


Research Article

Competitive Removal of Perchlorate Ions by Quaternary Amine Modified Reed in the Presence of Nitrate and Phosphate

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We report a kinetic and equilibrium study in which we examined the removal of perchlorate anions from water by adsorption onto modified reed (MR), an adsorption material constituted by giant reed (GR) particles whose anion adsorption properties have been enhanced by quaternary amine (QA) crosslinking. In particular, we examined how MR adsorption of perchlorate interacts competitively with concomitant adsorption of agriculture-derived phosphate and nitrate contaminants. Equilibrium and pH experiments were first conducted in single-component systems, the results of which were best described by the Langmuir-Freundlich (L-F) isotherm. Subsequent analyses of competitive effects on adsorption showed that although MR had a higher adsorption capacity for perchlorate alone than for nitrate or phosphate alone, the addition of either phosphate or nitrate to a perchlorate solution had a diminishing effect on MR adsorption of perchlorate within a natural-water pH range, with phosphate having the stronger competitive effect. Perchlorate adsorption on MR varied inversely with competing ion concentrations, providing direct evidence of the perchlorate diminution effect being attributable to anion competition. Finally, we developed a multicomponent isotherm model that describes the binary adsorption of perchlorate in the presence of each of these competing anions. The results of this work provide perchlorate removal efficiency information that is directly applicable to the design of water treatment systems.

1. Introduction

Modified reed (MR) particles are chemically stable, highly reactive agricultural byproducts formed by the addition of quaternary amine (QA) functional groups to giant reed (GR) plant materials [1]. The added QA functional groups enhance the adsorptive properties of GR greatly, thus enabling MR to bind a wide range of anionic contaminants, including perchlorate [2], phosphate [3, 4], and nitrate [5] ions (molecular formulas: ClO_4^- , PO_4^{3-} , and NO_3^- , respectively). Perchlorate removal by MR adsorption has been shown to depend on pH and the initial perchlorate concentration [2]. In real-world water treatment systems, perchlorate removal efficiency is affected by additional factors, including the presence of competing anions [6].

Phosphate and nitrate molecules are common in perchlorate-polluted waters and their ions, PO_4^{3-} and

NO_3^- , have been identified as major competing anions for adsorption in water treatment processes [7, 8]. Phosphate and nitrate are major constituents of natural water [9] in which they serve as nutrients for photosynthetic macro- and microorganisms [10, 11]. However, fertilizer overuse can elevate concentrations of phosphorus and nitrogen in domestic wastewater and agricultural effluents, giving rise to high phosphate and nitrate levels [1]. Excess phosphate and nitrate accumulation causes eutrophication, especially in closed water bodies [12–14]. Such eutrophication depletes water of dissolved oxygen, which has negative impacts on ecosystems [15]. Furthermore, nitrate concentrations above 10 mg/L in drinking water have been linked to methemoglobinemia (a.k.a. blue-baby syndrome), a potentially fatal blood disorder in infants characterized by an insufficient erythrocyte oxygen-carrying capacity [16]. There has been relatively limited investigation of anion competition on

functionalized adsorbents such as MR. Namasivayam and Höll [5] reported that both perchlorate and phosphate (both 100 mg/L) have been reported to impede the removal of nitrate (10 mg/L) by crosslinked Chinese reed (0.2 g/L) at a pH of 5.8. They found that perchlorate and phosphate competition reduced nitrate adsorption capacity by 30% and 25%, respectively. However, they did not explain the physical nature of the competition or its relation to experimental conditions, such as initial concentration and pH. In a study examining perchlorate removal by protonated crosslinked chitosan at a pH of 4, Xie et al. [8] found that nitrate (10 mg/L) competed with perchlorate (10 mg/L) for adsorption and that functionalized chitosan adsorbent (10 g/L) had a higher selectivity for perchlorate than for nitrate. The authors did not attempt to explain the competition effect or the preferential adsorption of perchlorate.

Because the presence of phosphate and nitrate ions in contaminated water requiring perchlorate removal may affect the efficiency of perchlorate removal, the effects of these ions on perchlorate adsorption should be investigated systemically. The objectives of this work were threefold: (1) to determine the MR adsorption capacity and equilibrium isotherm for phosphate and nitrate in single-component systems, (2) to investigate competition effects of phosphate and nitrate on MR adsorption capacity and equilibrium isotherm values for perchlorate, and (3) to develop a multicomponent isotherm model that describes the binary adsorption of perchlorate in the presence of phosphate and in the presence of nitrate. Experiments were conducted over a range of pH values and anion concentrations. The results of this work provide perchlorate removal efficiency information that is applicable to the design of perchlorate treatment systems.

2. Materials and Methods

2.1. Reagents. All chemicals used were of ACS grade (Fisher Scientific). All experiments were performed with tap water left at room temperature for 24 h. Conductivity measurements indicated that the water had an average ionic strength of 0.01 M. Perchlorate, phosphate, and nitrate stock solutions were prepared from sodium perchlorate monohydrate ($\text{NaClO}_4 \cdot \text{H}_2\text{O}$), potassium dihydrogen phosphate monohydrate ($\text{KH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$), and sodium nitrate (NaNO_3), respectively. All stock solutions were prepared in deionized water (18.2 M Ω cm, Millipore, Cambridge, MA) at an ionic concentration of 10,000 mg/L.

Raw GR and QA reagent were provided by Dr. Baoyu Gao (School of Environmental Science and Engineering, Shandong University, China). GR (whole stems, no leaves) contains 21.1% lignin, 31.1% cellulose, 30.3% hemicellulose, and 12.1% extractives [2, 17].

2.2. MR Particles. Adsorbent MR particles were prepared as described previously for wheat adsorbent particles [18] with minor modifications. Briefly, raw GR was rinsed with water, dried in an oven at 60°C for 48 h, and then passed through a fine-mesh sieve (100–250 μm). The sieve-passed GR was reacted with epichlorohydrin, ethylenediamine, and triethylamine to form cellulose ether, and QA groups were added to

GR by crosslinking with epichlorohydrin and dimethylamine [2, 19, 20]. For crosslinking, 5 g aliquots of GR residue were dispersed in 60 mL volumes of N,N-dimethylformamide, each in a 500 mL three-necked round-bottom flask. We added 50 mL of epichlorohydrin to each flask. After the mixture was stirred for 1 h while being heated to 100°C, we added 20 mL of pyridine catalyst and stirred the mixture for an additional 1 h at 100°C. Finally, 75 mL of 33% (*w/w*) dimethylamine was added to the mixture which was stirred for 3 h at 100°C. The product, consisting of QA-enhanced MR particles that were 100–250 μm in size, was washed until the eluent reached neutrality and then dried at 60°C in a vacuum dryer.

Sorbent yield was determined gravimetrically as the quotient of raw GR dry weight divided by MR dry weight multiplied by 100. Because MR total exchange capacity is associated with its nitrogen content, we used an element analyzer (Elementar, Germany) to determine the nitrogen content of the MR obtained [20], which was found to be 7.78% in MR (vs. 0.9% in GR). Based on the chemical composition of the QA group [$-\text{CH}_2\text{CHOHCH}_2\text{NHCH}_2\text{CH}_2\text{NHCH}_2\text{OHCHCH}_2\text{N}(\text{CH}_2\text{CH}_2)_3^+$], the QA charge content was estimated to be $\sim 1.64 \text{ eq}(+)/\text{g}$ ($\approx 162 \text{ mg ClO}_4/\text{g}$ exchange capacity) [2].

2.3. Anion Analysis. Perchlorate and nitrate concentrations were determined by ion chromatography as described previously [2]. For NO_3^- analysis, the following parameters were applied: 10 mM KOH eluent, 50 mA current suppression, 1.0 mL/min flow rate, 50 μL sample injection volume, and 10 min running time. The detection limit was 0.1 mg/L. The HACH testing method 8114, which was adapted from a standard method for wastewater [21], was employed. Total phosphate concentration was measured with a DR/2800 spectrometer supplied with Test 'N Tube™ vials (both from HACH, Loveland, CO).

2.4. Adsorption Studies. Following QA enhancement, MR particles were used at a concentration of 2 g/L. For adsorption studies, conditions typical for perchlorate contamination were set: concentration range 0–2,000 mg/L, room temperature (25°C), and pH of 7.0 ± 0.5 . The pH level was varied from 3 to 12 with 0.1 M HCl and NaOH. The pH and zeta potential [22] experiments used in the procedures and instrumentation used in our pH and zeta potential experiments are described in detail below (Section 2.5). A contact time of 24 h was sufficient to reach a steady state.

A previously described perchlorate adsorption procedure [2] was followed. Briefly, to determine the MR adsorption capacity for ClO_4^- , equilibrium tests were performed in binary perchlorate-phosphate and perchlorate-nitrate systems. MR (0.1 g) was added to 50 mL tap water containing 0, 3, 10, 30, 50, 100, 150, 300, 500, 700, or 900 mg/L ClO_4^- , with each sample containing either 250 mg/L nitrate or 50 mg/L phosphate, and mixed for 24 hours at 25°C and a pH maintained at 7.0 ± 0.5 with 0.1 M HCl or NaOH drops as necessary. Perchlorate and nitrate concentrations were determined by ion chromatography. For NO_3^- analysis, the following parameters were used: 10 mM KOH eluent concentration, 50 mA current suppression, 1.0 mL/min flow

rate, 50 μL sample injection volume, and 10 min running time. With this setup, the detection limit was 0.1 mg/L. Total phosphate concentration was measured with a DR/2800 spectrometer (HACH, Loveland, CO) and HACH-supplied Test 'N Tube™ vials in accordance with HACH method 8114, which was derived from Method 4500-P [21].

Kinetic studies were carried out with 0.1 g GR samples (50 mL suspension containing 10 mg/L ClO_4^-) and 0.1 g MR samples (50 mL suspension containing 10, 20, and 30 mg/L ClO_4^-). After mixing at 25°C in 125 mL bottles with magnetic bar stirring, samples were drawn at 0, 1, 3, 5, 7, 10, 14, 15, 20, 25, and 30 min and again at 24 h, with last sampling time being selected to ensure a steady state reading. A neutral pH (7.0 ± 0.5) was maintained with drops of 0.1 M HCl and 0.1 M NaOH as needed. Samples were collected in 1.5 mL microcentrifuge tubes and centrifuged for 10 min at 10,000 rpm in a Micromax® centrifuge, and 1.0 mL samples of the supernatant were transferred to 2.0 mL glass vials for perchlorate ion chromatography. The amount of adsorbed perchlorate, qt (mg/g), at time t was determined by multiplying the difference between concentrations initially versus at time t (mg/L), multiplying that difference by the volume of the solution and then dividing the product by the dry mass (g) of the adsorbent.

Isotherm tests were performed to determine MR adsorption capacity for ClO_4^- . MR (0.1 g) in 50 mL tap water containing 3, 10, 30, 50, 100, 150, 300, 500, 700, or 900 mg/L ClO_4^- was mixed at 150 rpm in 125 mL bottles on a rotary mixer (Glas-Col, 2128, Terre Haute, IN) for 24 h to reach equilibrium at room temperature (25°C). The pH of each sample was maintained at 7.0 ± 0.5 with 0.1 M HCl and NaOH. Perchlorate was analyzed in supernatant samples with an IC25 ion chromatograph equipped with an analytical pump, an EG40 eluent generator, a CD25 conductivity detector, an AS50 autosampler, an LC20 column enclosure, an Ion-Pac® AS16 column (4 × 250 mm; 0.1 mg/L detection limit), a sample injection loop with a 1000 μL capacity, and an ASRS Ultra II current suppressor. Chromeleon® version 6.4 software was used for instrument control and data collection. The chromatograph and all of the aforementioned accessory components of the instrument, including the software, were obtained from Dionex Corporation (Sunnyvale, CA). An EluGen® potassium hydroxide cartridge provided the eluent (50 mM KOH) at a pump flow rate of 1.0 mL/min. Current suppression was set at 100 mA, the sample injection volume was 250 μL , and the running time was 18 min. With this setup, the detection limit was 0.1 mg/L.

2.5. pH and Zeta Potential Effects. To examine pH effects on perchlorate removal, 0.1 g samples of MR suspended in 50 mL tap water with or without 30 mg/L ClO_4^- were prepared in 125 mL bottles with pH levels ranging from 3.5 to 10.5 and placed on a rotary mixer at 150 rpm for 24 h at 25°C. Samples were analyzed in triplicate for aqueous perchlorate and equilibrium pH determination by drawing aliquots of equilibrated suspensions into disposable zeta cells via a Luer-Lok syringe and injecting them into a Nanoseries® Zetasizer (Malvern Instruments, Worcester-shire, UK) with parameters set as follows: 25°C, dielectric

constant = 78.5, viscosity = 0.88 cP, and applied voltage = 150 mV. The zeta potential was determined by measuring the electrophoretic mobility (U_E), which is related to the dielectric constant (ϵ), zeta potential (ζ), and viscosity (μ) by way of Hunter's function, $f(Ka)$, by the following equation [23]:

$$U_E = \frac{2\epsilon\zeta f(Ka)}{3\mu}. \quad (1)$$

The Smoluchowski approximation [24–26], which supposes that $f(Ka) \approx 1.5$, was employed. Malvern's Dispersion tech® version 5.0 software was used for instrument control and for data collection.

3. Results and Discussion

3.1. MR Adsorption of Nitrate and Phosphate: Isotherm and pH Effects. To obtain a better understanding of the competitive effect of nitrate and phosphate on perchlorate adsorption by MR, equilibrium and pH experiments were first conducted in single-component systems. The experimental adsorption data were fitted with the Langmuir-Freundlich (L-F) isotherm (Equation (2)), which takes into account the nonideal, heterogeneous nature of an adsorbent surface. In our previous work [2], the L-F isotherm was shown to better fit adsorption data obtained by the present methods than either the Langmuir isotherm or the Freundlich isotherm owing to it having the lowest residual sum of the squared estimate of errors (SSE) value (16.34). The L-F isotherm optimized adsorption parameters of perchlorate, nitrate, and phosphate used are listed in Table 1. Notably, optimal perchlorate adsorption was observed within the pH range of 3.5 to 7.0.

The effects of isotherm and pH on MR adsorption of nitrate and phosphate are shown in Figure 1. Both phosphate and nitrate exhibited good adsorption characteristics on MR (Figure 1(a)). At the pH studied (7.0 ± 0.5), which is typical for natural water, both ions have a size and charge similar to that of the perchlorate ion (Table 2). Anions are adsorbed through electrostatic interaction with MR owing to it being a positively charged exchanger. Pan et al. [27] and Gao et al. [28] concluded that QA functional groups are mainly responsible for phosphate adsorption on QA-modified wheat residue. Similar findings for phosphate and nitrate adsorption on QA-modified agricultural adsorbents have been reported [1, 3–5].

Similar to the perchlorate adsorption data, the sorbed concentrations of phosphate and nitrate at equilibrium q_e (mg/g) increased with increases in the initial concentrations of phosphate and nitrate (Figure 1(a)). The isotherm curves of all three anions had the same shape, suggesting similar adsorption behavior. Perchlorate showed the highest adsorption on MR ($q_{\text{max}} = 206.9$ mg/g). For phosphate and nitrate, we obtained q_{max} values of 185.8 and 125.1 mg/g, respectively (Table 1). Compared to phosphate and nitrate, perchlorate has a lower hydration energy and larger ion size (Table 2; see values in [29]), factors which affect its separation and adsorption behavior [30]. Additionally, perchlorate has greater free energy of adsorption

TABLE 1: L-F model parameters for anion adsorption.

Parameter	Perchlorate	Anion Phosphate	Nitrate
K_{LF} (L/mg)	0.008	0.006	0.004
q_{max} (mg/g)	206.9	185.83	125.14
a	0.87	0.81	0.86
R^2	0.99	0.99	0.99
SSE	0.68	0.95	0.63

($\Delta \circ G_{ads} = -RT \ln K_{LF}$), at -16.59 kJ/mol, than either phosphate (-15.76 kJ/mol) or nitrate (-13.69 kJ/mole). Adsorption on MR was favorable for all three ions, as indicated by the negative $\Delta \circ G_{ads}$ values [31].

In the equilibrium experiments, adsorption on MR was higher for phosphate than for nitrate. At the experimental pH (7.0 ± 0.5), both monovalent ($H_2PO_4^-$) and divalent (HPO_4^{2-}) phosphate species are present (Figure 1(b)). The stronger charge on the divalent phosphate ions creates a relatively strong electrostatic force between these anions and the positively charged functional groups on MR, resulting in higher adsorption of phosphate than of nitrate. Axinte et al. [14] observed higher phosphate adsorption than nitrate adsorption on ammonium-functionalized MCM-48 mesoporous silica. They attributed this variation to the two ions having different ionic structures; the nitrate anion's negativity is delocalized among three oxygen atoms, each with a charge of $-1/3$, whereas the phosphate anion's negativity is discretely localized, with each oxygen atom having a charge of -1 and a greater ability to stabilize the charge by adsorbing on a positive surface [14].

The effects of varying pH from 2.5 to 12 on the removal of perchlorate (30 mg/L), phosphate (50 mg/L), and nitrate (250 mg/L) on MR (0.1 g) at room temperature (25°C) are illustrated in Figure 1(c). Within the acidic equilibrium pH range up to a pH of ~ 6.5 , removal percentages of nitrate and perchlorate tend to remain stable (see essentially flat regions of curves in Figure 1(c)). The MR surface is positively charged at low pH levels, which increases the electrostatic forces between QA functional groups and anions [8]. At neutral and basic equilibrium pHs, that is, levels above ~ 6.5 , removal percentages of nitrate and perchlorate show clear decreasing trends with increasing pH. These lesser removal rates at higher pH levels are likely due to competition with hydroxide ions for adsorption sites. In addition, a decreased surface charge at a high pH would be expected to weaken the electrostatic attraction between anions and the MR surface [2].

In contrast to the nitrate and perchlorate adsorption data, we observe a lopsided inverted-U curve for phosphate adsorption in relation to equilibrium pH (Figure 1(c)). That is, the phosphate removal percentage increases steadily within the pH equilibrium range of 2.5–7.0, with the phosphate removal percentage peaking at a neutral equilibrium pH of 7.0, possibly due to the formation of divalent HPO_4^{2-} (Figure 1(b)). The relatively low phosphate removal percentages obtained at equilibrium pH values below 5.5,

compared to rates seen in the neutral-to-acidic equilibrium pH range, could be consequent to the formation of non-charged H_3PO_4 species. Similar findings have been reported previously [6, 14, 26]. The MR surface is positively charged at low pH, increasing the electrostatic forces between QA functional groups and anions [8].

As shown in Figure 1(c), the maximum removal obtained for phosphate, 88%, occurred in the pH range of 6.5 to 7.5. Removal decreased significantly at lower pH levels (e.g., a 70% decrease in removal at a pH of 2.5). A speciation diagram for 50 mg/L total phosphate is shown in Figure 1(b) ($pK_1 = 2.2$, $pK_2 = 7.2$, and $pK_3 = 12.4$). A decrease in pH favors the formation of a more soluble, less negatively charged phosphate species, weakening the electrostatic attractions between phosphate anions and the MR surface. Similar to previous reports [14, 26, 32], in the present study, the magnitude of the decrease in phosphate removal was smaller at high pH than low pH values (e.g., a 15% decrease in removal at pH 11.5 compared to a 70% decrease at pH 2.5). This effect could be attributed to phosphate existing in more than one charge state, depending on the solution pH, and forming species that are more soluble at a low pH [33, 34]. It can be concluded that optimum phosphate removal by MR occurs within the normal pH range of groundwater and that removal is less favored at high pH values than at low pH values. Meanwhile, perchlorate removal followed the opposite trend, being less favored at low pH values. At high pH values, adsorption of the divalent ion $H_2PO_4^-$ predominates (Figure 1(b)), presumably owing to it forming stronger electrostatic interactions with the MR surface than monovalent perchlorate anions.

For nitrate (50 mg/L), a maximum removal rate of 43% was observed at a pH of 5.1 (Figure 1(c)). Removal decreased slightly at lower pH levels. For example, at a pH of 2.5, removal decreased by only 7.2% from its maximum value. Increasing the pH also reduced the removal rate, with a 36.7% rate being observed at a pH of 11.8. Nitrate and perchlorate adsorption followed similar patterns as a function of pH (Figure 1(c)). Nitrate and perchlorate ions have similar ionic charges and radii (Table 2), which could explain their similar adsorption behaviors. These two anions are often found together in nature [35].

3.2. Effect of Phosphate and Nitrate Concentration on Perchlorate Adsorption. The addition of either phosphate or nitrate (0–2000 mg/L) had a diminishing effect on perchlorate adsorption (30 mg/L) (Figures 2(a) and 2(b)), determined under the conditions described in previous work [2]. Perchlorate adsorption on MR varied inversely with phosphate and nitrate concentrations. The reduced perchlorate adsorption observed in the presence of phosphate or nitrate can thus be attributed to increasing anion competition for MR adsorption on MR as the added anion concentrations increased.

Adsorption of perchlorate (30 mg/L) was reduced slightly, by 2.5%, in the presence of 50 mg/L NO_3^- , compared to in the absence of nitrate loading (Figure 2(a)). Even with relatively high nitrate loading (500 mg/L), perchlorate adsorption was decreased by only 23.2% relative to the

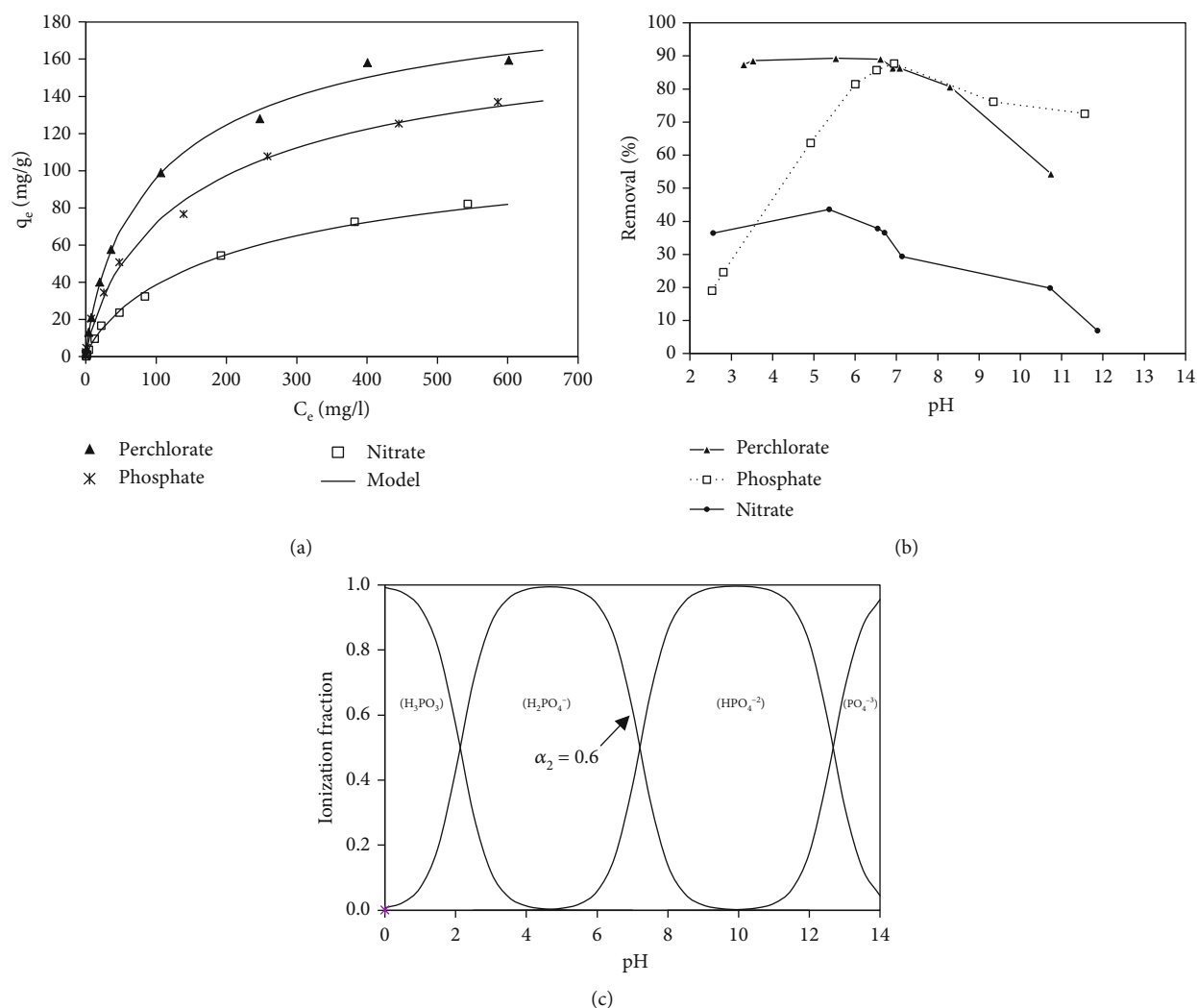


FIGURE 1: Isotherm and pH effects on MR adsorption of nitrate and phosphate. (a) Adsorption of anions by MR (2.0 g/L) and the fitted L-F isotherm model at $pH\ 7.0 \pm 0.5$ with a contact time of 24 h. (b) Effect of pH on anion removal by MR. Initial $[ClO_4^-] = 30\ mg/L$; initial $[NO_3^-] = 250\ mg/L$; initial $[PO_4^{3-}] = 50\ mg/L$; temperature = $25^\circ C$. (c) Phosphate speciation diagram as a function of pH in solution at an ionic strength of 0.01 M. At pH of 7.0 ± 0.5 , phosphate is present as $H_2PO_4^-$ and HPO_4^{2-} at a ratio of 1.0:0.6, respectively.

TABLE 2: Hydrated radius of common anions from Moyer and Bonnesen [29].

Anion	Radius (nm)	ΔG_h° (kJ/mol)
ClO_4^-	0.240	-205
PO_4^{3-}	0.238	-2765
NO_3^-	0.196	-300
HPO_4^{2-}	0.236	—
$H_2PO_4^-$	0.230	-465
OH^-	0.133	-430
Cl^-	0.172	-340
I^-	0.210	-275

non-nitrate-loaded condition. Only in the presence of $1000\ mg/L\ NO_3^-$ did perchlorate adsorption show a drop (38.3%). Interestingly, perchlorate adsorption was decreased by only 51% in the presence of $2000\ mg/L\ NO_3^-$, demon-

strating substantive perchlorate adsorption even at a large perchlorate-to-nitrate ratio. These results show that although nitrate would be expected to compete with perchlorate for similar MR adsorption sites, given that the two ions have similar charge and size properties, MR exhibits selectivity for perchlorate over nitrate, consistent with the findings of Xie et al. [8].

The presence of phosphate also decreased perchlorate adsorption, in a concentration-dependent manner, indicating that perchlorate and phosphate anions compete for similar adsorption sites. Perchlorate adsorption was decreased by 4.3%, 33.6%, and 47.8% with 50 mg/L, 500 mg/L, and 1000 mg/L PO_4^{3-} , respectively. Indeed, phosphate had a stronger effect on perchlorate adsorption than nitrate (Figure 2(b)), likely owing to greater electrostatic forces of phosphate consequent to its greater charge at the pH studied (7.0 ± 0.5). The stronger competitive effect of phosphate is also evidenced on an equimolar basis (Figure 2(c)). For example, perchlorate adsorption decreased by 10.8% in the

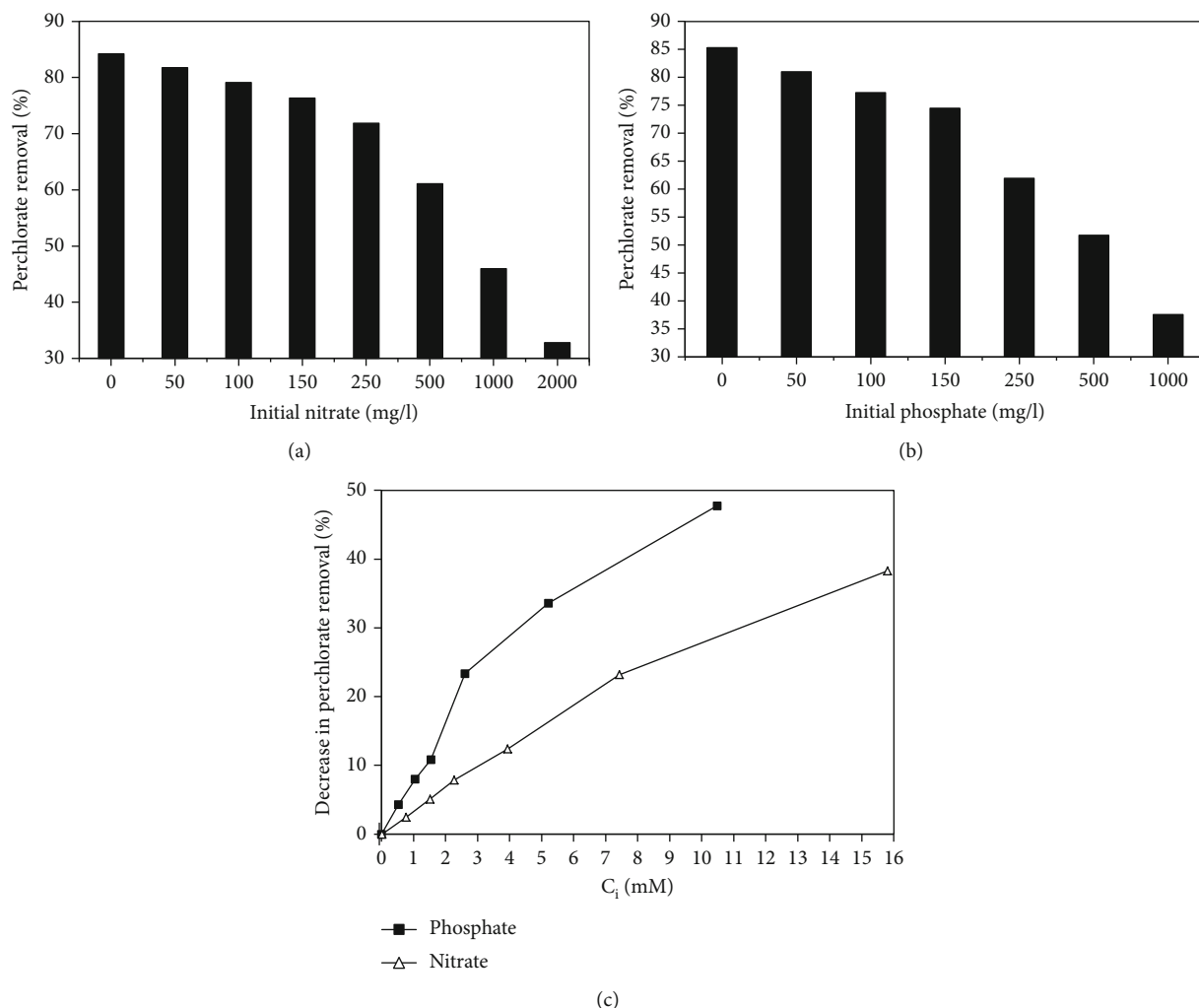


FIGURE 2: Anion competition effects on perchlorate removal by MR. (a) Nitrate concentration effect; initial $[\text{ClO}_4^-] = 30 \text{ mg/L}$, $\text{pH } 7.0 \pm 0.5$. (b) Phosphate concentration effect; initial $[\text{ClO}_4^-] = 30 \text{ mg/L}$, $\text{pH } 7.0 \pm 0.5$. (c) Effects of nitrate and phosphate concentrations (equimolar) on the decrease of perchlorate removal efficiency; initial $[\text{ClO}_4^-] = 30 \text{ mg/L}$ (0.3 mM), $\text{pH } 7.0 \pm 0.5$. Phosphate exhibited a greater competitive effect on perchlorate adsorption than nitrate.

presence of 1.5 mM PO_4^{3-} but decreased by only 5.11% in the presence of 1.5 mM NO_3^- . Within the range studied, the competitive effect of phosphate on perchlorate adsorption by MR was 1.5 ± 0.2 times greater than the effect of nitrate at the same molar concentration.

3.3. Perchlorate Isotherm Studies in the Presence of Competing Anions. Equilibrium tests were performed to determine the MR adsorption capacity for perchlorate in the presence of phosphate and nitrate in binary perchlorate-phosphate and perchlorate-nitrate systems (Figure 3). MR (0.1 g) was added to 50 mL of tap water containing $0, 3, 10, 30, 50, 100, 150, 300, 500, 700,$ or 900 mg/L ClO_4^- , with all samples containing either 250 mg/L NO_3^- or $50 \text{ mg/L PO}_4^{3-}$. As shown in Figure 3, the presence of either additional anion decreased perchlorate adsorption for the entire concentration range studied ($0\text{--}900 \text{ mg/L ClO}_4^-$), and the competitive effect was greater at higher initial perchlorate concentrations. That is, the perchlorate adsorption (q_e) values obtained for

the perchlorate-nitrate and perchlorate-phosphate systems showed quite small divergences from values obtained in the perchlorate-only system at low starting ion concentration (C_e) values (i.e., $\leq 50 \text{ mg/L}$). At C_e values $\geq 100 \text{ mg/L}$, the q_e values obtained in dual-ion system experiments were notably less than those seen with perchlorate alone. The perchlorate-nitrate system showed the widest gaps in q_e values versus perchlorate alone in the $100\text{--}500 \text{ mg/L } C_e$ range, while the perchlorate-phosphate system showed a progressively widening gap versus perchlorate alone at increasing C_e values from 100 ng/L onward (Figure 3). Similar findings have been reported in the literature [5].

Although equilibrium studies do not enable the identification of the forces affecting adsorption, they can reveal similarities of adsorption behaviors across ion species by demonstrating the relative affinities of each species to the adsorbent, a variable described by q_e . The competing phosphate and nitrate ions are both anionic, and they have similar ionic radii (Table 2). Therefore, theoretically, they can

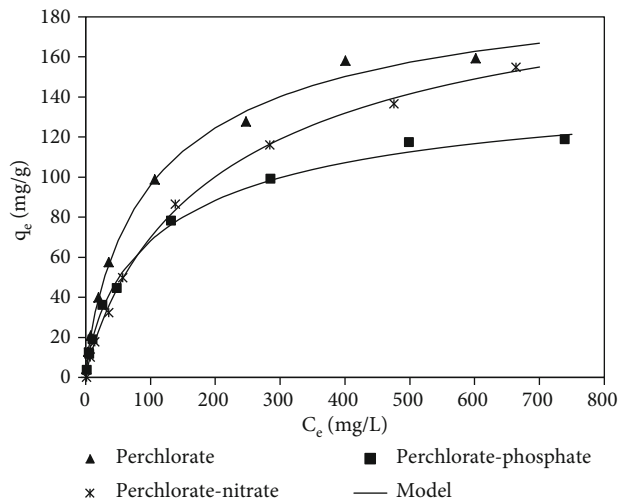


FIGURE 3: Effect of anions on perchlorate adsorption by MR and the fitted L-F model. Initial $[\text{NO}_3^-] = 250 \text{ mg/L}$; initial $[\text{PO}_4^{3-}] = 50 \text{ mg/L}$.

undergo ion-exchange onto MR based on electrostatic attraction [5, 26], thus limiting perchlorate adsorption through direct competition for adsorption sites.

Measured residual anion concentration data verify that nitrate and phosphate were indeed adsorbed by MR. Phosphate had a stronger competitive effect than nitrate on perchlorate adsorption (Figure 3). The fact that phosphate has a greater negative charge than perchlorate at the pH studied (7.0 ± 0.5) supports the hypothesis that electrostatic attraction is the main mechanism responsible for adsorption [30]. Upon demonstrating that nitrate competition with perchlorate for adsorption increases when an anion of a higher valence state is used, Xie et al. [8] likewise suggested that the adsorption of nitrate and phosphate on amine-functionalized chitosan occurs through electrostatic forces.

The L-F model [2] used to fit the equilibrium results of perchlorate adsorption on MR in the presence of competing anions assumes that each adsorption site is available for only one ion and that the number of available adsorption sites is constant. Because the concentration of the competing anion is constant (250 mg/L NO_3^- or $50 \text{ mg/L PO}_4^{3-}$), we assume that the number of adsorption sites available to perchlorate is reduced by a magnitude that remains constant throughout the entire perchlorate adsorption period as in a single-ion system containing only perchlorate.

The L-F equation (Equation (8)) was fitted to the experimental data using nonlinear regression (plot in Figure 3; isotherm parameters listed in Table 3). The perchlorate adsorption capacity (q_{max}) decreased from 206.90 mg/g in the perchlorate-only system to 185.86 mg/g in the perchlorate-nitrate system and to 156.89 mg/g in the perchlorate-phosphate system (Table 3). On the other hand, the residual SSE value increased from 0.68 , in the perchlorate-only system, to 11.14 in the perchlorate-nitrate system and to 23.65 in the perchlorate-phosphate system. The residual SEE indicates a model's deviation from experimental values when more than one type of anion is present. Although the per-

TABLE 3: L-F model parameters for anion adsorption.

Parameter	Alone	Perchlorate +phosphate	+nitrate
K_{LF} (L/mg)	0.008	0.006	0.007
q_{max} (mg/g)	206.9	156.89	185.86
a	0.87	0.76	0.96
R^2	0.99	0.99	0.99
SSE	0.68	23.65	11.14

chlorate adsorption capacity for all systems in this study was described accurately with the L-F model, the model becomes less useful for modeling as the number of interacting constituents increases. For example, the L-F model is unlikely to be useful in analyses of water in natural reservoirs due to the multitude of constituents present.

Favorability of adsorption is represented by the constant separation factor R_L [2]. For all systems, $R_L < 1$ was obtained, indicating favorable perchlorate adsorption [36]. When nitrate or phosphate was added to the perchlorate system, we obtained increased R_L values, indicating that perchlorate adsorption was less favored.

3.4. Modeling the Competitive Effect. The Langmuir equation describes the dependence of the surface coverage of the adsorbed species on its concentration at equilibrium and at a fixed temperature and pressure [37]. To model competitive effects, we modify the Langmuir isotherm equation and test its accuracy in predicting the binary sorption of perchlorate-nitrate and perchlorate-phosphate systems. For the modification, we assume that adsorption is competitive by including the adsorption of the additional competing anion at equilibrium.

The variables θ and q are adopted to represent surface coverage (of the adsorbing material) and rate of perchlorate adsorption, respectively. We define the surface coverage as being equal to the quotient q_e/q_{max} , where q_e is the sorbed concentration (mg/g) of perchlorate at equilibrium and q_{max} is the maximum adsorption capacity (mg/g). The maximum surface coverage at saturation is given by $\theta_{\text{max}} = 1$. The rate of adsorption r_{ads} of ion species on the surface of the adsorbent is proportional to the fraction of vacant adsorption sites, $(1 - \theta)$ and to the concentration of the ion species of interest in the liquid phase, C_e . The rate of adsorption can thus be written as

$$r_{\text{ads}} = k_a C_e (1 - \theta). \quad (2)$$

The rate of desorption r_{des} is proportional to the fraction of occupied adsorption sites (surface coverage):

$$r_{\text{des}} = k_d \theta, \quad (3)$$

where k_a and k_d are the equilibrium constants in the forward and reverse directions, respectively. At equilibrium, mass

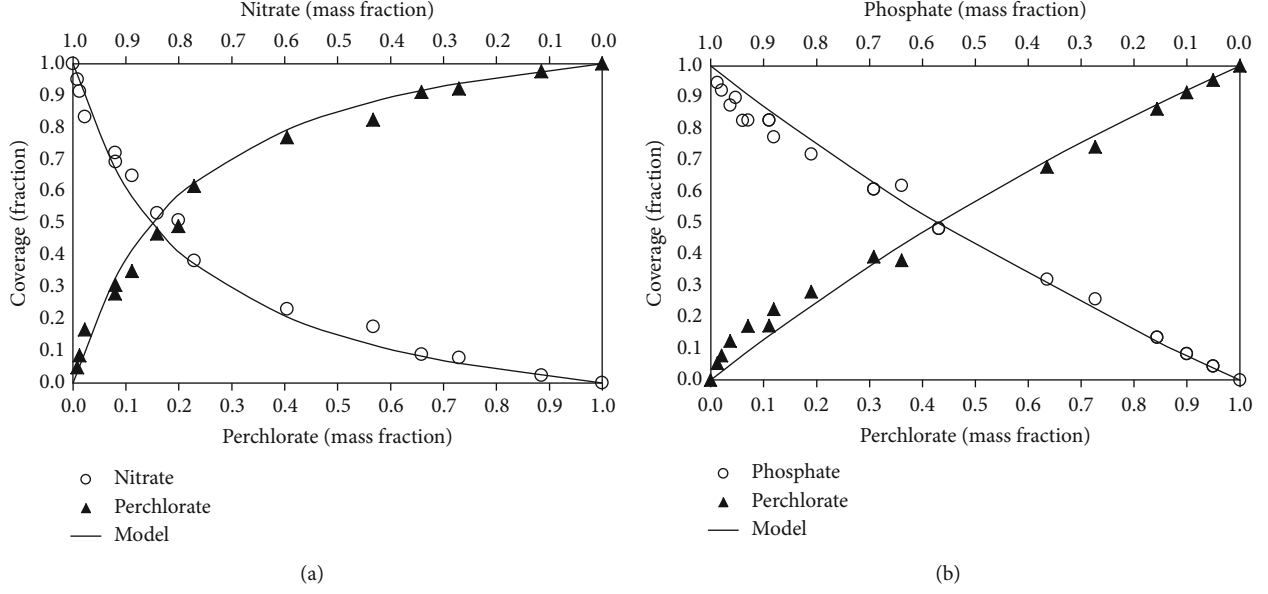


FIGURE 4: Adsorption fractions and modified Langmuir models in a binary anion system. (a) Ratio of sorbed perchlorate to sorbed nitrate. (b) Ratio of sorbed perchlorate to sorbed phosphate. For both graphs, MR = 2.0 g/L and pH 7.0 ± 0.5 .

balance at the interface yields

$$r_{\text{ads}} = r_{\text{des}}, \quad (4)$$

$$k_a C_e (1 - \theta) = k_d \theta, \quad (5)$$

$$\theta = \frac{k_a C_e}{k_d + k_a C_e}. \quad (6)$$

The Langmuir constant K_L is defined as

$$K_L = \frac{k_a}{k_d}. \quad (7)$$

Substituting in the constant K_L , the result is the Langmuir equation [37]:

$$\theta = \frac{K_L C_e}{1 + K_L C_e}, \quad (8)$$

$$K_L = \frac{k_a}{k_d}.$$

For the binary anion system, we extend the Langmuir equation to include two species (A and B). Because these two species are assumed to occupy the same adsorption sites, the fraction of vacant adsorption sites is equal to $(1 - \theta_A - \theta_B)$. Thus, for species A,

$$r'_{\text{ads}} = k'_a C_A (1 - \theta_A - \theta_B), \quad (9)$$

$$r'_{\text{des}} = k'_d \theta_A. \quad (10)$$

TABLE 4: Modified Langmuir isotherm parameters for adsorption in the presence of competing anions.

Parameter	Perchlorate	
	+phosphate	+nitrate
K_A (L/mg)	0.01	0.12
q_A (mg/g)	98.76	20.22
K_B	133.04	0.09
R^2	0.99	117.08
SSE	18.46	11.14

Anion A is perchlorate. Anion B is phosphate or nitrate, respectively.

At equilibrium, mass balance at the interface yields

$$r'_{\text{ads}} = r'_{\text{des}}, \quad (11)$$

$$k'_d \theta_A = k'_a C_A (1 - \theta_A - \theta_B), \quad (12)$$

$$K_A = \frac{k'_a}{k'_d}, \quad (13)$$

$$\theta_A = K_A C_A (1 - \theta_A - \theta_B). \quad (14)$$

Similarly, for species B,

$$\theta_B = K_B C_B (1 - \theta_A - \theta_B), \quad (15)$$

$$\frac{\theta_B}{K_B C_B} = (1 - \theta_A - \theta_B). \quad (16)$$

Substituting the mass-balance equations into Equation (4), we obtain

$$\theta_A = \frac{K_A C_A}{K_B C_B} \theta_B. \quad (17)$$

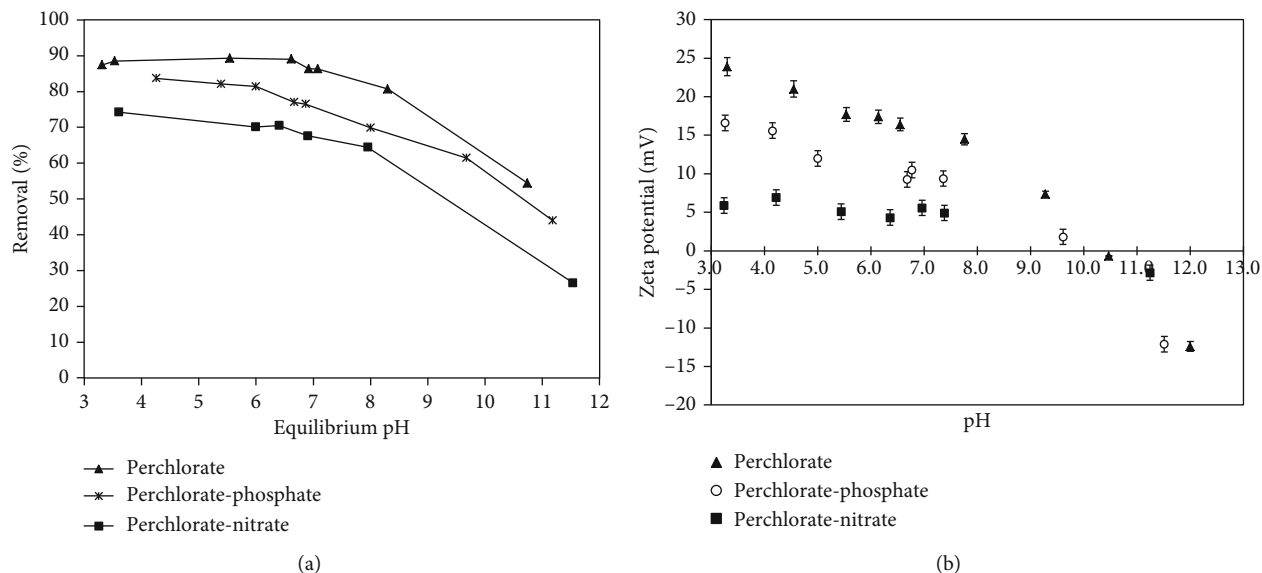


FIGURE 5: Effects of competing anions on MR properties. (a) Effect of competing anions on perchlorate removal at different pH values. (b) Effect of competing anions on the zeta potential of MR equilibrated with ClO_4^- for 24 hours (adsorbent dose = 2.0 g/L). For both graphs, initial conditions: $[\text{ClO}_4^-] = 30 \text{ mg/L}$, $[\text{NO}_3^-] = 250 \text{ mg/L}$, and $[\text{PO}_4^{3-}] = 50 \text{ mg/L}$.

Then, we substitute Equation (17) into Equation (16):

$$\theta_B = K_B C_B \left(1 - \frac{K_A C_A}{K_B C_B} \theta_B - \theta_B \right), \quad (18)$$

$$\theta_B = K_B C_B - K_A C_A \theta_B - K_B C_B \theta_B, \quad (19)$$

$$\theta_B + K_A C_A \theta_B + K_B C_B \theta_B = K_B C_B, \quad (20)$$

$$\theta_B (1 + K_A C_A + K_B C_B) = K_B C_B. \quad (21)$$

Finally, we obtain the following surface coverage values for both anions A and B:

$$\theta_B = \frac{K_B C_B}{(1 + K_A C_A + K_B C_B)}, \quad (22)$$

$$\theta_A = \frac{K_A C_A}{(1 + K_A C_A + K_B C_B)}. \quad (23)$$

Equations (22) and (23) were used to calculate fractional surface coverage. The parameter assessment for each binary system was obtained by nonlinear regression calculation (performed with the Solver tool in Microsoft Excel® 2003). The competition models for the perchlorate-nitrate and perchlorate-phosphate systems are shown in Figures 4(a) and 4(b), respectively. In both systems, ion coverage fractions increased in the presence of greater mass fractions of each respective ion as would be expected given that the greater presence of an ion produces more opportunities for it to interact with the adsorbent surface. The shapes of the curves differed between the two systems. In the case of the perchlorate-nitrate system, equivalent coverage between the two ions (coverage fraction of ~0.5) was seen at 0.1–0.2 mass fractions of perchlorate with 0.8–0.9 mass fractions of nitrate. Thus, nitrate competed effectively with perchlorate for adsorption sites when it

was the overwhelmingly predominant ion (>0.8 nitrate mass fraction) but became dramatically less competitive when it was not the overwhelming majority ion (i.e., with the progressive relative addition of perchlorate). This pattern is evidenced by steep coverage slopes at low perchlorate/high nitrate mass fraction levels that proceed to flatten gradually and then asymptote at high perchlorate mass fraction levels. Meanwhile, the coverage fraction curves obtained for the perchlorate-phosphate system were near linear with slopes near |1|, indicating that the mass fractions of each ion related directly to the coverage fractions observed for that ion. The coefficients of determination were all high ($R^2 > 0.99$) with low residual SSE values (Table 4), indicating that the model and the experimental data are in good agreement. This model developed will be beneficial to water treatment design.

3.5. pH and Zeta Potential Effects. The effect of pH on perchlorate removal was studied by comparing the perchlorate, perchlorate-nitrate, and perchlorate-phosphate systems at concentrations of $\text{ClO}_4^- = 30 \text{ mg/L}$, $\text{NO}_3^- = 250 \text{ mg/L}$, and $\text{PO}_4^{3-} = 50 \text{ mg/L}$. As shown in Figure 5(a), all three systems followed the same adsorption behavior as a function of pH: removal efficiency decreased as the equilibrium pH was increased. For all systems studied, maximum removal occurred in the pH range of 5.5 to 7.0, and minimum removal occurred in the pH range of 10.7 to 11.0. Decreased removal at high pH values can be attributed to competition from hydroxide ions, and decreased surface charge weakens the electrostatic attraction between the perchlorate anions and the MR surface. On average, the maximum removal for the perchlorate system decreased by 4.85% with the addition of phosphate and by 14.26% with the addition of nitrate (Figure 5(a)). Thus, nitrate had a stronger competitive effect on perchlorate removal than phosphate at the concentrations studied. The presence of either phosphate or nitrate

reduced perchlorate removal without altering perchlorate adsorption behavior, as exemplified by the similar curve shapes for the three systems.

The effects of competing anions on MR surface charge were studied by measuring the zeta potential [21] as a function of pH in each of the same three systems. As shown in Figure 5(b), the point of zero charge did not significantly shift when nitrate or phosphate anions were added to the perchlorate system, suggesting that anion interactions with MR are largely electrostatic in nature. The addition of either anion species did result in a decreased zeta potential, as expected given their negative charge, and perchlorate removal percentage correlated directly with the zeta potential value (compare Figures 5(a) and 5(b)). Nitrate had a stronger effect on surface charge than phosphate owing to our having used a higher nitrate concentration (250 mg/L).

4. Conclusions

The present findings show that although MR had a higher adsorption capacity for perchlorate alone than for nitrate or phosphate alone, the addition of either phosphate or nitrate to a perchlorate solution had a diminishing effect on MR adsorption of perchlorate within a natural-water pH range, with phosphate having the stronger competitive effect. Perchlorate adsorption on MR varied inversely with phosphate and nitrate concentrations providing direct evidence of this diminution effect being attributable to anion competition. The L-F isotherm described our perchlorate equilibrium results in two-ion systems accurately though we would not expect its utility to generalize to real water systems with numerous constituents.

Data Availability

Data is available upon request.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

Acknowledgments

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