2±0.1 and <0.025 for  $K$  at pH=10.4±0.1). As pH of the equilibrium solution rose from the acidic to alkaline range, P adsorption on the SMZ also increased. This increase was reflected in the estimated Langmuir parameters, the capacity parameter  $M$  and the affinity parameter  $K$ , which were significantly increased with the pH rise (Table 4).

Soluble inorganic P may be present in four different chemical forms, depending on pH. When solution pH is less than 2, P exists as H<sub>3</sub>PO<sub>4</sub>, between pH 3 and 6.5 the dominant chemical form is H<sub>2</sub>PO<sub>4</sub><sup>-</sup>, HPO<sub>4</sub><sup>2-</sup> dominates between 7.5 and 12 and when pH exceeds 12, P exists as PO<sub>4</sub><sup>3-</sup> (Tisdale et al. 1990). Consequently, when the pH of the equilibrium solution was acidic ( $4.2 \pm 0.1$ ), the univalent form of H<sub>2</sub>PO<sub>4</sub><sup>-</sup> was dominant, whereas at the alkaline pH ( $10.4 \pm 0.1$ ) P was mostly in the divalent form of HPO<sub>4</sub><sup>2-</sup>. According to Li and Bowman (1997), the anion adsorption mechanism on the SMZ (with HDTMA-Br) is anion exchange. Specifically, the anions are exchanged for

Br<sup>-</sup> originating from the HDTMA-Br on the surface of the zeolite and held by electrostatic bond. Furthermore, the electrostatic bond is stronger for the polyvalent anions than the univalent and for anions with a smaller hydrated ionic radius (Schroeder 1984). Based on this and taking into account that the univalent and divalent P anions have similar hydrated ionic radii estimated at 0.4 nm (Dean 1979), the increase in P adsorption in response to a rise in pH could be due to a stronger electrostatic bond between the SMZ and the divalent P anions than the univalent P anions.

Phosphorus adsorption on the SMZ in the presence of NO<sub>3</sub><sup>-</sup> was conformed satisfactorily to the Langmuir equation (for NO<sub>3</sub><sup>-</sup>=25 mgL<sup>-1</sup> SE=18,  $F=77$ ,  $p<0.001$  and for NO<sub>3</sub><sup>-</sup>=50 mgL<sup>-1</sup> SE=9.6,  $F=247$ ,  $p<0.001$ ;  $p$  values of the  $t$  tests were <0.001 for  $M$  in both cases, <0.05 for  $K$  at NO<sub>3</sub><sup>-</sup>=25 mgL<sup>-1</sup> and <0.005 for  $K$  at NO<sub>3</sub><sup>-</sup>=50 mgL<sup>-1</sup>) and reduced (Fig. 4). However, the reduction was significant only when there was 50 mgL<sup>-1</sup> of NO<sub>3</sub><sup>-</sup> in the external solution, i.e. the estimated Langmuir parameters,  $M$  and  $K$  were significantly decreased with the NO<sub>3</sub><sup>-</sup> concentration increase from 0 to 50 mgL<sup>-1</sup> (Table 5). In all cases, the amount of P removed by the SMZ was substantial. More than 50 and 80 % of the added P was

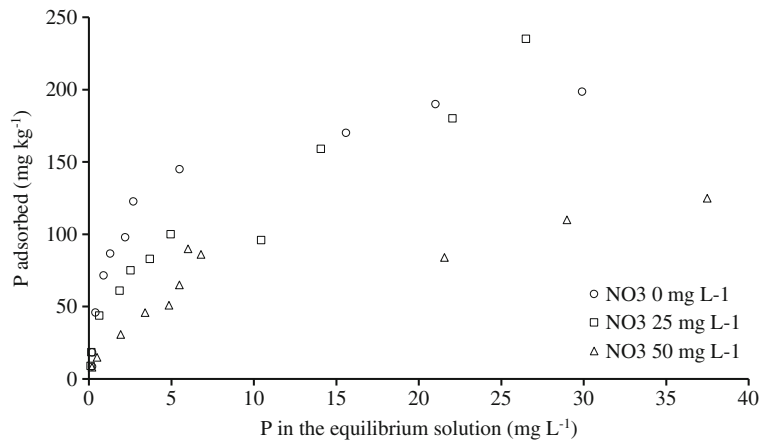
**Table 4** Parameters of the Langmuir equation, at the two pH values of the equilibrium solution

pH	$M$ (mean±SE mgkg <sup>-1</sup> )	$K$ (mean±SE Lmg <sup>-1</sup> )
4.2±0.1	235±13 b	0.15±0.02 b
10.4±0.1	407±23 a	0.31±0.05 a

Values followed by different letter, within the same column, are significantly different, at  $p \leq 0.05$ , using  $t$  test

SE standard error

**Fig. 4** Isotherms of P adsorption on the SMZ, at the two  $\text{NO}_3^-$  concentrations in the external solution adsorption isotherm at  $0 \text{ mg L}^{-1} \text{NO}_3^-$  is the same with that presented in Fig. 1, for  $25 \pm 1 \text{ }^\circ\text{C}$



removed when the P concentration in the external solution was less than 30 and  $5 \text{ mg L}^{-1}$ , respectively.

According to Schroeder (1984), adsorbent's affinity for anions depends mainly on the anion's valence and size. The higher the valence and the smaller the hydrated ionic radius, the stronger is the adsorption. Phosphorus anions commonly found in a pH, like the pH of the equilibrium solution,  $6.9 \pm 0.3$  (see first paragraph of this section), are  $\text{H}_2\text{PO}_4^-$ ,  $\text{HPO}_4^{2-}$ . Although  $\text{HPO}_4^{2-}$  have valence higher than  $\text{NO}_3^-$ , both P anionic species have hydrated ionic radius ( $0.4 \text{ nm}$ ) larger than  $\text{NO}_3^-$  ( $0.3 \text{ nm}$ ) (Dean 1979). Consequently, the reduction of P adsorption on the SMZ in the presence of  $\text{NO}_3^-$  may be due to the size difference of the specific anions.

Contradictory results are reported in the literature with respect to the adsorption of competing anions on SMZs. Specifically, Li and Bowman (1997) reported that  $\text{CrO}_4^{2-}$  adsorption was decreased in the presence of  $\text{NO}_3^-$ ,  $\text{HCO}_3^-$ ,  $\text{SO}_4^{2-}$  and  $\text{HPO}_4^{2-}$ , whereas Zhang et al. (2007), reported that, from the anions studied,  $\text{Cl}^-$ ,

$\text{OH}^-$ ,  $\text{NO}_3^-$ ,  $\text{CO}_3^{2-}$  and  $\text{SO}_4^{2-}$ , only  $\text{NO}_3^-$  reduced  $\text{ClO}_4^-$  adsorption on the SMZ, and only when the concentration of  $\text{ClO}_4^-$  in the external solution was low.

### 3.2 Phosphorus Desorption from the SMZ

The data obtained from the short-term desorption experiments, performed using deionised water or  $0.01 \text{ M KCl}$  as external solution, showed that P desorption from the SMZ within 12 h, was not affected by the kind of the external solution. For this reason, only the data obtained using deionised water are presented.

The results of both (short-term and long-term) desorption experiments showed that P desorption from the SMZ was affected only by time and not by the initial P concentration added to the SMZ (Table 6; Fig. 5). As it can be seen from the desorption data, especially from Table 6, P desorption from the SMZ was a slow reaction and this is in agreement with the findings of Bansiwali et al. (2006) who studied P release from a SMZ by leaching experiments. At both rates of P addition, the greatest part of the total desorbed P was released within 24 h and found to be 37 and 51 % of the total desorbed P, for P addition at 50 and  $200 \text{ mg kg}^{-1}$ , respectively. After the 24 h, the cumulative amounts of desorbed P continued to increase and at the end of the last desorption step (96 h) reached the  $7.5 \text{ mg kg}^{-1}$ , in both cases of P addition. Consequently, the SMZ retained a large amount of added P.

At both rates of P addition, P concentration in the equilibrium solution ranged between  $0.1$  and  $0.4 \text{ mg L}^{-1}$ . The above outcome is an indication that in the case of using SMZ for reducing P levels from P enriched waters, after P adsorption on the SMZ, the concentration in waters will be less than  $2 \text{ mg L}^{-1}$ ,

**Table 5** Parameters of the Langmuir equation, at the two  $\text{NO}_3^-$  concentrations in the external solution

$\text{NO}_3^-$ ( $\text{mg L}^{-1}$ )	$M$ (mean $\pm$ SE $\text{mg kg}^{-1}$ )	$K$ (mean $\pm$ SE $\text{L mg}^{-1}$ )
0	194 $\pm$ 10 a	0.55 $\pm$ 0.10 a
25	157 $\pm$ 26 a, b	0.36 $\pm$ 0.17 a, b
50	141 $\pm$ 12 b	0.17 $\pm$ 0.04 b

Parameters at the  $0 \text{ mg L}^{-1}$  are the same with those reported in Table 2, for  $25 \pm 1 \text{ }^\circ\text{C}$ . Values followed by different letter, within the same column, are significantly different, at  $p \leq 0.05$ , using  $t$  test

SE standard error

**Table 6** Amounts of desorbed P from the SMZ, after P addition at 50 and 200 mg kg<sup>-1</sup>

Desorption time (h)	P added (mg P kg <sup>-1</sup> of SMZ)	
	50	200
	P desorbed (mean±SE mg kg <sup>-1</sup> )	
0.25	1.83±0.06 e, f, g	1.73±0.13 f, g
0.50	1.80±0.17 e, f, g	1.99±0.04 b, c, d, e
1	1.79±0.14 f, g	1.72±0.06 f, g
2	1.81±0.09 e, f, g	1.88±0.03 c, d, e, f
4	1.86±0.09 d, e, f, g	1.67±0.01 g
6	1.71±0.11 f, g	1.90±0.09 b, c, d, e, f
8	1.84±0.08 e, f, g	1.88±0.06 c, d, e, f
10	2.05±0.16 b, c	2.04±0.06 b, c, d
12	2.23±0.15 a	2.07±0.10 a, b

Values followed by different letter are significantly different, at  $p \leq 0.05$ , using the Duncan's multiple range test

SE standard error

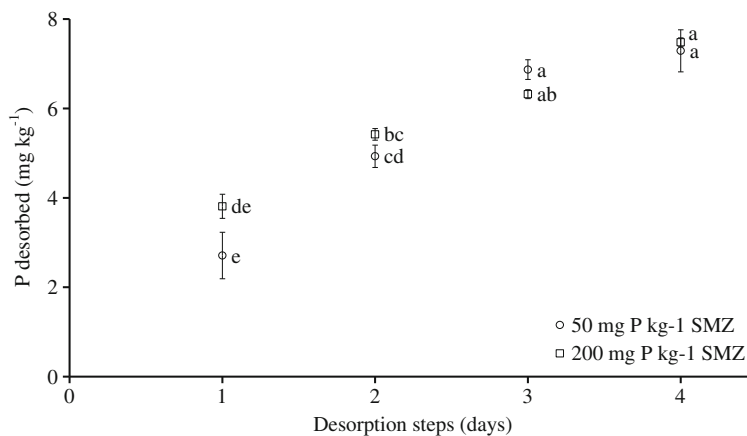
above which environmental risks are likely (Council Directive 91/271/EC 1991). Furthermore, according to Tisdale et al. (1990) who reported that P concentrations in the soil solution between 0.2 and 0.3 mg L<sup>-1</sup> are adequate for a variety of crops, it seems that if P-laden SMZ is applied to soils after its use for removing P from waters could supply soil solution and plants with probably sufficient P. This is also supported by the findings of Bansiwali et al. (2006) who reported that SMZ has a great potential as a fertiliser carrier for slow release of P.

#### 4 Conclusions

In conclusion, the SMZ exhibited high adsorption capacity for P, which was comparable to certain

other materials, used as adsorbents for P. The P adsorption capacity of the SMZ increased with pH increase and although decreased with temperature increase and in the presence of a relative high NO<sub>3</sub><sup>-</sup> concentration, remained appreciable in all cases. In addition, the SMZ retained the greatest amount of added P and the P desorbed concentrations ranged at levels below than those above which environmental risks are likely. Taking into account zeolite's high availability, its low cost and the simplicity of the techniques that can be used for its surface modification, it was concluded that SMZ can be a promising adsorbent for cleaning up waters enriched with P. However, further research, including additional laboratory experiments, economical analysis and especially large-scale experiments, is needed.

**Fig. 5** Cumulative amounts (mean and standard deviation) of desorbed P from the SMZ, after addition of 50 and 200 mg P kg<sup>-1</sup> of SMZ. Each step represents a 24-h desorption interval. Values followed by different letter are significantly different, at  $p \leq 0.05$ , using the Duncan's multiple range test





**Acknowledgment** The funding for this work provided by the Greek State Scholarships Foundation is gratefully appreciated.

## References

- Agyei, N. M., Strydom, C. A., & Potgieter, J. H. (2002). The removal of phosphate ions from aqueous solution by fly ash, slag, ordinary Portland cement and related blends. *Cement and Concrete Research*, *32*, 1889–1897.
- Allred, B. J. (2010). Laboratory batch test evaluation of five filter materials for removal of nutrients and pesticides from drainage waters. *Soil and Water of American Society of Agricultural and Biological Engineers*, *53*, 39–54.
- Bansiwal, A. K., Rayalu, S. S., Labhasetwar, N. K., Juwarkar, A. A., & Devotta, S. (2006). Surfactant-modified zeolite as a slow release fertilizer for phosphorus. *Journal of Agricultural and Food Chemistry*, *54*, 4773–4779.
- Bowman, R. S., Sullivan, Z., & Li, Z. (2000). Uptake of cations, anions and nonpolar organic molecules by surfactant modified clinoptilolite rich tuff. In C. Collela & A. Mumpton (Eds.), *Natural zeolites for the third millennium* (pp. 287–297). Napoli: De Frede.
- Correll, D. (1998). The role of phosphorous in the eutrophication of receiving waters: a review. *Journal of Environmental Quality*, *27*, 261–266.
- Council Directive (EC) 91/271/EC of 21 Mai 1991 on concerning urban waste water treatment.
- Daniel, T. C., Sharpley, A. N., & Lemunyon, J. L. (1998). Agricultural phosphorous and eutrophication. A symposium overview. *Journal of Environmental Quality*, *27*, 251–257.
- Dao, T. H. (2003). Competitive anion sorption effects on dairy wastewater dissolved phosphorus extraction with zeolite-based sorbents. *Food Agriculture and Environment*, *1*, 263–269.
- Dean, J. A. (1979). *Lange's handbook of chemistry*. New York: McGraw-Hill.
- Denaix, L., Van Ort, E., Pernes, M., & Jongmans, A. G. (1999). Transmission X-ray diffraction of undisturbed soil micro-fabrics obtained by microdrilling in thin sections. *Clays and Clay Minerals*, *47*, 637–646.
- Dimirkou, A., Ioannou, A., & Doula, M. (2002). Preparation, characterization and sorption properties for phosphates of hematite, bentonite and bentonite-hematite systems. *Advances in Colloid and Interface Science*, *97*, 37–61.
- Dou, Z., Ramberg, C. F., Toth, J. D., Wang, Y., Sharpley, A. N., Boyd, S. E., Chen, C. R., Williams, D., & Xu, Z. H. (2009). Phosphorus speciation and sorption-desorption characteristics in heavily manured soils. *Soil Science Society of America Journal*, *73*, 93–101.
- Drizo, A., Frost, C. A., Grace, J., & Smith, K. A. (1999). Physico-chemical screening of phosphate-removing substrates for use in constructed wetland systems. *Water Research*, *33*, 3595–3602.
- Faghihian, H., Ghannadi, M., & Kazemian, M. H. (1999). The use of clinoptilolite and its sodium form for removal of radioactive cesium and strontium from nuclear wastewater and  $Pb^{2+}$ ,  $Ni^{2+}$ ,  $Cd^{2+}$ ,  $Ba^{2+}$  from municipal wastewater. *Applied Radiation and Isotopes*, *50*, 655–660.
- Frenay, J., Lambert, C., & Bastin, D. (2000). Use of surface-modified zeolite to clean industrial effluents containing metal cation and anions. Public Report for European Research program with acronym METASEP No. EVK1-CT-2000-00083. Brussels: European Union
- Grubb, D. G., Guimaraes, M. S., & Valencia, R. (2000). Phosphate immobilization using an acidic type F fly ash. *Journal of Hazardous Materials*, *76*, 217–236.
- Haggerty, G. M., & Bowman, R. S. (1994). Sorption of chromate and other inorganic anions by organozeolite. *Environmental Science and Technology*, *28*, 452–458.
- Hengpeng, Y., Fanzhong, C., Yanqing, S., Guoying, S., & Jiamo, F. (2006). Adsorption of phosphate from aqueous solution onto modified palygorskites. *Separation and Purification Technology*, *50*, 283–290.
- Hesterberg, D., & Beauchemin, S. (2000). Changes in phosphate bonding as affected by level of adsorption on oxide minerals. *National Synchrotron Light Source Activity Report No 2*. New York: Brookhaven National Laboratory
- Hosni, K., & Srasra, E. (2010). Evaluation of phosphate removal from water by calcined-LDH synthesized from the dolomite. *Colloid Journal*, *72*, 423–431.
- Ioannou, A., Dimirkou, A., & Ioannou, Z. (2001). Comparison of kinetic models for phosphate reaction in goethite, bentonite-goethite and kaolinite-goethite systems. *Journal of Colloid and Interface Science*, *4*, 35–55.
- Khadhraoui, M., Watanabe, T., & Kuroda, M. (2002). The effect of the physical structure of a porous Ca-based sorbent on its phosphorus removal capacity. *Water Research*, *36*, 3711–3718.
- Li, Z. (2003). Use of surfactant-modified zeolite as fertilizer carriers to control nitrate release. *Microporous and Mesoporous Materials*, *61*, 181–188.
- Li, Z. (2004). Influence of solution pH and ionic strength on chromate uptake by surfactant-modified zeolite. *Journal of Environmental Engineering*, *130*, 205–208.
- Li, Z., & Bowman, R. (1997). Counterion effects on the sorption of cationic surfactant and chromate on natural clinoptilolite. *Environmental Science and Technology*, *31*, 2407–2412.
- Li, Z., Anghel, I., & Bowman, R. (1998). Sorption of oxyanions by surfactant-modified zeolite. *Journal of Dispersion Science and Technology*, *19*, 843–857.
- Li, Z., Beachner, R., McManama, Z., & Hanlie, H. (2007). Sorption of arsenic by surfactant-modified zeolite and kaolinite. *Microporous and Mesoporous Materials*, *105*, 291–297.
- Mercer, B. W., & Ames, L. L. (1978). Zeolite ion exchange in radioactive and municipal wastewater treatment. In L. B. Sand & F. A. Mumpton (Eds.), *Natural zeolites: occurrence, properties, use* (pp. 451–462). Oxford: Pergamon Press.
- Ming, D. M., & Dixon, J. B. (1987). Quantitative determination of clinoptilolite in soils by a cation-exchange capacity method. *Clays and Clay Minerals*, *35*, 463–468.
- Misaclides, P., Godelitsas, A., & Filippidis, A. (1995). The use of zeoliferous rocks from Metaxades-Thrace, Greece, for the removal of caesium from aqueous solutions. *Fresenius Environmental Bulletin*, *4*, 227–231.
- Murphy, J., & Riley, I. P. (1962). A modified single solution method for the determination of phosphate in natural waters. *Analytica Chimica Acta*, *27*, 31–36.

- Oguz, E., Gurses, A., & Yalcin, M. (2003). Removal of phosphate from waste waters by adsorption. *Water, Air, and Soil Pollution*, 148, 279–287.
- Rajec, P., Macasek, F., Feder, M., Misaelides, P., & Samajova, E. (1998). Sorption of caesium and strontium on clinoptilolite and mordenite containing sedimentary rocks. *Journal of Radioanalytical and Nuclear Chemistry*, 229, 49–55.
- Saad, R., Hamoudi, S., & Belkacemi, K. (2008). Adsorption of phosphate and nitrate anions on ammonium-functionalized mesoporous silicas. *Journal of Porous Materials*, 15, 315–323.
- Schroeder, D. (1984). *Soils, facts and concepts*. Bern: Int. Potash Institute.
- Sei, J., Jumas, J. C., Olivier-Fourcade, J., Quiquampoix, H., & Staunton, S. (2002). Role of iron oxides in the phosphate adsorption properties of kaolinites from the Ivory Coast. *Clays and Clay Minerals*, 50, 217–222.
- Shin, E. W., Han, J. S., Jan, M., Min, S. H., Park, J. K., & Rowell, R. M. (2004). Phosphate adsorption on aluminium-impregnated mesoporous silicates: surface structure and behaviour of adsorbents. *Environmental Science and Technology*, 38, 912–917.
- Sparks, D. L. (1984). *Environmental soil chemistry*. New York: Academic.
- Sullivan, E. J., Bowman, R. S., & Legiec, I. A. (2003). Sorption of arsenic from soil-washing leachate by surfactant-modified zeolite. *Journal of Environmental Quality*, 32, 2387–2391.
- Tanada, S., Kabayama, M., Kawasaki, N., Sakiyama, T., Nakamura, T., Araki, M., & Tamura, T. (2002). Removal of phosphate by aluminum oxide hydroxide. *Journal of Colloid and Interface Science*, 257, 135–140.
- Tisdale, S. L., Nelson, W. L., & Beaton, J. D. (1990). *Soil fertility and fertilizers*. New York: Macmillan Publishing Company.
- United States Environmental Protection Agency (USEPA) (1986). *Nonpoint source pollution in the US. Report to Congress*. Washington, DC: US Environmental Protection Agency, Office of Water Criteria and Standards Division.
- Valsami-Jones, E. (2001). Mineralogical controls on phosphorus recovery from wastewaters. *Mineralogical Magazine*, 65, 611–620.
- Vujakovic, A., Tomasevic-Canovic, M., Dakovic, A., & Dondur, V. T. (2000). The adsorption of sulphate, hydrogenschromate and dihydrogenphosphate anions on surfactant-modified clinoptilolite. *Applied Clay Science*, 17, 265–277.
- Vujakovic, A., Dakovic, A., Lemic, J., Radosavljevic-Michaljovic, A., & Tomasevic-Canovic, M. (2003). Adsorption of inorganic contaminants on surfactant modified minerals. *Journal of the Serbian Chemical Society*, 68, 833–841.
- Widiastuti, N., Hongwei, W., Ang, M., & Zhang, D. (2008). The potential application of natural zeolite for greywater treatment. *Desalination*, 218, 271–280.
- Zhang, P., Avudzeza, D., & Bowman, R. S. (2007). Removal of perchlorate from contaminated waters using surfactant-modified zeolite. *Journal of Environmental Quality*, 36, 1069–1075.