

Article

Phosphate Removal Using Polyethylenimine Functionalized Silica-Based Materials

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Abstract: In water and wastewater, phosphate anions are considered critical contaminants because they cause algae blooms and eutrophication. The present work aims at studying the removal of phosphate anions from aqueous solutions using silica particles functionalized with polyethylenimine. The parameters affecting the adsorption process such as pH, initial concentration, adsorbent dose, and the presence of competitive anions, such as carbonate, nitrate, sulfate and chromate ions, were studied. Equilibrium studies were carried out to determine their sorption capacity and the rate of phosphate ions uptake. The adsorption isotherm data fitted well with the Langmuir and Sips model. The maximum sorption capacity was 41.1 mg/g at pH 5, which decreased slightly at pH 7. The efficiency of phosphate removal adsorption increased at lower pH values and by increasing the adsorbent dose. The maximum phosphate removal was 80% for pH 5 and decreased to 75% for pH 6, to 73% for pH 7 and to 70% for pH 8, for initial phosphate concentration at about 1 mg/L and for a dose of adsorbent 100 mg/L. The removal rate was increased with the increase of the adsorbent dose. For example, for initial phosphate concentration of 4 mg/L the removal rate increased from 40% to 80% by increasing the dose from 0.1 to 2.0 g/L at pH 7. The competitive anions adversely affected phosphate removal. Though they were also found to be removed to a certain extent. Their co-removal provided an adsorbent which might be very useful for treating waters with low-level multiple contaminant occurrence in natural or engineered aquatic systems.

Keywords: phosphate; adsorption; polyethylenimine; sorption capacity; nitrate; chromate



Citation: Xanthopoulou, M.; Giliopoulos, D.; Tzollas, N.; Triantafyllidis, K.S.; Kostoglou, M.; Katsoyiannis, I.A. Phosphate Removal Using Polyethylenimine Functionalized Silica-Based Materials. *Sustainability* **2021**, *13*, 1502. <https://doi.org/10.3390/su13031502>

Academic Editor: Luca Di Palma

Received: 31 December 2020

Accepted: 28 January 2021

Published: 1 February 2021

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1. Introduction

Phosphorus, as a nutrient in water, enters the environment from municipal, industrial, human and natural sources. Phosphorus enters water systems naturally by dissolving out of rock, but phosphates are also mined and made into chemical fertilizers to grow crops. The fertilizer industry, household laundries and washings produced wastewaters are enriched in phosphate ions. Human activities like improper disposal of municipal and industrial effluents and indiscriminate applications of agrochemicals in agriculture are the main factors contributing to the deterioration of water quality [1]. Elevated phosphate concentrations cause an adverse effect on the environment, favoring algae growth and subsequently eutrophication. Although concentrations of phosphorus are currently unregulated in drinking water, phosphate concentrations ranging from 0.03 to 0.1 mg/L is associated with algae blooms [2]. However, lack of phosphate in the environment can also cause side effects. For instance, phosphorus deficiency is a plant disorder associated with the insufficient supply of phosphorus [3]. The natural resources of phosphate, which are phosphate ores, are rapidly being exhausted. In ecological terms, because of its important role in biological systems, phosphate is a highly sought-after resource. Hence, nowadays removal of phosphate as well as recovery of phosphate, are both of great significance [4].

In general, phosphorus is present in waters in the form of phosphate in solution, including organic phosphate, metaphosphates, orthophosphate and polyphosphate. Among these four forms, the most predominant species of phosphate in natural waters and wastewaters are orthophosphates which have three acid ionization constants ($pK_{a1} = 2.1$, $pK_{a2} = 7.2$ and $pK_{a3} = 12.3$), indicating that at pH values of most natural waters, phosphate is present in the form of anions [5].

Several physicochemical and biological processes have been investigated for the removal of phosphate from waters and wastewater [6–8]. The techniques include adsorption methods, chemical precipitation (with aluminum, iron and calcium salts) followed by filtration and biological processes that rely on biomass growth (bacteria, algae, plants) or intracellular bacterial poly-phosphate accumulation. Among them, adsorption is a very promising technique, especially when treating low concentrations of pollutants, since this allows simple and economical operation resulting in less sludge production and disposal problems and offers the chance for recovery and reuse [9–11].

Although a variety of materials have been applied to remove phosphorus from aqueous solutions, such as zeolite [12], hydrotalcite [13], bentonite [14] and metal oxides [15], it is imperative to develop materials, which are effective in phosphate removal but also can offer multiple contaminant removal, since phosphate is usually present in waters with other pollutants [16]. In our study, we applied materials made up of silica, which we modified with the use of polyethylenimine, to provide plenty of cationic functional groups, which could enhance phosphate removal from waters.

Silica normally has characteristics of a highly specific surface, high adsorption capacity and porous structure, which make it a very promising material for the treatment of water and sewage. However, because of the negatively charged surface of silica, due to the presence of Si-OH groups, the adsorption of anions is not efficient [17] and past studies have shown poor phosphate retention [18]. An attractive approach to obtain high-capacity silica-based adsorbents involves the functionalization of silica with organic or inorganic groups of suitable properties for desired environmental applications [19].

Phosphate possesses a negative charge and hence the adsorbent should possess a high positive charge. Polyethyleneimine (PEI) is a polymer with a high cationic charge [20]. It can bind negatively charged ions due to the electrostatic interaction between PEI and the anions and has been used to modify surfaces for the removal of contaminants such as cadmium, Cd (II), nickel, Ni (II) [21], nitrate ions [22] and anionic dyes [23], from waters and wastewaters.

Previous research demonstrated that non modified silica showed low phosphate adsorption capacity. Agrawal et al. (2011) studied the phosphate removal capability of silica sand, applying 40 g/L of the material for treating initial phosphate concentrations of 0–68 mg/L and exhibited phosphate removal efficiency ranging from 21–58% [24]. Han et al. (2015) studied phosphate removal from water by using ordered mesoporous silica loaded with samarium oxide. MCM-41 did not adsorb phosphate in measurable quantities; thus, the phosphate adsorption was attributed to the Sm incorporation [25]. Also, Kang et al. (2015) studied the removal of phosphate using ammonium-functionalized MCM-41. The results showed that the phosphate removal in the MCM-41 (initial P conc. = 2 mg P L⁻¹) was negligible with the percent removal of $\leq 1.0\%$ at the adsorbent dosages between 0.5 and 2.0 g/L [26]. Hamoudi et al. (2007) synthesized mesoporous silica functionalized with ammonium groups (MCM-48-NH₃⁺) and proved that it is an effective high-capacity adsorbent for the removal of nitrate and phosphate anions from aqueous solutions. Maximal removals of 70% and 88% were obtained for the nitrate and phosphate, respectively [27]. In the case of ammonium-MCM-41, the percent removal for phosphate anions increased from 73.6 to 100% as the adsorbent dose increased from 0.5 to 2.0 g/L for phosphates up to 100 mg/L [26].

Also, PEI has been used as a material functionalization agent and applied for the adsorption of phosphates. Anirudhan et al. (2012) studied the removal of the phosphate as well as its recovery from water and wastewater by cellulose grafted epichlorohydrin

functionalized polyethylenimine graft copolymer and found that the removal of phosphates reached the maximum, 99.6%, at pH 4.5 [4].

More recently, Suzaimi et al. (2020), also, studied the adsorption of phosphate ions on silica from rice husk modified with polyethyleneimine (RSi-bPEI). It was shown that the modification of the silica with polyethyleneimine increased the positive charge of the silica surface. The adsorption capacity was 123.46 mg/g, at pH 4.5. In terms of adsorption isotherms, the Langmuir model fitted the experimental data and the pseudo-second-order model fitted the kinetic data. The effect of the presence of sulfate, nitrate, chloride and carbonate anions were also studied. Sulfate ions showed the greatest negative effect among others, while chloride and carbonate ions showed almost negligible effect on the adsorption and removal of phosphate ions [22]. Li et al. (2020) studied the mechanism of phosphate adsorption by PEI-modified biochar. After modification with PEI, the phosphate adsorption capacity of phosphate of biochar was increased. Furthermore, the phosphate adsorption capacity was highly dependent on ionic strength, indicating that phosphate adsorption occurs at the outer sphere [28].

The purpose of this study was to investigate the use of amorphous silica materials functionalized with polyethyleneimine for the effective removal of phosphate anions from aqueous solutions, with prominence on treating water with phosphate concentrations less than 20 mg/L, and the study of the possible co-removal of other anionic pollutants that may be simultaneously present in the water. It is of great importance to examine the selectivity of the SiO₂-PEI materials against phosphates among other coexisting anions since the presence of other anions may interfere with phosphate adsorption. Some typical anionic species, such as carbonate, sulfate, nitrate and chromate ions, that commonly exist in waters were chosen to assess their interference on phosphate adsorption.

Apart from the scientific objectives, the practical aim of our study was to investigate the development of an adsorption material, which will be able to remove phosphate and other co-occurring anions from natural or engineered waters with multiple contaminations such as drainage waters resulting from rice irrigation. These waters normally contain phosphates and nitrate, and in some cases also arsenic and chromate [29].

2. Materials and Methods

2.1. Materials

Tetraethyl orthosilicate (TEOS) reagent grade 98% (Merck) was used as the silica source. Branched polyethylenimine (PEI) with an average molecular weight (Mw) of ~800 and ~25,000 was supplied from Aldrich.

All stock solutions were prepared with distilled water. Phosphate ions solution was prepared with KH₂PO₄ (98%, Panreac), from which an appropriate amount was dissolved in an appropriate volume of distilled water. The reagents K₂CO₃ (Fluka AG, >99%), KNO₃ (Merck, >99%), K₂SO₄ (Merck, 99%) and K₂Cr₂O₇ (Carl Roth GmbH, >99.5%) were used to study the effect of the presence of other anions.

For phosphate ions determination, concentrated sulfuric acid, H₂SO₄, (Sigma-Aldrich, 95–98%), potassium antimony tartrate, K(SbO)C₄H₄O·1/2H₂O (Merck, 99%), ammonium molybdate, (NH₄)₆Mo₇O₂₄·4H₂O (Merck, 99%) and L-ascorbic acid (Sigma-Aldrich, 99.7%) were used. Also, sulfuric acid, H₂SO₄, for preparation of concentration 10% solution, diphenyl carbazide (Carl Roth GmbH, >97%) and acetone (Carl Roth GmbH, >99.8%) were used for the determination of chromium ions. Test kits HI 93755-0 and HI 93751-0 from Hanna Instruments were used to determine carbonate and sulfate ions.

2.2. Synthesis of Adsorbents

The synthesis of PEI-SiO₂ materials was conducted via sol-gel reaction. In a typical procedure, PEI is dissolved in deionized water at room temperature, followed by TEOS addition dropwise and the solution is left under stirring for 24 h, at 30 °C. The formed material is recovered by vacuum filtration, rinsed firstly with ethanol and then with

deionized water and, finally, allowed to dry in air. The respective inorganic materials are formed after calcination of PEI-silicas at 550 °C, for 6 h, with a 1 °C/min heating rate.

2.3. Phosphate Adsorption Experiments

Two silica materials grafted with polyethylenimine of two different molar masses, 800 and 25,000, and the corresponding calcined silica materials, were synthesized. Then, we examined the adsorption capacity of the four silicate materials. Phosphate ion adsorption experiments were performed in batch mode and different parameters were studied in each cycle of experiments. The adsorption capacity of the four materials was initially studied. Isotherm study was conducted by applying the Langmuir, Freundlich and Sips isothermal models on experimental data. Then, the effect of pH, the effect of the initial concentration of phosphate ions, the effect of the increasing concentration of the adsorbent material and the effect of carbonate, nitrate, sulfate and chromium anions on the removal rate were studied. The experiments were performed using distilled water.

To study the adsorption capacity, 35 mL of phosphate ion solution at concentrations of 0.15–15 mg/L and 0.0035 g of adsorbent (100 mg/L in solution) were placed in 50 mL falcon conical plastic tubes. The adsorption isotherm experiments of phosphate onto the samples were carried out at 20 °C.

The anion effect study was performed for an initial concentration of 4 mg/L phosphate ions and 100 mg/L of adsorbent at pH 7, in 50 mL falcon tubes with 35 mL solution at 32 rpm for 24 h. Concentrations of 10–300 mg/L for carbonate, nitrate and sulfate ions and concentrations of 10–100 µg/L for chromium ions were studied. At pH 7, phosphate ions compete with these forms of anions, bicarbonate, $\text{HCO}_3^{\text{superscript-}}$, sulfate, SO_4^{2-} , nitrate, NO_3^- and chromate, CrO_4^{2-} .

2.4. Analytical Determinations

The determination of phosphate ions was conducted by the ascorbic acid method and the measurement of the absorbance of the samples was performed at 880 nm [28]. Also, the determination of chromium ions was conducted by the diphenyl carbazide method and the measurement of the absorbance of the samples was performed at 540 nm and the determination of nitrate ions was performed by measuring the absorbance of the samples at 220 and 275 nm [30]. For the measurement of the absorption the spectrophotometer Uv-Vis model U-2000, Hitachi, (Tokyo, Japan) was used. The photometer HI 83099 COD and Multiparameter was used to measure carbonate and sulfate ions using test kits. The experiments were performed using the Rotary stirrer RS-RR 5 Phoenix Instrument.

The textural properties of the materials PEI-SiO₂ and the calcined counterparts were determined by N₂ porosimetry. Nitrogen adsorption/desorption experiments were performed at −196 °C to determine the BET surface area (multi-point BET method), total pore volume (at P/P₀ = 0.99) and pore size distribution (BJH method using the adsorption data) of the samples, which were previously outgassed at 120 °C or 150 °C (hybrid and calcined silicas respectively) for 16 h under 5.9×10^{-9} Torr vacuum using an Automatic Volumetric Sorption Analyzer (Autosorb-1, Quantachrome, Boynton Beach, FL 33426 USA).

Scanning electron microscopy (SEM), JEOL JSM-6390LV (0.5–30 KV) with 10 nm resolution, equipped with EDS resolution system and Oxford INCA EDS Software, was used for the determination of the morphology (size and shape) of the primary silicate nanoparticles, as well as the agglomerates they form. The sample particles were immobilized on a metal sampler on a thin layer of conductive carbon and were also coated with carbon to make them conductive.

2.5. Isotherm Models and Phosphate Removal

Adsorption isotherms describe how the adsorbed components interact with the adsorbents and are thus critical to optimizing the use of the adsorbent. Therefore, the correlation of equilibrium data with either theoretical or empirical equations is necessary for the practical design and operation of adsorption systems. In the present study, the experimental data

of equilibrium isotherms were compared with the equations of the Langmuir, Freundlich and Sips models.

For this purpose, plots of the uptake of phosphate ions on the adsorbent material in relation to the concentration of phosphates in the solution in equilibrium were made. The uptake of phosphate ions from the adsorbent was calculated by the following equation:

$$q_e = \frac{(C_o - C_e)V}{m} \quad (1)$$

where q_e is the uptake of phosphate ions (mg/g), C_o and C_e the initial concentration of phosphates in the solution and concentration at equilibrium, respectively, (mg/L), V the volume of the solution (L) and m the mass of the adsorbent (g).

According to Langmuir's theory, the process of adsorption on a solid surface is based on a kinetic principle in which a continuous bombardment of molecules on the surface occurs with simultaneous desorption of the corresponding molecules from the surface, with zero accumulation rate on the surface [31]. In other words, the adsorption and desorption rates must be equal. The Langmuir model is an empirical model that assumes that the thickness of the adsorbed layer consists of a molecule (single-layer adsorption) in which the adsorption process takes place on flat homogeneous surfaces consisted of equivalent defined locations. The maximum adsorption capacity results from the monolayer coverage. The forces between the adsorbed molecules are negligible with respect to the forces between the adsorbed molecules and the surface, not allowing interactions between the molecules. This means that the already adsorbed molecules do not affect the adsorption rate per active site. The equation describing the Langmuir isotherm is as follows [32]:

$$q_e = q_{max} * \frac{K_L * C_e}{1 + K_L * C_e} \quad (2)$$

where q_e is the uptake of phosphate ions in monolayer per unit weight of adsorbent at equilibrium (mg/g), q_{max} is the maximum uptake of phosphate ions that can be adsorbed in monolayer per unit weight of adsorbent (mg/g), K_L is a constant associated with the adsorption capacity (L/mg) and C_e the concentration of phosphate ions in solution at equilibrium (mg/L).

The Freundlich model describes the reversible and non-ideal adsorption process. Unlike the Langmuir isotherm model, the Freundlich model is not limited to the formation of monolayers but can be applied to the adsorption of multiple layers [33]. The Freundlich model expression defines surface heterogeneity as well as the exponential distribution of active sites. Described by the non-linear equation [34]:

$$q_e = K_F * C_e^{\frac{1}{n}} \quad (3)$$

where q_e is the uptake of phosphate ions adsorbed per unit weight of adsorbent at equilibrium (mg/g), K_F is a constant related to adsorption capacity (L/mg) and C_e is the concentration of phosphate ions in the solution at equilibrium (mg/L). The ratio $1/n$ is the intensity of adsorption or surface heterogeneity indicating the energy distribution and heterogeneity of the adsorption sites. When $1/n$ is greater than zero ($0 < 1/n < 1$) the adsorption is favorable, when $1/n$ is greater than 1, the adsorption process is unfavorable and it is irreversible when $1/n = 1$.

The Freundlich model is an empirical model based on the hypothesis of heterogeneity of the surface to which the adsorption energy is distributed. Adsorption energy is the energy produced due to the interaction of adsorbent and adsorbate. The adsorbed molecules in one position do not interact with each other and each such position is independent of the others.

The Sips model is also a combination of the Langmuir and Freundlich models, which is inferred to predict the heterogeneity of adsorption systems as well as to bypass the constraints associated with the increased concentrations of the adsorbed component of

the Freundlich model. This, in turn, leads to the production of an expression that has a finite limit at high concentration. The Sips equation is given by the following non-linear expression [35].

$$q_e = \frac{K_S b C_e^{\frac{1}{n}}}{1 + b C_e^{\frac{1}{n}}} \quad (4)$$

where q_e is the uptake of phosphate ions per unit weight of adsorbent at equilibrium (mg/g), C_e is the concentration of adsorbent in solution equilibrium (mg/l), K_S and b are constants of the Sips model (L/mg) and $1/n$ is the exponent of the Sips model.

The rate of removal ($R\%$) of phosphate ions was calculated as follows

$$R\% = \frac{C_o - C_e}{C_o} \times 100 \quad (5)$$

where C_o is the initial concentration of phosphates and C_e is the concentration in solution equilibrium (mg/L).

3. Results and Discussion

3.1. Materials Characterization

The morphology of PEI-SiO₂ and calcined materials was examined with SEM (Figure 1). Although the two polyamines used vary only in their molecular weight, the resulting siliceous materials have completely different morphologies. More specifically, the PEI₈₀₀ silicas (both as-synthesized, H-800 and calcined, C-800) consist of almost spherical primary particles (Figure 1a,b) that aggregate into bunch-shaped clusters, while the PEI₂₅₀₀₀ silicas (as-synthesized, H-25000 and calcined, C-25000) consist of larger, almost monolithic, particles that have a geometrically irregular shape and multifaceted morphology (Figure 1c,d). Furthermore, the morphology of the hybrid materials remains unchanged after the calcination process, indicating the thermal stability of the siliceous materials.

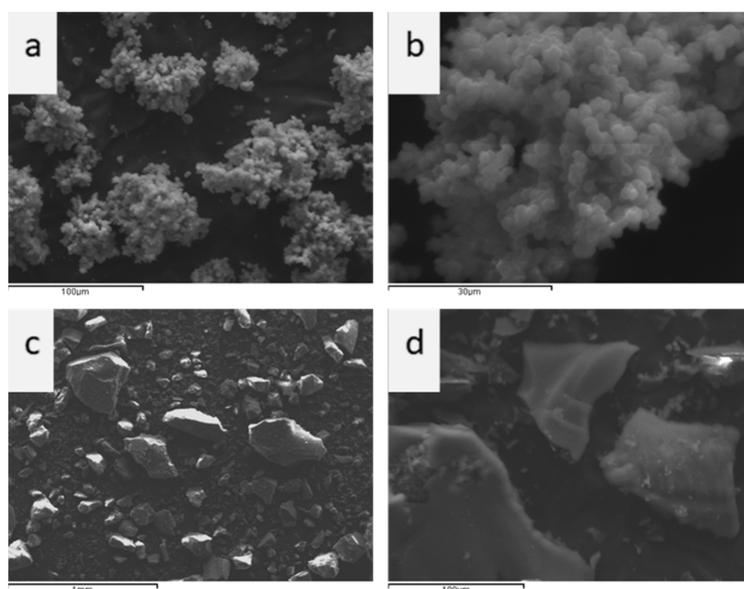


Figure 1. SEM images of as-synthesized PEI-SiO₂ and calcined materials (a) H-800, (b) C-800, (c) H-25000 and (d) C-25000.

The PEI-SiO₂ materials, both as-synthesized and calcined, have different textural properties depending on the PEI analog they were produced from. The N₂ adsorption/desorption isotherms and the porosimetry results are presented in Figure 2 and Table 1 below, respectively. More specifically, as it can be seen in Figure 2a, the as-synthesized SiO₂-PEI₈₀₀ (H-800) is a non-porous material since the PEI-800 macromolecules are blocking all

the pores. After the removal of PEI via calcination, it can be seen that the produced C-800 sample exhibit a highly microporous structure, having 446 m²/g BET (total) surface area with more than half being micropore area (280 m²/g). On the other hand, the as-synthesized SiO₂-PEI₂₅₀₀₀ (H-25000) exhibits remarkable porosity, that is, 185 m²/g BET area, even in the presence of the relatively large MW PEI₂₅₀₀₀, being mainly meso/macropore area with an average mesopore size of 34.6 nm. Upon calcination of H-25000, the BET surface area of the formed C-25000 increases significantly to 590 m²/g, owing to the increase of both micropore and mesopore area (342 m²/g and 248 m²/g, respectively). The average mesopore size of C-25000 decreased slightly to 28.7 nm, due to the removal of PEI-25000 chains and further condensation of silica upon calcination. The sharp increase in the adsorbed nitrogen volume at relative pressure $P/P_0 > 0.9$ for both H-25000 and C-25000 samples corresponds to nitrogen condensation in inter-(nano)particle voids which generate the measured mesoporosity.

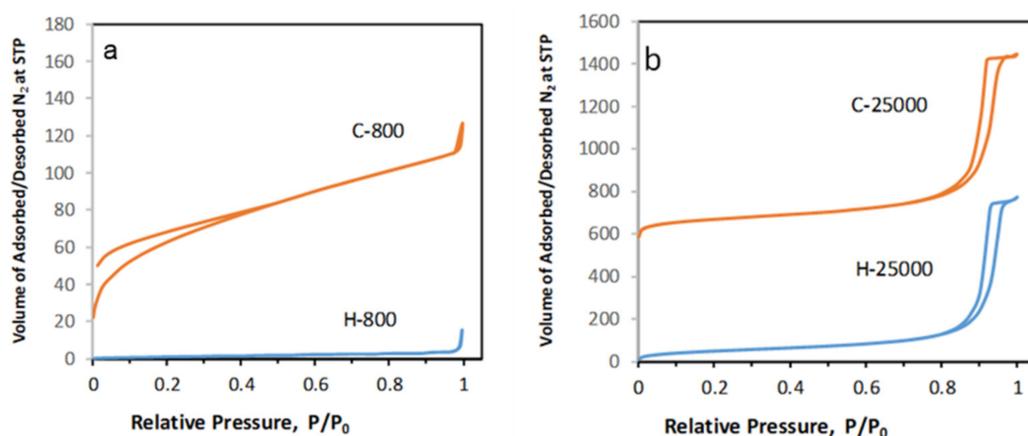


Figure 2. N₂ adsorption/desorption isotherms of microstructured silicas, (a) PEI-800 and (b) PEI-25000 derived materials.

Table 1. N₂ porosimetry results of PEI-SiO₂ materials.

Sample	Surface Area	Total Pore Volume	Micropore Volume	Micropore Area	Meso/Macro-Pore and External Surface Area	Average Mesopore Size (BJH, Adsorption Data)
	(m ² /g)	(cc/g)	(cc/g)	(m ² /g)	(m ² /g)	(nm)
H-800	4	0.025	0	0	4	-
C-800	446	0.304	0.134	280	166	-
H-25000	185	1.194	0	18	167	34.6
C-25000	590	1.461	0.157	342	248	28.7

3.2. Phosphates Adsorption Capacity

The results of the adsorption capacities of the four silica materials are shown in Figure 3. As shown in Figure 3, for the material of silica grafted with polyethylenimine of molar mass 800 (PEI-800) the maximum uptake of phosphates is up to 1.2 mg P/g and for the corresponding calcined material, it is up to 1.6 mg P/g. This value is much higher for the silica material grafted with polyethylenimine of molar mass 25,000 (PEI-25000), that is 26.9 mg P/g and for the corresponding calcined material it is up to 3 mg P/g.

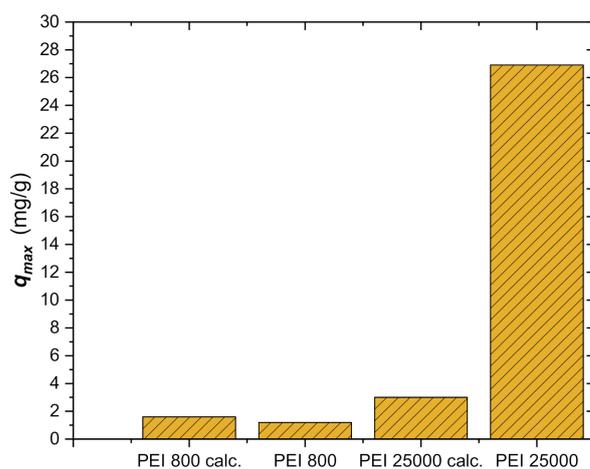


Figure 3. Phosphate adsorption capacities of the four adsorbents. Experimental conditions: Adsorbent dose 100 mg/L, phosphate concentration 4 mg/L, at pH 7 in buffered deionized water.

The material of polyethylenimine of molar mass 25,000 was the most efficient adsorbent for phosphate adsorption while the amorphous silica (calcined materials) was not efficient for the process of adsorption. As the molecular weight of polyethylenimine increases, so does the content of amino groups with which phosphate ions interact. For this reason, this material was used for the rest of the study of phosphate ion adsorption. The present results agree with other relevant studies, which used the PEI-25000 for the experiments, such as the study of the mechanism of phosphate ion adsorption on biochar modified with PEI [28] and the study of polyethylenimine-modified graphene oxide hydrogel as an adsorbent for heavy metal ions [36].

3.3. Adsorption Isotherms

The adsorption isotherms data at 20 °C for the adsorbent silica material grafted with polyethylenimine of molar mass 25,000, are shown in Figures 4–6. This increase in the adsorption capacity is mainly attributed to the fact that the higher the phosphate concentration, the larger the number of active sites of SiO₂-PEI (25,000) involved, and thus the greater the uptake capacity. At higher concentrations, phosphate ions are adsorbed on the active sites until saturation occurs and the remaining ions remain in the solution [25].

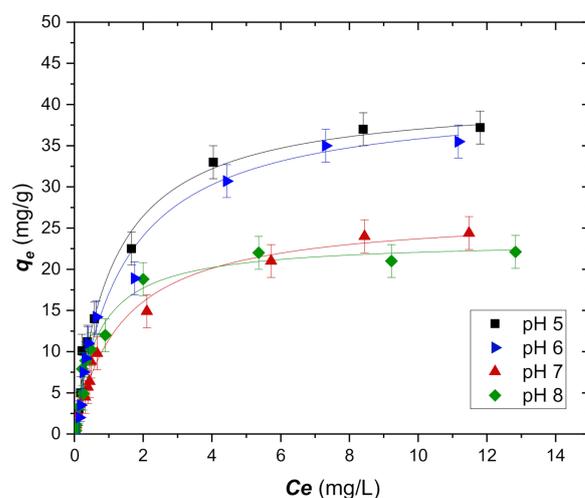


Figure 4. Adsorption data fitted in Langmuir model. Experimental conditions: Adsorbent dose 100 mg/L, phosphate concentration 0.15–15 mg/L, at pH 5–8 in deionized water.

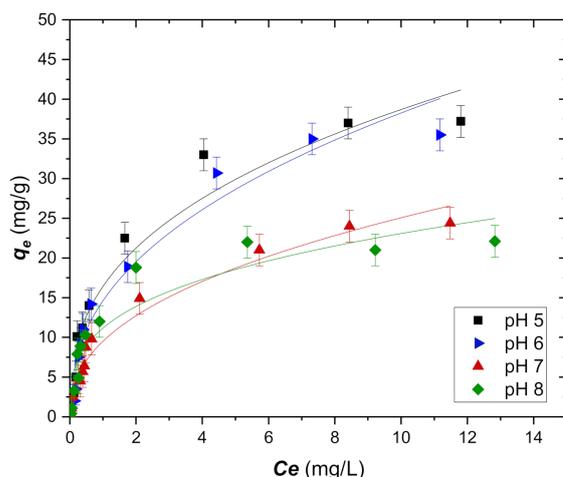


Figure 5. Adsorption data fitted in Freundlich model. Experimental conditions: Adsorbent dose 100 mg/L, phosphate concentration 0.15–15 mg/L, at pH 5–8 in deionized water.

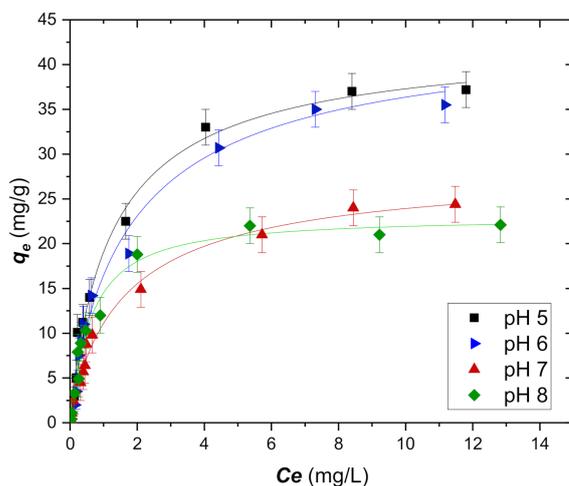


Figure 6. Adsorption data fitted in Sips model. Experimental conditions: Adsorbent dose 100 mg/L, phosphate concentration 0.15–15 mg/L, at pH 5–8 in deionized water.

Figure 4 represents adsorption data fitted in the Langmuir model, Figure 5 shows fitted data for the Freundlich model and Figure 6 the data fitted in the Sips model. The relevant values of the isotherm models constants and their corresponding linear regression correlation coefficient (R^2 value) are summarized in Tables 2–4.

As shown in Figures 4 and 6, the data of phosphate adsorption onto $\text{SiO}_2\text{-PEI}$ (25000) fit well with the Langmuir, and Sips isotherm models regarding the correlation coefficient (R^2), as compared with that produced by the isotherm models. The fittings of Langmuir isotherm for the adsorption process indicates that a homogenous and monolayer adsorption occurs [31]. Concerning the Sips model, the exponent n values are close to one, and the R^2 is only slightly larger than the one of Langmuir. This suggests that the Langmuir model describes best the adsorption of phosphate on the applied material since it gives similar fit quality with the Sips but with a smaller number of parameters.

The maximum phosphate adsorption capacity at 20 °C as suggested by Langmuir isotherm was 41.1 mg P/g at pH 5, 40.8 mg P/g at pH 6 which is the isoelectric point of polyethyleneimine [37], 26.9 mg P/g at pH 7 and 23.5 mg P/g at pH 8. Results in Figure 4 clearly indicated that pH increase had an adverse effect on the maximum adsorption capacity of phosphate. The coefficient K_L is more or less constant for pH up to 7 and then rises to a much larger value at pH 8.

Table 2. Langmuir Model Isotherm Constants for adsorption.

pH	q_{max} (mg/g)	K_L (L/mg)	R^2
5	41.1	0.89	0.985
6	40.8	0.71	0.977
7	26.9	0.74	0.987
8	23.5	1.5	0.979

Table 3. Freundlich Model Isotherm Constants for adsorption.

pH	K_F (L/g)	n	R^2
5	16.4	2.7	0.942
6	14.6	2.4	0.946
7	9.5	2.37	0.960
8	11.2	3.16	0.882

Table 4. Sips Model Isotherm Constants for adsorption.

pH	K_S	b	n	R^2
5	47	0.6	1.2	0.987
6	44.9	0.58	1.15	0.979
7	28.8	0.63	1.12	0.988
8	23	1.72	0.93	0.979

Other researchers showed as well, that the Langmuir model fits well in the adsorption of phosphates on materials such as biochar with polyethyleneimine-25000 [28], clay composites (dolomite, montmorillonite) [25], and the porous silica from rice husk modified with polyethyleneimine [22].

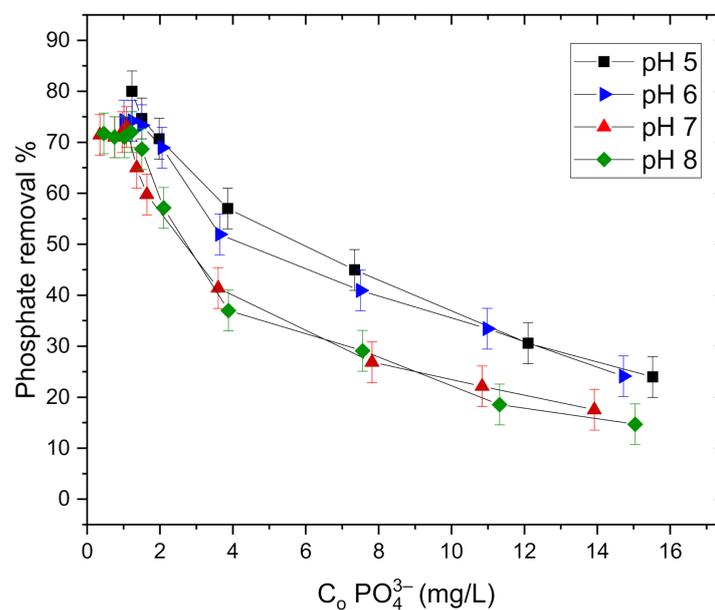
According to Table 5, silica, in the form of silica sand, is an adsorbent material that in the case of phosphate ions does not remove them to a sufficient extent from an aqueous solution. When silica is modified with functional groups such as ammonium and samarium, a much higher phosphate adsorption capacity is observed, which is due to ion exchange and coulomb and/or acid-base Lewis force interactions. It also appears that, although silica modification is an effective solution for increasing adsorption capacity, polyethyleneimine is a good substrate for the binding of negatively charged phosphate ions. The adsorption capacity of Cell-g-E/PEI material was 232.46 mg P/g, at low pH value, for Biochar-PEI₂₅₀₀₀ was 9.2 mg P/g, at about neutral pH and 123.46 mg P/g for RSi-bPEI material, for low pH values [4,22,28]. In the present work for the SiO₂-PEI₂₅₀₀₀ material, the highest adsorption capacity was 41.1 mg P/g at pH 5 and decreased to 26.7 mg P/g at pH 7. This is considerably higher than the maximum sorption capacity reported for the Biochar-PEI₂₅₀₀₀ material at pH 7.

3.4. Effect of the pH and the Initial Concentration of Phosphates

Batch tests were carried out with various phosphate concentrations (0.15–15 mg/L) and constant conditions (T = 20 °C, adsorbent dose 100 mg/L, mixing time 24 h) at pH 5–8. Figure 7 shows the removal efficiency as the initial concentration of phosphates is increased. At all the pH values examined, the removal efficiency decreased by increasing the initial phosphate concentration at a constant adsorbent dose. This can be attributed to the increase in the amount of phosphate ions compared to those competing for the available active sites on the adsorbent since for a given dose of adsorbent, the total number of available active sites is constant and not sufficient for the high initial phosphate concentrations [25]. Results showed that the maximum removal rate is up to 80% at pH 5 and at about 70–75% at pH 6, 7 and 8. Similar results were observed also in other studies [4,22,27]

Table 5. Overview of phosphate ion removal studies using silica and/or polyethyleneimine modified materials.

Adsorbent (dose g/L)	C_0 of Phosphate Ions (mg/L)	Removal %	Adsorption Capacity (mg P/g)	pH	Reference
Silica sand (40)	5–100	21–58	0.9	7–8	[24]
MCM-48-NH ₃ ⁺ (10)	100–700	88	35	4–6	[27]
Sm _x MCM-41 (1,5)	30	100	20	7	[25]
Ammonium-MCM-41 (1)	0–100	94.7–97.6	14.97	3.5–7.4	[26]
Cell-g-E/PEI (1)	0–250	99.6	232.8	4.5	[4]
Biochar-PEI ₂₅₀₀₀ (1)	5–100	-	9.2	6.5	[28]
RSi-bPEI (0,5)	5–200	99	123.46	4	[22]
SiO ₂ -PEI ₂₅₀₀₀ (0,1)	1.5–15	40	26.9	7	Present work
SiO ₂ -PEI ₂₅₀₀₀ (0,1)	1.5–15	82	41.1	5	Present work

**Figure 7.** Effect of initial phosphate concentration on the removal efficiency of phosphate as affected by pH variation (adsorbent dosage = 100 mg/L).

The effect of pH on the removal of phosphate by polyethylenimine functionalized silica is ascribed to the fact that changes in pH cause significant changes to the surface charge and the behavior of the functional groups on the adsorbent surface. Under acidic conditions, amino groups on polyethylenimine are easier to protonate, while when the pH of the solution increases, the adsorbent surface becomes more negatively charged, and therefore becomes unfavorable to phosphate ions adsorption due to electrostatic repulsion [27].

For phosphate anions, the pH dependence profile indicates an optimal adsorption process at pH values between 5 and 6. At low pH, the amino groups in PEI are protonated so it is a very positively charged polyelectrolyte, but at high pH (>9), it is essentially a neutral polymer [37], indicating that at lower pH values, electrostatic attraction is strong but weak at high pH values.

3.5. Effect of the Adsorbent Dose

Figure 8 shows the effect on phosphate removal by increasing the concentration of the adsorbent material PEI (25000). As it is observed, the removal rate is increased from 40% to 80% at pH 7 and from 50% to 80% at pH 6 as the adsorbent concentration is increased from 100 mg/L to 2 g/L. This increase in the adsorbent efficiency at pH 7 is very promising since it shows that the application of this material can be effective for phosphate removal even at circumneutral pH values, which corresponds to pH values of most natural and engineered

aquatic systems. The increase at removal efficiency would be expectable as an increase in the adsorbent dosage would lead to more available binding sites on the adsorbent [27]. At a low adsorbent dose, 100 mg/L, a low phosphate removal rate was observed due to the limited active sites available for adsorption. At higher adsorbent doses, there were plenty of active sites for adsorbent-phosphate interaction and thus the removal efficiency increased [22].

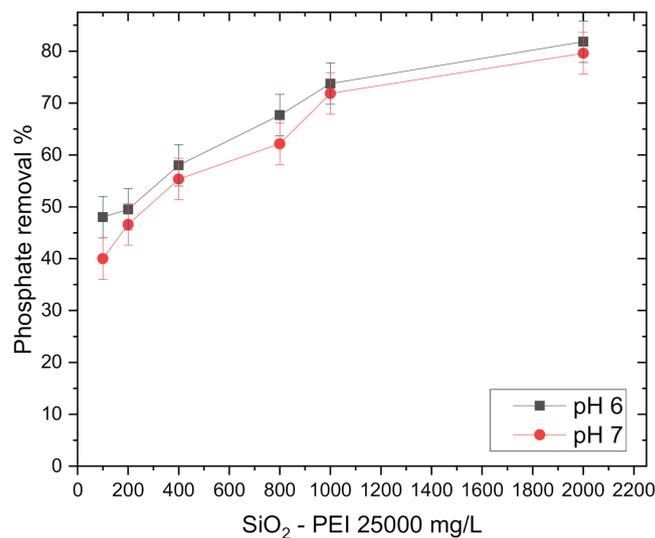


Figure 8. Effect of adsorbent concentration on the removal efficiency. (Initial phosphate concentration 4 mg/L).

3.6. Effect of Coexisting Anions

Figures 9–12 show the effect of coexisting anions on phosphate removal efficiency. Specifically, Figure 9 represents the effect of carbonate ions, Figure 10 shows the effect of sulfate ions, Figure 11 the effect of nitrate ions and Figure 12 the effect of chromate ions, for experiments carried out at pH 7, initial phosphates concentration 4 mg/L and SiO₂-PEI (25000) dose 100 mg/L.

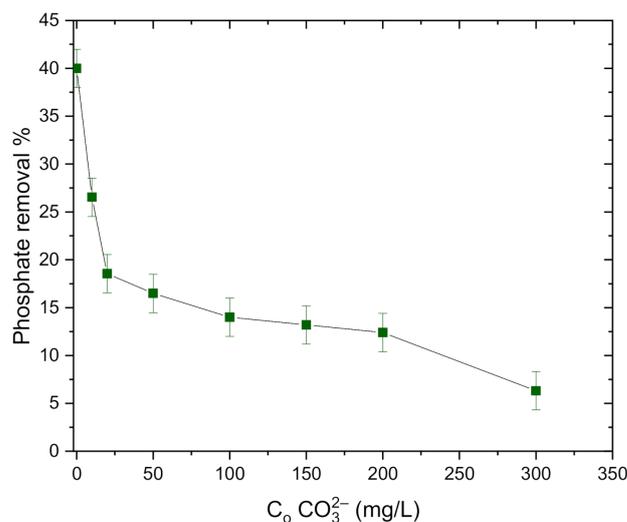


Figure 9. Effect of carbonate concentration on the removal efficiency of phosphates. (pH 7, initial phosphates concentration 4 mg/L, SiO₂-PEI (25000) dose 100 mg/L).

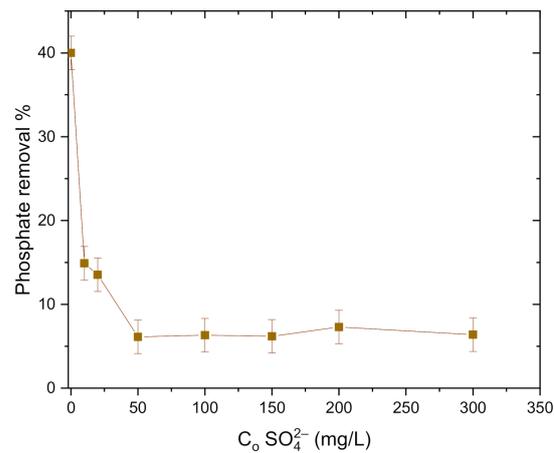


Figure 10. Effect of sulfate concentration on the removal efficiency of phosphates. (pH 7, initial phosphates concentration 4 mg/L, SiO₂-PEI (25000) dose 100 mg/L).

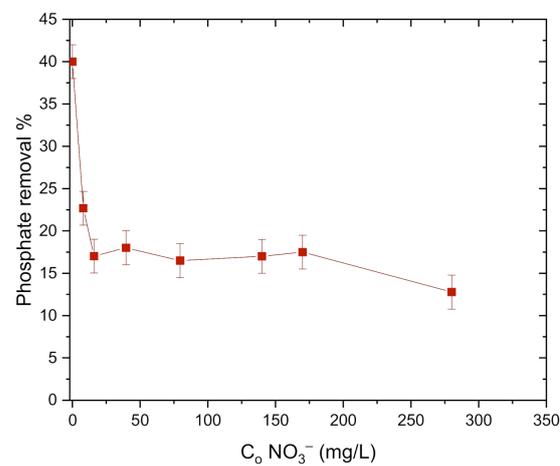


Figure 11. Effect of nitrate concentration on the removal efficiency of phosphates. (pH 7, initial phosphates concentration 4 mg/L, SiO₂-PEI (25000) dose 100 mg/L).

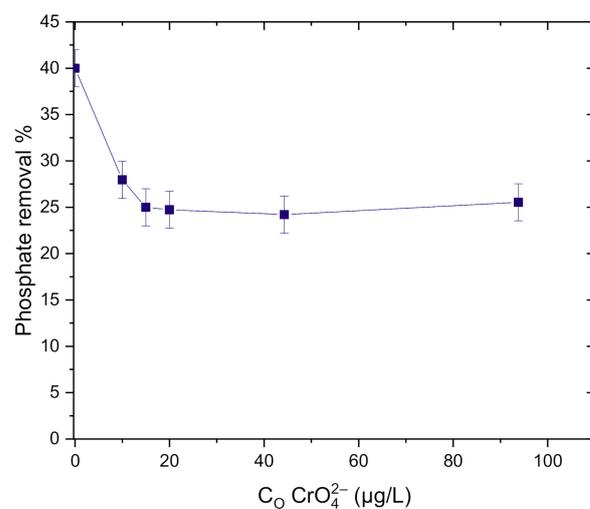


Figure 12. Effect of chromate concentration on the removal efficiency of phosphates. (pH 7, initial phosphates concentration 4 mg/L, SiO₂-PEI (25000) dose 100 mg/L).

The presence of SO_4^{2-} at 10 mg/L decreases the removal rate of phosphates from 40% to 15% compared to the absence of those. Similar to the presence of sulfate, phosphate

removal decreased from 40%, in the absence of the ions, to 27%, 23% and 28% for the CO_3^{2-} , NO_3^- and CrO_4^{2-} ions respectively, at 10 mg/L of CO_3^{2-} , NO_3^- and at 10 $\mu\text{g/L}$ of CrO_4^{2-} . As the concentration of the ions increases from 10 mg/L to 300 mg/L for the SO_4^{2-} , CO_3^{2-} and NO_3^- ions and from 5 $\mu\text{g/L}$ to 100 $\mu\text{g/L}$ for the CrO_4^{2-} ions, the removal rate of phosphates was further decreased. Therefore, it could be concluded that the competition of coexisting anions on phosphate adsorption follows the order: $\text{SO}_4^{2-} > \text{CO}_3^{2-} > \text{NO}_3^- > \text{CrO}_4^{2-}$. These results are in agreement with findings from a study of phosphate adsorption in the presence of other ions, in which the SO_4^{2-} ions provided the most inhibitory effect on phosphorus adsorption on porous rice husk silica modified with polyethyleneimine [22].

3.7. Removal of Chromate and Nitrate Ions in the Presence of Phosphate

In the present work, we also studied the possible co-removal of other anionic pollutants that may be present in the water, such as chromates and nitrates. Figures 13 and 14 show the removal of chromate and nitrate ions, respectively, in the presence of phosphate ions using the adsorbent $\text{SiO}_2\text{-PEI}_{25000}$.

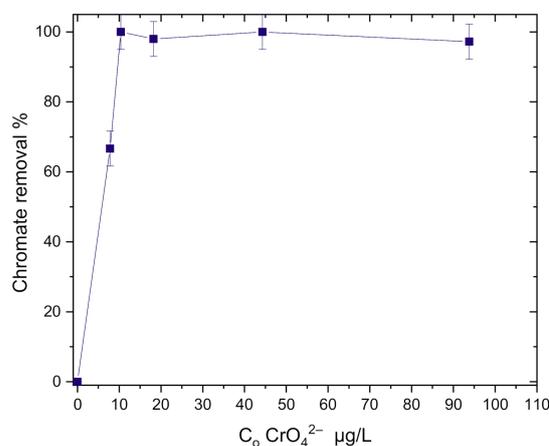


Figure 13. Removal of chromate ions in the presence of 4 mg/L of phosphate ions (pH 7 and adsorbent dose at 100 mg/L).

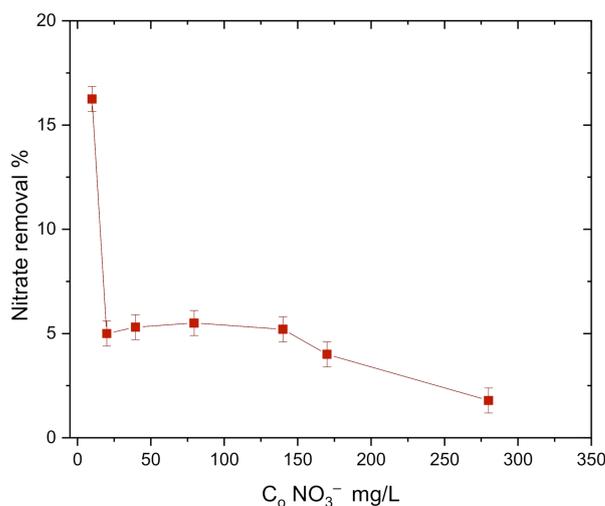


Figure 14. Removal of nitrate ions in the presence of 4 mg/L of phosphate ions (pH 7 and adsorbent dose at 100 mg/L).

For chromium ions, maximum removal of 100% was observed from the solution in the presence of 4 mg/L phosphate ions and for the adsorbent dose of 100 mg/L. Apparently,

phosphate ions did not affect the adsorption of chromates in the range of chromate concentrations examined, which corresponds to chromium concentrations found in contaminated groundwaters [38]. These results are in agreement with a previous publication studying by Chen et al. (2018), in which the presence of phosphate ions resulted in a very small reduction, 6%, in the adsorption of chromates in polyethylenimine- and phosphorus-codoped porous carbons for initial chromium concentration of 200 mg/L, adsorbent dosage 1 g/L and 2 g/L of phosphates at pH 2 [39]. It has also been found that chromium ions can be removed up to 100%, over a wide pH range (3–9), from solutions using polyethyleneimine in materials such as ultrafiltration membranes [40]. In contrast, Figure 14 shows, that the removal rate for nitrate ions, in the presence of 4 mg/L phosphate, was only 16% for low concentrations of nitrate ions and sharply decreased to 5% and finally to 2.5% for the highest concentrations. These results were in agreement with findings from other relevant studies in the presence of nitrate ions, in which the adsorption capacity was 20.3 mg/g and 17.2 mg/g for nitrates and phosphates, respectively, while for the same conditions without the coexistence of the two ions the adsorption capacity was, respectively, 25 mg/g and 20 mg/g [41].

4. Conclusions

The silica-polyethyleneimine adsorbent materials proved to be effective for the removal of phosphate anions from aquatic solutions in the pH range 5–7. Comparing the present study with other studies reported in the literature of phosphate ion adsorption on silica and/or polyethyleneimine materials (Table 5), it can be noted that the use of polyethyleneimine increased the adsorbed phosphate concentration. The role of polyethyleneimine was very important for the adsorption of phosphate ions since it increased drastically the adsorptive efficiency of pure silica. In particular, polyethyleneimine with a molecular weight of 25,000 was shown to be more effective than polyethyleneimine with a molecular weight of 800, while silica used without the active amino groups of polyethyleneimine is not capable of adsorbing phosphate ions. The morphology results showed that the SiO₂-PEI (25000) consists of almost monolithic particles having a geometrically irregular shape and a multifaceted morphology, with a porosity of 185 m²/g BET area, being mainly meso/macropore area with an average mesopore size of 34.6 nm.

According to the results of the present study, phosphate removal follows quite well the Langmuir model with decreasing efficiency as the pH increased. The maximum sorption capacity was 41.1 mg P/L at pH 5 which decreased to 26.9 mg P/L at pH 7. At pH 7, for the initial concentration of phosphate 2 mg/L and the adsorbent dose of 100 mg/L, the removal recorded was about 70%, which is considered as an efficient result. This was shown also by comparison of the results with similar literature findings, which showed that the proposed material is very competitive at circumneutral pH values, which represents pH values of natural and engineered aquatic systems. At all the examined pH values, the removal efficiency decreased from 70–80% to 20–30% by increasing the initial phosphate concentration from 1 to 15 mg/L at a constant adsorbent dose. The removal rate is increased from 40–50% to 80% as the adsorbent concentration is increased from 100 mg/L to 2 g/L, at pH 6 and 7. The presence of other anions such as sulfate, carbonate, nitrate and chromate, reduced the removal efficiency of phosphate ions and the SO₄²⁻ ions provided the most inhibitory effect on phosphorus adsorption. However, it was shown that the proposed material was able in removing simultaneously chromate and nitrate in the presence of 4 mg/L phosphate. This shows that this material can be potentially used for the removal of multiple contaminants when present at low concentrations but still above the regulation limits.

Author Contributions: Conceptualization, I.A.K. and N.T, Methodology, K.S.T., D.G. and M.X., Data Curation, M.K., Validation, M.K., Writing original draft, M.X., writing-review and editing, M.X., I.A.K., M.K., K.S.T., D.G. and N.T., Supervision, I.A.K. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Not applicable.

Conflicts of Interest: The authors declare no conflict of interest.

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