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Sorption of phosphate from innovative composite material focusing on physicochemical interactions

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ABSTRACT

A modified inorganic bentonite (Zenith/Fe) based on natural bentonite has been evaluated for phosphate uptake under various physicochemical conditions prevailing in natural water bodies. The effects of material fraction size, solution alkalinity, dissolved organic matter (DOM), solution potential (E_h), ionic strength on the adsorption of phosphate on modified bentonite are investigated by bench-scale batch techniques. The role of anions and cations has been also evaluated. Modified inorganic bentonite had the most prominent effect on phosphate ion removal at an alkalinity close to that of soft water (low alkalinity), followed by moderate and hard waters (high alkalinity). Hence the phosphate-adsorption capacity (PAC) followed the order: [soft] > [moderate] > [hard] water. The kinetics of phosphate uptake by Zenith/Fe is influenced by DOM: Phosphate is captured during the first 60 min of adsorption while equilibrium is attained after approximately 120 min. However, the PAC of Zenith/Fe in the presence of DOM (74%) is lower than the PAC onto modified bentonite in the absence of DOM (87%). Metal cations in solution have a positive effect on phosphate uptake by Zenith/Fe. The PAC increased with the increase of cation concentration, following the order: $Na^+ > K^+ > Mn^{2+} > Mg^{2+}$. Contrarily, PAC decreased with the increase of anion concentration following the order: [carbonate] > [chloride] > [sulfate]. In addition, phosphate adsorption was found to be not influenced by ionic strength, suggesting formation of strong inner-sphere complexes. Finally, solution potential does not change the maximum adsorption capacity of modified inorganic bentonite; however, it changes the adsorption rate in the first minutes.

Keywords: Alkalinity; Dissolved organic matter; Solution potential; Eutrophication; Restoration

1. Introduction

Today there is growing interest in developing low-cost and effective natural materials, as specific phosphorus adsorbents from natural eutrophic water bodies [1–4]. Physicochemical parameters such as dissolved organic matter (DOM), solution potential (E_h), alkalinity, concentration of metal cations (e.g., Mg^{2+}, Na^+, Mn^{2+}, K^+) and anions (such as carbonate, sulfate, chloride) describe important aspects of eutrophic water bodies and for this reason should be taken into account in the implementation study of novel P-adsorbents. Although, eutrophication is related to high nutrient loads, the definition also stresses that eutrophication is an increase in the supply rate of organic matter [5]. DOM is the basis for microheterotrophic activity in aquatic ecosystems [6]. DOM in aquatic processes depends on its sources, which in most natural eutrophic waters include both terrestrial organic matter from degrading plant and soil material delivered from the watershed and microbial organic matter from the breakdown products of bacterial and algal matter in the water column [7].

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The proliferation of aquatic plants and the subsequent decomposition of organic matter usually lead to low dissolved oxygen concentrations in bottom waters and sediments of eutrophic aquatic ecosystems with low water renewal rates. Hypoxic/anoxic conditions occur in stratified lakes, reservoirs, estuaries and coastal waters that receive high loadings of nutrients from anthropogenic sources, affecting many natural ecosystems worldwide [8–12]. These aquatic environments often create reductive conditions resulting in higher adverse effects on aquatic animals [13–14]. Alkalinity is a measure of the bicarbonate and carbonate content of water and therefore the buffering capacity of an aquatic ecosystem. This parameter is usually strongly influenced by both photosynthetic activity and the delivery of inorganic buffering compounds of the watershed. Moyel [15] recorded 40 mg/L total alkalinity as a natural separation point between soft and hard waters. In general, the more oligotrophic (low nutrient) lakes tend to have lower alkalinity while eutrophic (high nutrient) lakes tend to have higher alkalinity.

Modified bentonite is a low-cost composite material embedding Fe, Cu ions in the interlayer space of a natural bentonite. Its basic physicochemical properties have been studied in detail in our recent work [16]. This composite clay-material was highly efficient for phosphorus removal from water at a wide range of pH values (5–9). Its efficiency is maintained at alkaline pH (pH 8–9) in contrast with most materials, whose ability in adsorbing phosphorus drops dramatically under these conditions. This is of particular importance as in eutrophic waters the pH conditions that dominate are between 8 and 9. In addition, the adsorption capacity for phosphate followed the order [16]: fresh water > brackish > marine water. Thus, modified bentonite is a low-cost material prepared by environmentally friendly components that is potent for removal of phosphate at low concentrations such as in natural water ecosystems.

Nevertheless, due to the complexity of natural water contents, it is important to map its phosphate adsorption capacity (PAC) in relation to physicochemical parameters in natural eutrophic water bodies. For example, one may envisage that due to this complexity, there might be competition from some parameters which may largely affect the phosphate removal performance on modified bentonite.

The objective of the present study was to examine the feasibility of using modified inorganic bentonite – based on natural bentonite – as adsorbent for phosphate under various physicochemical conditions pertaining in natural eutrophic ecosystems. Here, the effects of fraction size, DOM, solution potential (E_h) and ionic strength for phosphate uptake by modified bentonite have been studied. Moreover, the effects of metal cations and anions on PAC by modified bentonite were also studied. Critical parameters aiming to simulate a eutrophic natural ecosystem were screened, for example, the initial phosphate concentration, concentration of DOM and concentrations of metal cations and anions.

2. Materials and methods

2.1. Reagents

All solutions were prepared with analytical grade chemicals and purified water Milli-Q produced by Millipore Academic system with a conductivity of demineralized water of 18.2 μS. Moreover, potassium dihydrogen phosphate [KH_2PO_4] was used for phosphate stock solutions. $Fe(NO_3)_3.9H_2O$, $Cu(NO_3)_2$, $AlCl_3$, Na_2CO_3, HEPES (4-(2-hydroxyethyl) piperazine-1-ethanesulfonic) acid, $K_3[Fe(CN)_6]$, $K_4[Fe(CN)_6]$ and sodium ascorbate (sodium (2*R*)-2-[(1*S*)-1,2-dihydroxyethyl]-4-hydroxy-5-oxo-2*H*-furan-3-olate), were obtained from Sigma-Aldrich (Germany). The material used in this work was a modified inorganic bentonite (Zenith/Fe) based on natural bentonite that was prepared by embedding Fe ions in the interlayer space of bentonite. The properties of this modified clay have been published in detail previously [16].

2.2. Batch experiments

Phosphate stock solution of 50 mg/L was prepared by dissolving 0.2197 g of potassium dihydrogen phosphate [KH_2PO_4] in 1.0 L deionized water and dilutions of the stock solution were used in subsequent experiments.

Modified bentonite was ground manually using a pestle and mortar. The resulting fraction size was determined using sieve in a sequence ranging from 0 to 0.2 mm (0.1 ± 0.1 mm), from 0.2 to 0.5 mm (0.35 ± 0.15 mm), from 0.5 to 2 mm (1.25 ± 0.75 mm) and from 2 to 5 mm (3.5 ± 1.5 mm). The influence of fraction size was studied using optimized conditions: pH 7, phosphate concentration 0.1 mg/L, adsorbent mass 0.02 g dispersed in a solution volume of 60 mL H_2O and 25°C ± 1°C temperature.

To assess the effect of alkalinity, batch experiments were conducted in order to simulate three different water bodies; soft waters (low alkalinity), moderate and hard waters (high alkalinity). Alkalinity expressed as the concentration of calcium carbonate [$CaCO_3$] using 20, 80 and 150 mg/L to simulate soft, moderate and hard waters, respectively. Adsorption kinetic data of phosphate on Zenith/Fe in contact times ranging between 15 and 1,440 min were studied in the three different alkalinities using optimized conditions: pH 7, phosphate concentration 0.1 mg/L, adsorbent mass 0.02 g dispersed in a solution volume of 60 mL H_2O and 25°C ± 1°C temperature.

The effect of DOM on PAC of modified bentonite was studied out by determining the phosphate uptake of modified bentonite in contact times ranging between 15 and 1,440 min adding 50 mg/L a well characterized soil humic acid [17] at pH 7, phosphate concentration 0.1 mg/L, adsorbent mass 0.02 g dispersed in a solution volume of 60 mL H_2O, and 25°C ± 1°C temperature.

Chloride ion, sulfate ion and hydrogen carbonate ion solutions were prepared from sodium chloride, sodium sulfate and sodium hydrogen carbonate, respectively, in concentrations ranging from 50 to 250 mg/L. The optimized conditions were: pH 7, phosphate concentration 0.1 mg/L, adsorbent dose 0.02 g dispersed in a solution volume of 60 mL H_2O, and 25°C ± 1°C temperature.

Standard stock solutions of magnesium (Mg^{2+}), manganese (Mn^{2+}), sodium (Na^+) and potassium (K^+) were prepared in concentrations ranging from 0.5 to 5 mg/L. The optimized conditions were: pH 7, phosphate concentration 0.1 mg/L, adsorbent dose 0.02 g dispersed in a final volume of 60 mL H_2O and 25°C ± 1°C temperature.

The effect of ionic strength was investigated in the ionic strength ranges of 0–0.2M $NaClO_4$ at 25°C ± 1°C for 0.1 mg/L of phosphate, at initial pH 7 and contact time of 24 h.

To study the effect of solution potential (E_h), milli-Q water was degassed using pure nitrogen (99.999%) before use for 6 h. The experiments were carried out under N_2 atmosphere. To obtain reductive environment (E_h = –90 mV in pH 7), 50 mM of sodium ascorbate solution was used, or 50 mM of $K_3Fe(CN)_6$, to obtain oxidative potential (E_h = +310 mV in pH 7). Solution potentials were measured using a redox platinum Metrohm electrode (6.00401.300) calibrated vs. solution 10 mM $K_3Fe^3(CN)_6$: 10 mM $K_2Fe^2(CN)_6$: 3 M KCl that correspond to a redox value of $E_{h\text{ reference}}$ = +228 mV. All redox potentials were calculated using the equation $E_{h\text{ real}} = E_{h\text{ measured}}$ + (228 mV – $E_{h\text{ reference}}$). The redox potential value for milli-Q was E_h = +110 mV in pH 7.

In all batch experiments, after equilibration, the suspension was separated by centrifugation and the concentration in supernatant (c_e) was measured by the molybdate blue spectrophotometric method [18] using a Lambda 25 UV–Vis spectrophotometer (PerkinElmer, Germany). The detection limit of the analytical method was 0.01 mg PO_4^{-3}/L.

The amount of adsorbed phosphate (q_e) was calculated from the difference in concentration between initial (c_o) and the final concentration. Blank samples without any adsorbent were prepared and monitored as control.

To adjust the pH, a buffer system of 10 mM MES: (*N*-morpholino-ethanesulfonic acid), HEPES: (4-(2-hydroxyethyl) piperazine-1-ethanesulfonic) acid was used in all samples [16,19–21]. This system presented a significant buffer capacity at pH range 5–8.5, with an average deviation from the adjusted pH value of <5%. Screening experiments indicated that under the above experimental conditions, the buffer molecules caused no interference on the adsorption phenomena. Prior to starting the experiment, the pH was adjusted from 5 to 9 at 25°C ± 1°C, using small volume of 0.1 M HCl and NaOH solutions. All experiments were repeated in duplicates.

Desorption tests were conducted at different pH conditions to assess the stability of modified bentonite. 0.1 g Zenith/Fe was added to each 250 mL Erlenmeyer flask containing 100 mL of distilled water, adjusted to pH levels within the range of 2.0–7.0. The mixture was continuously shaken for 24 h at 25°C ± 1°C after which the supernatant was collected and filtered prior to analysis by inductively coupled plasma-atomic emission spectroscopy (ICAP 6000 Radial, Thermo, USA).

3. Results and discussion

3.1. Influence of fraction size of Zenith/Fe on phosphate adsorption

Experiments were conducted with samples having four different average fraction sizes for Zenith/Fe, ranging from 0 to 5 mm in order to determine the effect of fraction size on adsorption process. The results are given in Fig. 1; they reveal that phosphate removal efficiency rises with decrease in fraction size. It was observed that removal efficiency of phosphate increased from 76% to 87% with reduction in the modified bentonite fraction size range from <1 to 5 mm. For scientists working with lake restoration efforts, it is very important to evaluate the effect of the fraction size of adsorbent material. During the application of the material in a lake/pond/reservoir, a potential adverse effect is caused by the settling of the material, which is the smothering of the lake bed. Consequently, authors are interested to find a good performance of material in relatively large fraction sizes to avoid negative impacts of this phenomenon. The results were encouraging for a possible lake restoration treatment.

3.2. Effect of alkalinity on adsorption process

The effect of alkalinity of phosphate adsorption by Zenith/Fe at contact times ranging between 15 and 1,440 min (24 h) are presented in Fig. 2. The plots represent the amount of phosphorus adsorbed onto modified bentonite vs. time in relation to the effect of alkalinity representing three different water bodies (soft, moderate and hard waters, $CaCO_3$ = 20, 80 and 150 mg/L). As shown in Fig. 2, most of the phosphate is captured during the first 4 h of the adsorption process, while the rate of removal slowed down considerably with increase of contact time and after 8 h was almost negligible. In general, the removal kinetics

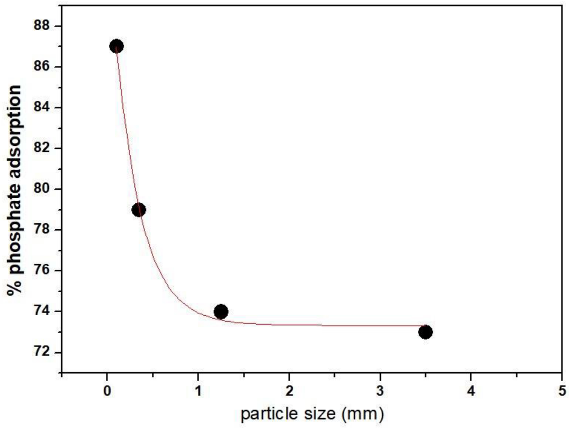

Fig. 1. Effect of fraction size on phosphate uptake by modified material Zenith/Fe. Phosphate concentration 0.1 mg/L, adsorbent dose 0.02 g, T = 25°C and contact time 24 h.

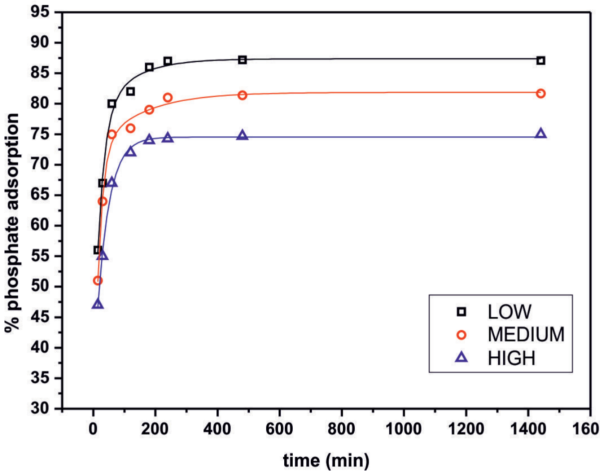

Fig. 2. Effect of alkalinity on phosphate uptake by modified material Zenith/Fe at different contact times. Phosphate concentration 0.1 mg/L, adsorbent dose 0.02 g, T = 25°C.

of hydrogen phosphate HPO_4^{2-} by Zenith/Fe at all alkalinities were biphasic, with an initially faster phase (4 h) where at least 80% of the maximum removal has been achieved.

Fig. 2 illustrates that at an alkalinity close to that of soft water (80 mg/L $CaCO_3$) Zenith/Fe had the most prominent effect on phosphate ion removal, followed by moderate and hard waters (high alkalinity). Hence the phosphate capacity followed the order: soft > moderate > hard water. The effect of different alkalinities is relatively small; however it is not negligible. Thus, this is attributed to the competitive adsorption between P-containing anions ($H_2PO_4^-$ and HPO_4^{2-}) and HCO_3^- anion [22].

3.3. Influence of DOM in phosphate adsorption

The removal of phosphate from natural waters onto modified bentonite as a function of DOM is illustrated in Fig. 3. As shown, in both cases, for example, in the presence or in the absence of DOM, most phosphate is captured during the first 60 min of reaction. Adsorption maximum was attained after 100 min. However, the maximum PAC by modified bentonite in the presence of DOM (74.7%) is lower than the PAC in the absence of DOM (87%). This effect can be attributed to the carboxylates groups that are known to exist in DOM [23]. At natural pH values 7–8, these groups are in anionic form (pKas of the COOH are in the range of 2–5 [23]. Thus the R–COO^- inhibit phosphate anions ($H_2PO_4^-$ and HPO_4^{2-}) uptake by the active Fe^{3+} sites embedded in the structure of Zenith/Fe as shown previously [18,19].

3.4. Effect of dissolved metal cations

The effect of dissolved magnesium (Mg^{2+}), manganese (Mn^{2+}), sodium (Na^+) and potassium (K^+) ions on PAC is shown in Fig. 4. The data reveal that there is a small increase in the PAC in the presence of metal ions. As shown in Fig. 4, when the concentrations of Mg^{2+}, Mn^{2+} and Na^+ increased from 0 to 5 mg/L, the removal efficiency of phosphate anions ($H_2PO_4^-$ and HPO_4^{2-}) increased from 87.5% to 88%, and from 88.4% to 89%, respectively. However, the difference in P adsorption in the presence of different cations is less than 2%, thus it can actually be considered negligible. However, since the material adsorbs the phosphate ions better in the range of pH 5 to 9, $H_2PO_4^-$ is the ion that Zenith/Fe better binds.

At identical concentration of metal cations, the removal efficiency of phosphate was highest for Na^+ present in the solution, followed by K^+, Mn^{2+} and Mg^{2+} ($Na^+ > K^+ > Mn^{2+} > Mg^{2+}$). It is known that Na^+ and K^+ are non-coordinating ions resulting in electrostatic weak binding with high exchange rate, whereas the larger bivalent Mn^{2+} and Mg^{2+} result in lower exchange rates [24], and therefore lower binding efficiency. Moreover, between Na^+ and K^+, it is known that potassium is more reactive; therefore Na^+ can result in even weaker binding [25].

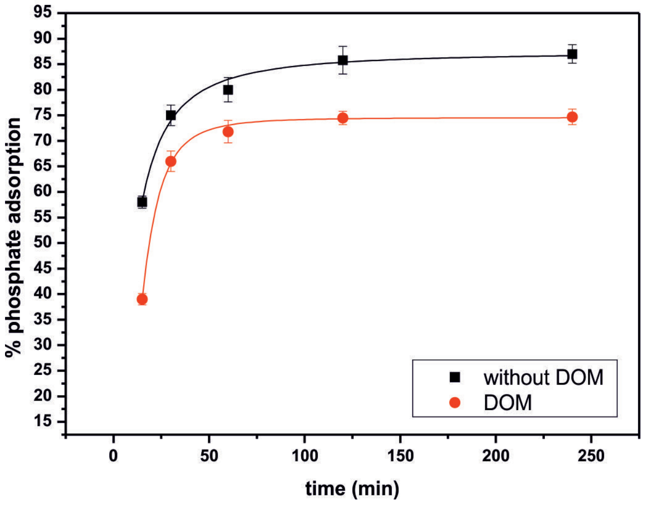

Fig. 3. Effect of 50 mg/L DOM at pH 7, on phosphate uptake by modified material Zenith/Fe. Phosphate concentration 0.1 mg/L, adsorbent dose 0.02 g, $T = 25°C$ and contact time 4 h.

3.5. Anion effect on phosphate adsorption by Zenith/Fe

Due to the complexity of natural water contents, there might be competition from other anionic species which may potentially affect the phosphate removal performance on Zenith/Fe. Anions, such as carbonate (H_2CO_3 and HCO_3^- anion), sulfate and chloride, are commonly present in eutrophic water bodies and might interfere with the phosphate adsorption on modified material. The effects of these anions on PAC shown in Fig. 5 are rather small, affecting it by less than 10% at most.

It is seen that PAC was decreased with the increase of anion concentration. At identical phosphate ($H_2PO_4^-$ and HPO_4^{2-}) concentrations, the effect of carbonate was greatest, and was followed by those of chloride and sulfate, in that order. When the initial phosphate ($H_2PO_4^-$ and HPO_4^{2-}) concentration was raised from 50 to 300 mg/L with only carbonate present in solution, PAC fell from 86% to 73.8%; however, when chloride or sulfate, were present, PAC declined from 86% to 77% and 79.4%, respectively. This indicates that the order of anion effect on phosphate removal is carbonate > chloride > sulfate.

We underline that, as shown in Fig. 5, PAC by Zenith/Fe was not impaired by the anion and only a minor decrease, at most 10%, in PAC was observed.

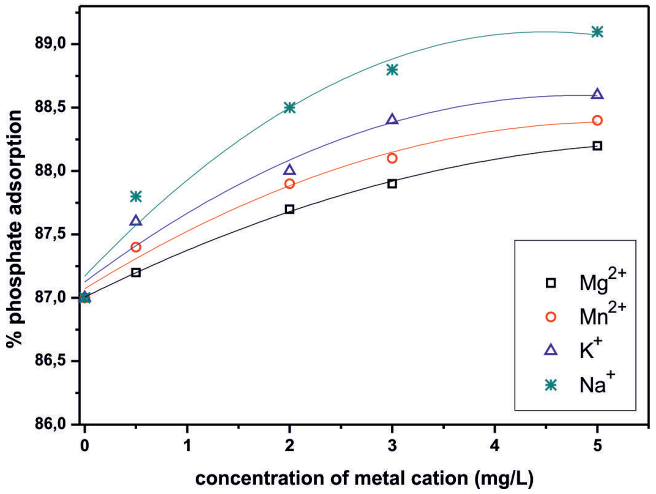

Fig. 4. Cation effect on phosphate adsorption by Zenith/Fe.

3.6. Effect of ionic strength on phosphate adsorption by Zenith/Fe

Investigation of the effect of ionic strength on adsorption is an approach to distinguish possible adsorption processes involved either in inner-sphere or outer-sphere surface complexes [26]. Here, the solution set for ionic strength (IS) effect was adjusted by the addition of an "indifferent electrolyte" [26] $NaClO_4$ that does not apply any coordination phenomena in the system. Fig. 6 shows that PAC was almost unaffected for the tested IS up to 0.02. We notice that the IS values tested were low; however they were deliberately chosen to represent eutrophic freshwaters.

According to McBride [27] and Xu et al. [28], the adsorption of phosphate would decrease upon the increase of ionic strength if the phosphate formed outer-sphere surface complexes, while the adsorption of phosphate would either not change or increase with the increase of ionic strength if the phosphate formed inner-sphere complexes. Thus, the results in this study demonstrated that the adsorption of phosphate on Zenith/Fe follows the inner-sphere complex mechanism at the Fe^{3+} active sites of Zenith/Fe.

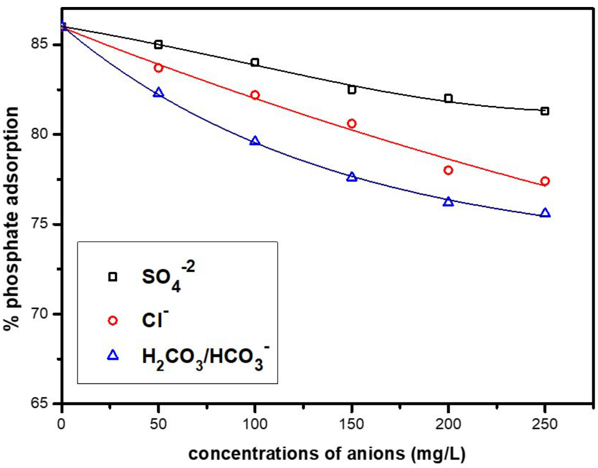

Fig. 5. Anion effect on phosphate adsorption by Zenith/Fe.

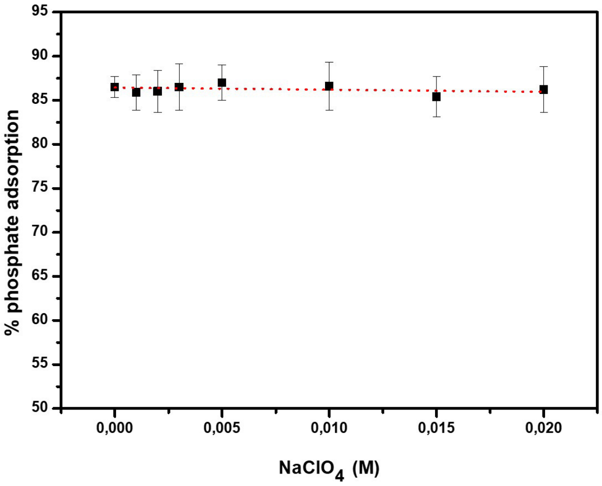

Fig. 6. Effect of ionic strength on phosphate adsorption by Zenith/Fe. Phosphate concentration 0.1 mg/L, adsorbent dose 0.02 g, $T = 25^{\circ}C$ and contact time 24 h.

3.7. E_h effect on phosphate adsorption by Zenith/Fe

In order to monitor the effect of solution potential on PAC of Zenith/Fe, adsorption was carried out at pH 7.0. Redox potential E_h was adjusted using sodium ascorbate and potassium ferricyanide. From Fig. 7, it is obvious that solution

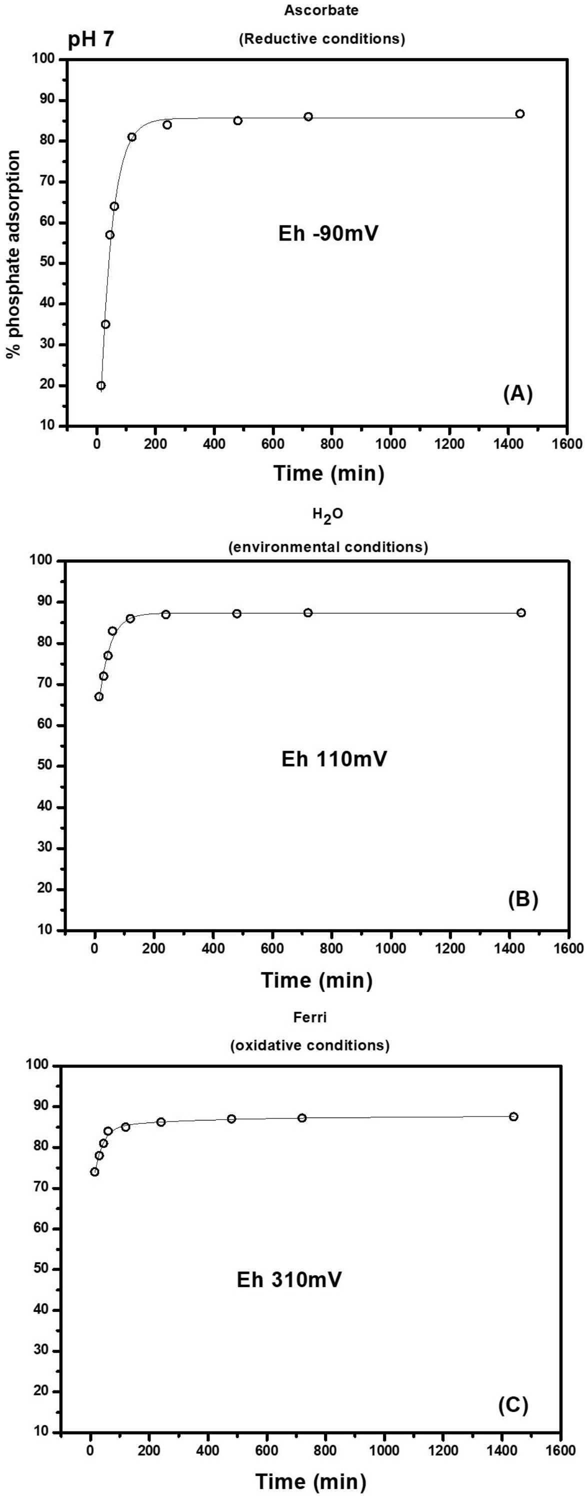

Fig. 7. Effect of redox potential on phosphate adsorption by Zenith/Fe.

potential does not change the maximum PAC obtained after 24 h. However, what is really changing is the adsorption rate in the first minutes. After the first 15 min under reductive conditions, the adsorption percentage rises to ~20%, while under oxidative conditions this percentage rises to ~75%.

3.8. Stability of Zenith/Fe

Modified bentonite Zenth/Fe was prepared for desorption experiments. Leaching of phosphate from the adsorbent was not observed. A series of experiments were performed to determine the influences of pH on the stability of the Zenith/Fe. It was found that there was no leakage of phosphate from the adsorbent in a pH range 2.0–7.0. However, a small amount of phosphate leached out from the adsorbent at pH > 10. The leaching of phosphate from the adsorbent increased from 3% to 8% with increasing pH from 10.0 to 12.0. Since in eutrophic natural waters, the optimum pH range for is 6.0–9.0, a small amount of phosphate leaching at higher pH ranges may not create problems in Zenith/Fe applications.

4. Conclusions

This work is part of a continuing attempt to develop innovative approaches to phosphate removal, supporting restoration of degraded natural water ecosystems. A novel low-cost composite material Zenith/Fe was evaluated in detail for phosphate uptake under various physicochemical conditions prevailing in eutrophic water bodies. Modified bentonite had the most prominent effect on phosphate ion removal at low-alkalinity water, followed by moderate and hard waters (high alkalinity). Removal of phosphate onto Zenith/Fe as a function of DOM shows that the adsorption capacity is not impaired severely by DOM, since the difference of presence and absence of DOM affected PAC only by 12%. Interestingly, PAC increased by 10% in the presence of dissolved cations, following the order: $Na^+ > K^+ > Mn^{2+} > Mg^{2+}$. On the other hand, PAC decreased by 10%, in the presence of environmentally occurring anions following the order: carbonate > chloride > sulfate.

PAC was independent of low ionic strength while solution potential did not change the maximum adsorption capacity of Zenith/Fe; however, it changes the adsorption rate in the first minutes. All these phenomena are attributed to the strong binding affinity of phosphate ($H_2PO_4^-$ and HPO_4^{2-}) to the Fe active sites that are embedded in the structure of modified material.

According to present results together with preceding publications [16,21], it is obvious that Zenith/Fe – a low-cost composite material prepared by environmentally friendly components – can function reliably under a wide range of physicochemical conditions pertaining in natural waters. Therefore, authors recommend and encourage the application of modified bentonite for removal of phosphate ions from eutrophic waters.

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