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Abstract

Three commercial resins bearing sulfonic, amino phosphonic, or phosphonic/sulfonic reactive groups have been tested for the removal of iron and cadmium from phosphoric acid solutions. The sorption properties are compared for different experimental conditions such as sorbent dosage (0.5–2.5 g L^{-1}), phosphoric acid concentration (from bi-component solutions, 0.25–2 M), and metal concentrations (i.e., in the range 0.27–2.7 mmol Cd L^{-1} and 0.54 mmol Fe L^{-1}) with a special attention paid to the impact of the type of reactive groups held on the resins. The sulfonic-based resin (MTC1600H) is more selective for Cd (against Fe), especially at high phosphoric acid concentration and low sorbent dosage, while MTS9500 (aminophosphonic resin) is more selective for Fe removal (regardless of acid concentration and sorbent dosage). Equilibrium is reached within 2–4 h. The resins can be ranked in terms of cumulative sorption capacities according the series: MTC1600H > MTS9570 > MTS 9500. Sulfuric acid (0.5–1 M) can be efficiently used for the desorption of both iron and cadmium for MTC1600H, while for MTS9570 (phosphonic/sulfonic resin) sulfuric acid correctly desorbs Cd (above 96% at 1 M concentration), contrary to Fe (less than 30%). The aminophosphonic resin shows much poorer efficiency in terms of desorption. The sulfonic resin (i.e., MTC1600H) shows much higher sorption capacity, better selectivity, comparable uptake kinetics (about 2 h equilibrium time), and better metal desorption ability (higher than 98% with 1 M acid concentration, regardless of the type of acid). This conclusion is confirmed by the comparison of removal properties in the treatment of different types of industrial phosphoric acid solutions (crude, and pre-treated H$_3$PO$_4$ solutions). The three resins are inefficient for the treatment of crude phosphoric acid, and activated charcoal pre-treatment (MTC1600H reduced cadmium content by 77%). However, MTC1600H allows removing over 93% of Fe and Cd for H$_3$PO$_4$ pre-treated by TBP solvent extraction, while the others show much lower efficiencies (< 53%).

Keywords Phosphoric acid purification · Metal removal · Sorption isotherms · Uptake kinetics · Effect of reactive groups

Introduction

Phosphoric acid is widely used in industry for applications such as fertilizer, metal surface cleaner (rust removal), and catalyst, but also as ingredient for food, pharmacy, cosmetics, and electronics. The manufacturing of phosphoric acid may be operated through two main processes: (a) wet way or (b) thermal way. The thermal processing usually limits the presence of metal impurities, but the technique is highly expensive, nevertheless wet processing is the most frequently used at industrial scale. Its main drawback consists of the presence of relatively high concentrations of hazardous metals (such as uranium, cadmium, mercury, arsenic, and other heavy metals) or other organic (humic acid, for example) and inorganic substances (such as sulfate) (El Zrelli et al. 2018). The requirements and regulations for phosphoric acid grade are of increasing complexity when target application concerns fertilizers < food < pharmacy < electronics. The quote for the different grades of H$_3$PO$_4$ is logically following the same scale of purity requirements.

For preparation of technical phosphoric acid, the wet process usually consists of the following (EFMA 2000): (a)

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phosphate rock grinding, (b) sulfuric acid leaching, (c) filtration (to remove calcium sulfate di-hydrate, or phosphogypsum), and (d) concentrating step (produced diluted liquor is concentrated by evaporation to reach 50% *w/w* P_2O_5 merchant grade acid, MGA). Phosphogypsum residue that may contain substantial amounts of valuable metals, including rare earths, constitutes one of the most important by-products of the wet process.

The origin of phosphate rock is thus of critical importance since some areas are reputed for the presence of high concentrations of these hazardous metals that decrease substantially the commercial value of produced phosphoric acid. In addition, the high concentration of these impurities affect negatively the filtration of phosphoric acid, and the solubility of the produced fertilizers (in the case of iron) (Abdel-Ghafar et al. 2019) and have a harmful impact on the environment as well as the human health (in the case of cadmium) (Roberts 2014). Several processes have been designed for the purification of phosphoric acid including precipitation (Abdel-Ghafar et al. 2019; Kouzbour et al. 2019), solvent extraction (Ahmed et al. 2007; Ahmed et al. 2019; Chen et al. 2018; Li et al. 2017a; Li et al. 2017b; Sanghani 2014; Ye and Li 2013), and extractant-impregnated resins (Reyes et al. 2001). However, in the case of solutions containing low levels of metal ions (below a few hundred mg L^{-1}), sorption processes may be interesting and competitive. Activated carbon and clays are frequently used for the purification of phosphoric acid from organic impurities (Nasr et al. 2005; Trabelsi and Tlili 2017) or metal ions (El-Bayaa et al. 2011; Kussainova et al. 2019; Kussainova et al. 2016; Tjioe et al. 1988), including metal-loaded clays (Hamza et al. 2016). However, sorbents can be also operated for metal removal from crude phosphoric acid (Alexandratos and Zhu 2016; El-Bayaa et al. 2011; Heres et al. 2018; Kouzbour et al. 2019; Zhu and Alexandratos 2015).

Metal recovery from phosphate rock processing is thus considered a way to limit environmental and health issues associated with application of metal-loaded phosphoric acid, and to improve the cost of valorization of processed phosphoric acid. However, the treatment of both phosphoric acid and phosphogypsum can also be regarded as an opportunity to recover valuable and strategic metals (Khayambashi et al. 2016; Reddy and Kumar 2016; Virolainen et al. 2019). Indeed, wastes and sub-products of industrial production and mining activities may be considered for valorization of secondary resources (Gomes et al. 2016; Islam et al. 2015). Biopolymer composites (Abasiyan et al. 2019), clays (Lan et al. 2019) biochars (Yin et al. 2019) have been successfully tested for cadmium sorption.

In this work, a special attention is paid to the removal of cadmium and iron from phosphoric acid solutions using three commercial resins (supplied by Purolite) bearing different reactive groups. The three spherical resins are supported on macroporous polystyrene crosslinked with divinylbenzene.

Puromet MTC1600H bears sulfonic acid reactive groups, aminophosphonic reactive groups are supported on Puromet MTS9500, while Puromet MTS9570 is a bi-functional resin constituted of phosphonic and sulfonic acid groups. The study compares the effects of these different reactive groups on the removal of cadmium and iron from phosphoric acid through the evaluation of the influence of H_3PO_4 concentration, sorbent dosage, uptake kinetics and sorption isotherms from bi-component synthetic solutions; metal desorption is also tested using acid solutions (HNO_3, HCl, H_2SO_4). In a second part of the work, the resins are applied to the treatment of an industrial phosphoric acid solution produced by Abu Zaabal Fertilizer and Chemicals Company (AZFC) in Egypt. Metal recovery is processed, as a polishing treatment, on solutions pre-treated with either activated carbon or solvent extraction (using tributyl phosphate extractant, TBP). TBP has been used for the purification of phosphoric acid for fluoride removal, metal recovery and acid separation (phosphoric acid *vs.* sulfuric acid) (Lembrikov et al. 2004; Li et al. 2017a; Liu et al. 2016; Zuo et al. 2019).

Materials and methods

Materials

Selected resins were supplied by Purolite (King of Prussia, PA, USA). They were used as supplied. Table AM1 (see Additional Material Section) summarizes the main properties of the resins (commercial data). For the study of synthetic solutions, phosphoric acid (analytical grade) was purchased from Merck KGaA (Darmstadt, Germany). Other acids, namely nitric, hydrochloric, and sulfuric acids (analytical grade), used for desorption tests, were supplied by Sigma-Aldrich (Saint-Louis, MO, USA). Cadmium ($CdSO_4$) and iron ($FeSO_4 \cdot 7H_2O$) salts were obtained from Merck KGaA. Stock solutions of 1.0 g metal L^{-1} were prepared in Milli-Q water (acidified by a few drops of nitric acid to prevent metal precipitation at long storage). Freshly prepared solutions for experiments were obtained by dilution with phosphoric acid at the appropriate concentration prior to sorption tests. When relevant, pH was measured using Cyber Scan pH 6000 pH-meter (Eutech Instruments, Nijkerk, Netherlands).

Sorption and desorption processes

The sorption tests were carried out in batch reactor. Although the primary step in the design of a sorbent process is the study of the pH effect on metal binding, in the current work, the strategy focused on the development of preferred process based on unchanged pH (the only variation dealt with the effect of phosphoric acid dilution in the relevant section investigating the effect of acid concentration). A fixed volume

(V, L) of solution containing 50 mg L^{-1} of both cadmium and iron (C$_0$, 0.44 mmol Cd L^{-1}; 0.90 mmol Fe L^{-1}) was mixed for 24 h with a fixed amount of resin (m, g) (agitation speed 150 rpm). The concentration of phosphoric acid was varied between 0.25 M and 2.0 M. In most cases, the sorbent dosage (SD = m/V, g L^{-1}) was set to 1.5 g L^{-1}. When relevant, the sorbent dosage was varied (in the range 0.5–2.5 g L^{-1} for the study of the effect of sorbent dosage), as well as the initial concentration. For the study of sorption isotherms, the initial concentration (C$_0$) varied in the range 30–300 mg metal L^{-1}, 0.27–2.7 mmol Cd L^{-1}, and 0.53–5.3 mmol Fe L^{-1}. The concentration ranges were selected to reach the saturation of the resins and evaluate maximum sorption capacities (though sorption is probably not competitive when metal concentration exceeds a few hundred mg L^{-1}). For the uptake kinetics, the contact time was varied between 0 and 1440 min (1 day) with samples collected at fixed contact times for building the kinetic profiles. After filtration (filter membrane, pore size 1.2 μm), the residual metal concentration (C$_{eq}$) was analyzed by ICP-AES (inductively coupled plasma atomic emission spectrometer, Activa M, Horiba-Jobin Yvon, Longjumeau, France). The sorption efficiency was calculated as well as the sorption capacity (q$_{eq}$, mmol g^{-1}) using the mass balance equation: q$_{eq}$ = (C$_0$-C$_{eq}$) × V/m.
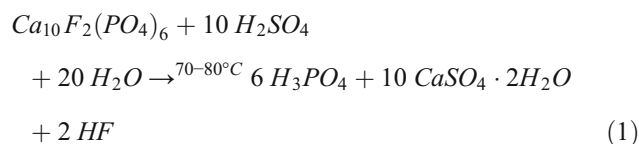
For desorption investigation, similar experimental procedure was used. Metal loading was performed using the procedure described above, and the effective amount of metal present on the resin was calculated from the mass balance equation. Metal sorption was carried out by contact of the resins (SD 1.5 g L^{-1}) with metal solutions containing both iron and cadmium (C$_0$ 50 mg L^{-1}) in 0.25 M H$_3$PO$_4$ solution (pH$_0$ 1.5) at room temperature for 24 h. Metal resins were washed with demineralized water before processing the elution step. Bi-metal-loaded sorbents were mixed for 24 h with the eluent, setting the sorbent dosage to 0.5 g L^{-1}. After filtration, the concentration in the eluate was analyzed to calculate the amount released, and to calculate the desorption efficiency.

The modeling of uptake kinetics was performed using conventional equations: (a) pseudo-first order rate equation (PFORE), (b) pseudo-second order rate equation (PSORE) (Ho and McKay 1999; Spies and Wewers 2020; Wieszczycka et al. 2020), and (c) the Crank equation (associated with the resistance to intraparticle diffusion, assuming the homogeneous diffusion of the sorbate at the surface of the sorbent, with constant surface diffusivity condition (Crank 1975)). The parameters were determined by non-linear regression analysis using the facilities of Mathematica ® software.

Application to treatment of industrial phosphoric acid solutions

El-Sebaeya phosphate deposits of the Nile Valley are recognized among the most important sources of phosphate rock in Egypt (Yassien and Elameer 2014). El-Sebeaya plateau is located between latitudes 25° 30′–26° 30′ and longitudes 32° 30′–33° 30′ on both sides of the Nile Valley (Elmaadawy et al. 2015; NMA 2010). Abu Zaabal Fertilizer and Chemicals Company (AZFC) produces phosphoric acid using the wet di-hydrate process; phosphate rock is completely acidified using concentrated sulfuric acid to produce di-hydrate phosphoric acid (∼ 25% P$_2$O$_5$%) and insoluble di-hydrate calcium sulfate precipitate (phosphogypsum) (Shweikani et al. 2013), according Eq. 1:

$$Ca_{10}F_2(PO_4)_6 + 10\,H_2SO_4$$
$$+ 20\,H_2O \rightarrow^{70-80°C} 6\,H_3PO_4 + 10\,CaSO_4 \cdot 2H_2O$$
$$+ 2\,HF \tag{1}$$

Crude phosphoric acid supplied by AZFC was pre-treated using two different processes: (a) sorption onto activated carbon (case a), and (b) solvent extraction using TBP (case b).

Activated charcoal (AC, Loba Chemie Pvt. Ltd., Mumbai, India) was mixed with crude phosphoric acid (≈ 22.5% w/w P$_2$O$_5$) in an agitated tank reactor for 24 h; the sorbent dosage was 5 g AC L^{-1} (NMA 2017). Filtrated pre-treated solution was used for polishing treatment with ion-exchange resins.

For solvent extraction, tri-butyl phosphate (TBP, Loba Chemie Pvt. Ltd., Mumbai, India) was diluted in kerosene (extractant concentration: 2.55 M) and shaken with concentrated phosphoric acid (≈ 45% w/w P$_2$O$_5$) for 15 min at room temperature with a 4/1 org./aq. volume ratio. After phase separation, loaded organic phase was scrubbed with pure phosphoric acid (≈ 35% w/w P$_2$O$_5$) with a 1/1 org./aq. volume ratio, for 5 min. Finally, the scrubbed organic phase was stripped with double distilled water at room temperature, for 10 min; the org./aq. volume ratio was set to 1/1 (NMA 2018). The eluted sample was used for polishing treatment with the resin.

For the polishing treatment of pre-treated phosphoric acid solutions, the solution was mixed with the resin for 24 h. The sorbent dosage was 1.5 g L^{-1}. After filtration, the residual concentration of the metals was evaluated by ICP-AES, and the mass balance equation was used for calculating the sorption efficiency and the sorption capacity. Fluoride concentration was measured by a fluoride ion-selective electrode (Orion Star A215 pH/Conductivity Benchtop Meter, Thermo Fisher Scientific, Waltham, MA USA) coupled to an 8157BNUMD Orion ROSS Ultra Triode pH/ATC electrode. The P$_2$O$_5$ concentration was determined using spectrophotometer-type Shimadzu UV 1208 by a specific colorimetric method (ammonium molybdate and ammonium metavanadate) (Marczenko and Balcerzak 2000). The same procedure was applied to the treatment of crude phosphoric acid supplied by AZFC.

Results and discussion

Synthetic phosphoric acid solutions

Effect of phosphoric acid concentration

The increasing concentration of phosphoric acid decreases both the efficiency of cadmium and iron sorption, regardless of the resin (Fig. 1), and their relevant sorption capacities (Figure AM1, see Additional Material Section). However, the responses significantly differ for the systems resin/metal. Table AM2 shows the relative variation of the sorption capacities (compared with the q_m at 0.25 M H_3PO_4 concentration): for cadmium sorption, MTC1600H sulfonic resin is less sensitive to acid concentration, while for iron removal most stable performances are obtained with MTS9500 aminophosphonic resin. On the opposite hand, high concentration of phosphoric acid drastically reduces the sorption of cadmium on aminophosphonic resin and iron sorption is strongly depreciated by high concentrations for the sulfonic resin. The phosphonic/sulfonic resin (i.e., MTS9570) shows an intermediary behavior; being sensitive to acid concentration for both cadmium and iron.

Alexandratos' group documented the relative importance of polarizability (Alexandratos and Zhu 2015), hydrogen bonding (Alexandratos and Zhu 2017; Zhu and Alexandratos 2011), and bi-functionality (Alexandratos and Smith 2004) on the sorption performance of ligands (especially those bearing phosphonate and amidoxime groups) (Alexandratos et al. 2016). The electronegativity of Cd (II) (i.e., χ_{aq} 2.660) is close to that of Fe (II) (i.e., χ_{aq} 2.636), while Fe(III) has a much higher χ_{aq} value (i.e., 3.835) (Li et al. 2012). Persson (Persson 2010) reported a Shannon radius for hydrated cadmium (Cd $(OH)_6^{2+}$) close to 0.95 Å, while iron hydrated radius was much lower (i.e., 0.78 Å for Fe $(OH)_6^{2+}$, and 0.645 Å for Fe $(OH)_6^{3+}$). Cadmium is classified among
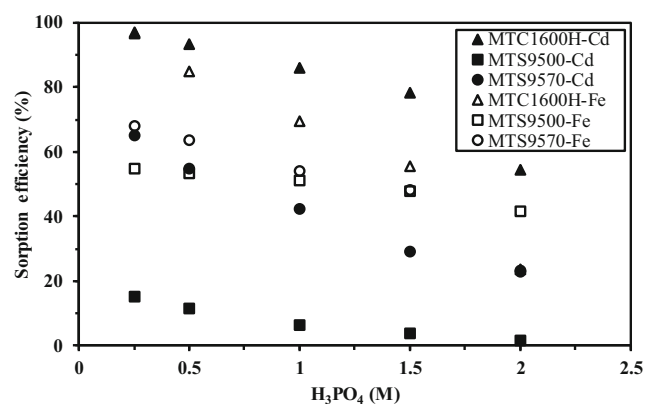

Fig. 1 Effect of phosphoric acid concentration on Cd and Fe removal using selected commercial resins (bi-component solutions, C_0 50 mg L^{-1}, i.e., 0.445 mmol Cd L^{-1} and 0.895 mmol Fe L^{-1}; contact time 24 h; sorbent dosage (SD) 1.5 g L^{-1}; T 20 ± 1 °C)

the so-called soft acids (Pearson 1966), while Fe(III) is part of hard acids and Fe(II) is assimilated to borderline acid. Based on the HSAB principle (hard and soft acid and base theory), strong acids will preferentially react with strong bases (such as N >> P; O >> S) (and reciprocal: weak acids with weak bases). The introduction of sulfonic groups, which bring hydrophilic properties, may affect the intraligand bonding, and, in turn, the affinity of the sorbent for target metal ions (Alexandratos and Smith 2004). Another important parameter may affect the affinity of the resin for metals: the speciation of the metal ions in complex solutions (including in phosphoric acid) may strongly influence the binding of metal species in solution onto reactive groups (Figure AM2). Iron forms stable complexes with phosphate: the cationic complex $FeH_2PO_4^+$ represents 91–96% of total Fe(II) in 0.25–2 M H_3PO_4 solutions (free Fe^{2+} varies between 8.6 and 3.8%). On the opposite hand, cadmium is not forming stable species: in 0.25–2 M H_3PO_4 solutions, the fraction of $CdHPO_4$ is negligible (less than 0.02%). Free Cd^{2+} species largely predominates (97.9–99.4%), aqueous cadmium sulfate counts for 2% at low acidic concentration and its fraction progressively decreases below 0.6% at 2 M H_3PO_4 concentration. The two metals form predominating cationic species: monovalent $FeH_2PO_4^+$ and divalent free Cd^{2+} under selected experimental conditions. The charge difference and the size of metal cations may influence the interaction mode with reactive groups (thermodynamics/equilibrium) but also the accessibility to reactive groups (kinetics).

These different synergic or anti-synergic interactions/effects make complex the interpretation of the variations in the affinity of the different resins for the two metals with increasing phosphoric acid concentration.

Figure AM3 shows the log-log plots of the distribution ratios (D = q_{eq}/C_{eq}, L g^{-1}) with the concentration of phosphoric acid for the different systems. Linear trends are observed: the slope of this type of plot in usually associated, in ion-exchange processes, with the stoichiometry of proton exchange. For Cd(II), the slopes vary between − 0.87 (MTS9570 dual sulfonic/phosphonic resin) and − 1.44 (MTC1600H sulfonic); the aminophosphonic resin (MTS9500) shows a slope close to − 1.1. The stoichiometric ratio is thus close to 1. This is not consistent with the predominance of the divalent cations (free Cd^{2+}). For iron, the slope of the linear plots varies much more: − 1.99 for MTC1600H resin, − 0.79 for MTS9570, and down to − 0.22 for MTS9500. The resins bearing two reactive groups show much lower slopes and lower distribution ratios for iron sorption; especially at low phosphoric acid concentration, the differences tend to level off in 2 M H_3PO_4 solutions. For Cd(II), the resins can be clearly ranged according the series: MTC1600H (sulfonic) > MTS9570 (phosphonic/sulfonic) > MTS9500 (aminophosphonic).

Figure AM4 plots the selectivity coefficient, $SC_{Cd/Fe}$ (i.e., $SC_{Cd/Fe} = D_{Cd}/D_{Fe}$) as a function of phosphoric acid concentration for the three resins. The SC coefficient is less than 0.15 for MTS9500 aminophosphonic resin: the sorbent has a marked preference for Fe, especially at low H_3PO_4 concentration. On the opposite hand, MTC1600H sulfonic resin shows a preference for Cd that increases with acid concentration. The dual phosphonic/sulfonic resin (MTS9570) cannot separate the two metals, whatever the concentration of the acid: the SC varies between 0.44 and 1. The closer the SC value to 1, the more difficult the separation of the metal ions on selected resins. The resin has little preference for Fe at low phosphoric concentration, while at higher concentration the two metals ions are almost equally sorbed.

Effect of sorbent dosage

As expected, increasing sorbent dosage improves the sorption of both Cd and Fe, regardless of the sorbent. It is noteworthy that the curves are almost overlapped for MTC1600H for the two metal ions, and the sorption efficiency is significantly higher than for the other systems (resin/metal) (Fig. 2). For a sorbent dosage of 2 g L^{-1}, both cadmium and iron are completely removed from 0.25 M H_3PO_4 solution. For the other resins, even at 2.5 g L^{-1} sorbent dosage, it is not possible achieving the complete removal of the metals. Iron is more efficiently sorbed than cadmium and MTS9570 phosphonic/sulfonic resin shows higher performance than MTS9500 aminophosphonic resin.

Table AM3 shows that the sulfonic resin (MTC1600H) allows much higher distribution ratios for both cadmium and iron than the alternative resins. Highest D values are reached for SD 2.5 g L^{-1} for Cd (D: up to 46.4 L g^{-1}) and SD 2.5 g L^{-1} for Fe (D: up to 43.5 L g^{-1}). At the highest SD, the D values for Cd are about 230 to 30 times higher for MTC1600H than for MTS9500 and MTS9570, respectively, while for Fe, the improvements are about 27 and 14 times, respectively.

Figure AM5 shows the effect of sorbent dosage on the selectivity coefficient $SC_{Cd/Fe}$. These results confirm that MTS9570 resin is poorly selective ($SC_{Cd/Fe}$ varies between 0.35 and 0.58) and that MTS9500 resin has a preference for Fe over Cd ($SC_{Cd/Fe}$ varies between 0.09 and 0.14); for these two resins, the sorbent dosage has a limited effect. The sulfonic resin (MTC1600H) shows a preference for Cd over Fe at low sorbent dosage ($SC_{Cd/Fe}$ is close to 1.6), while at higher sorbent dosage (in the range 1.5–2.5 L g^{-1}) the SC remains close to 1.08: the two metal ions are equally sorbed by the sulfonic resin. At high sorbent dosage, the full sorption of both Cd and Fe tends to limit the selectivity effect.

Therefore, the selection of experimental conditions (type of sorbent and sorbent dosage) depends on the target: purification (large spectrum of metals to be removed) or recovery (selectivity is preferred).
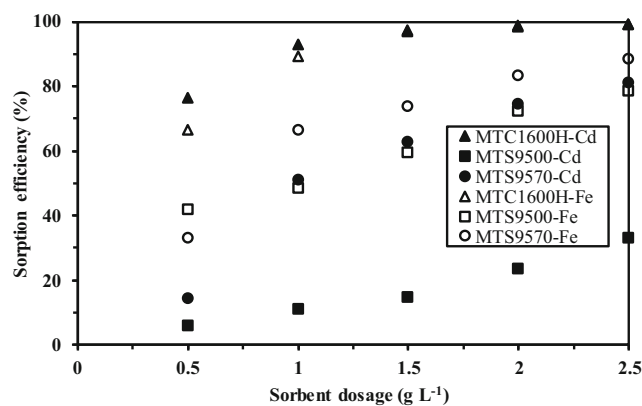

Fig. 2 Effect of sorbent dosage on Cd and Fe removal using selected commercial resins (bi-component solutions, C_0 50 mg L^{-1}, i.e., 0.445 mmol Cd L^{-1} and 0.895 mmol Fe L^{-1}; [H_3PO_4] 0.25 M; contact time 24 h; sorbent dosage (SD) 1.5 g L^{-1}; T 20 ± 1 °C)

Uptake kinetics

Under selected experimental conditions (SD, 1.5 g L^{-1}; [H_3PO_4], 0.25 M; C_0, 0.445 mmol Cd L^{-1} and 0.895 mmol Fe L^{-1}; pH_0 1.45), the equilibrium is reached within 2–8 h, depending on the system (Fig. 3). Faster kinetics are achieved within 2 h for MTC1600H sulfonic resin for both cadmium and iron (the curves are overlapped for the two metals). The kinetic profiles for cadmium and iron uptake are almost overlapped in the case of MTS9570 resin. MTS9500 aminophosphonic resin shows a different trend with similar profiles for the two metals but the equilibrium concentrations are substantially different. This is consistent with previous observations on the preference of the sorbent for iron vs. cadmium.

The uptake kinetics can be controlled by the resistance to film diffusion, to intraparticle diffusion and by the proper reaction rate. The PFORE, PSORE, and RIDE (crank equation) have been fitted to kinetic profiles (Fig. 3 and
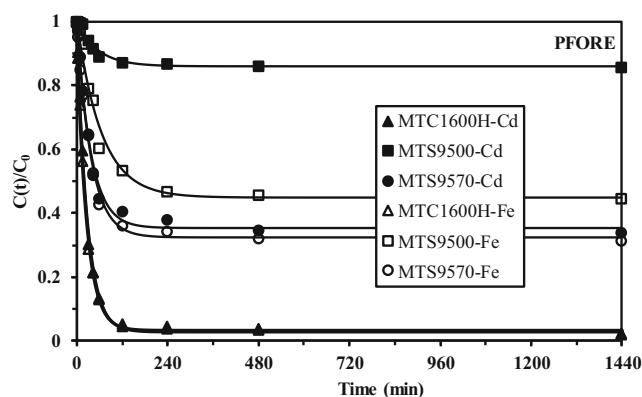

Fig. 3 Uptake kinetics for Cd and Fe removal using selected commercial resins—modeling with the PFORE (bi-component solutions C_0 50 mg L^{-1}, i.e., 0.445 mmol Cd L^{-1} and 0.895 mmol Fe L^{-1}; [H_3PO_4] 0.25 M; sorbent dosage (SD) 1.5 g L^{-1}; T 20 ± 1 °C)

Figure AM6). Figure AM7 also shows the fit of PFORE and PSORE to uptake kinetics with the representation of sorption capacity (i.e., q(t)) as a function of contact time. The parameters of the models are summarized on Table 1 (PFORE), and Tables AM4 and AM5 (PSORE and RIDE, respectively). The comparison of the fitted curves with experimental profiles, and the determination coefficients show that the PFORE fits better experimental data. In addition, the values of $q_{eq,1}$ (calculated sorption capacities for PFORE) are very close to the experimental values of the equilibrium sorption capacities: the variation never exceeds 3.5%. The PFORE is usually associated to physical sorption mechanism such as ion-exchange. The apparent rate coefficients (k_1, min^{-1}) are of the same order of magnitude for cadmium and iron, while the equilibrium sorption capacities are significantly higher for iron than for cadmium; this is consistent with the difference in molar concentration for the two metals.

Although the RIDE fits less accurately the profiles, the general trends are respected: the resistance to intraparticle diffusion contributes to control uptake kinetics. The model allows determining the effective diffusivity (D_e, m^2 min^{-1}) for cadmium and iron with the different resins (Table AM5). The diffusivity coefficients are of the same order for cadmium and iron for MTC1600H: 0.45×10^{-10} and 0.38×10^{-10} m^2 min^{-1}, respectively. The same conclusion can be deduced for MTS9570: 3.22×10^{-10} and 3.01×10^{-10} m^2 min^{-1}, respectively. The diffusivity is about an order of magnitude greater for the phosphonic/sulfonic resin (MTS9570) compared with the sulfonic resin (MTC1600H). The diffusivity of cadmium in MTS9500 aminophosphonic resin is almost doubled compared with iron (i.e., 4.23×10^{-10} and 2.23×10^{-10} m^2 min^{-1}, respectively). The order of magnitude is comparable for the two resins bearing phosphonic reactive groups. The self-diffusivity in water for both Cd^{2+} and Fe^{2+} is 4.23×10^{-8} m^2 min^{-1} (3.62×10^{-8} m^2 min^{-1} for Fe^{3+}, for counteranions such as HPO_4^{2-} and $H_2PO_4^{-}$, the self-diffusivities are: 4.55×10^{-8} m^2 min^{-1} and 5.75×10^{-8} m^2 min^{-1}, respectively) (Buffle et al. 2007). This means that the diffusivity coefficients for the metal ions in the resins are two or three orders of magnitude lower that their self-diffusivity in water. This confirms that the resistance to intraparticle diffusion cannot be neglected, especially for MTC1600 sulfonic resin. The presence of sulfonic groups is supposed to improve the hydrophilic behavior of the resin and therefore water (and metal ions) transfer. Other parameters probably influence this mass transfer resistance.

The predominant species (Cd^{2+} and $FeH_2PO_4^{+}$) have substantially different ionic sizes in solution: the complexation of iron with dihydrogen phosphate means a larger ionic size for predominant iron species compared to free divalent cadmium species. However, the variations of the rate parameters (k_1 and D_e) are not very marked.

Sorption isotherms

The sorption isotherms in bi-component solutions (0.25 M phosphoric acid) appear in Fig. 4. The curves are characterized by a steep initial section that shows the affinity of the resins for cadmium and iron. The curves tend to reach a plateau for residual concentrations in the range 0.5–1.5 mmol L^{-1}. Unexpectedly, above this limit range of concentration the sorption capacity tends to decrease. This behavior is sometimes explained, in multi-component solutions, by a difference in the affinity of the sorbent for a solute, which is displacing at high concentration another solute initially bound onto the sorbent. However, Figure AM8 shows the plots of the cumulative sorption capacity against the cumulative concentration of the residual metal ions. This figure clearly shows that the same trend is observed on the cumulative isotherm: at high residual metal concentration, the sorption capacity tends to decrease. The replacement of solutes is not sufficient for maintaining the total sorption capacity at a constant plateau.

In order to rank the resins, the sorption capacities are compared for $C_{eq} = 1$ mmol metal L^{-1}. In the case of Cd(II), the resins are ranked according: MTC1600H (0.61 mmol Cd g^{-1}) > MTS9570 (0.25) > MTS9500 (0.063). The same classification is observed in the case of Fe(II) but with higher sorption capacities: MTC1600H (0.93 mmol Fe g^{-1}) > MTS9570 (0.65) > MTS9500 (0.51). The predominant species is a monovalent species for iron (i.e., $FeH_2PO_4^{+}$) while divalent free cadmium predominates for cadmium. The stoichiometric ratio between metal species and reactive groups at the surface of the resins is more favorable for iron.

Table 1 Modeling of Cd and Fe uptake kinetics with the pseudo-first-order rate equation (bi-component solutions)

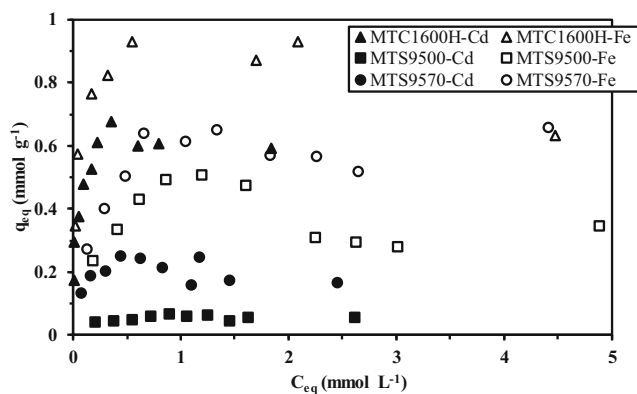| Metal	Cadmium			Iron		
Resin	MTC1600H	MTS9500	MTS9570	MTC1600H	MTS9500	MTS9570
$q_{eq,exp}$ (mmol g^{-1})	0.285	0.042	0.193	0.590	0.333	0.414
$q_{eq,1}$ (mmol g^{-1})	0.284	0.041	0.189	0.582	0.331	0.408
$k_1 \times 10^2$ (min^{-1})	3.61	1.80	2.72	3.80	1.53	2.66
R^2	0.995	0.971	0.990	0.994	0.985	0.995

Fig. 4 Sorption isotherms for Cd and Fe removal using selected commercial resins (bi-component solutions, C_0 30–300 mg L^{-1}, i.e., 0.27–2.7 mmol Cd L^{-1} and 0.534–5.41 mmol Fe L^{-1}; [H$_3$PO$_4$] 0.25 M; sorbent dosage (SD) 1.5 g L^{-1}; T 20 ± 1 °C)

The selectivity coefficient for cadmium over iron increases with total metal concentration for MTC1600H (around 2), while for MTS9570, it tends to decrease (the sorbent progressively enhances the preferential binding of iron) (Figure AM9). MTS9500 resin maintains a preference for iron, independently of total concentration.

Compared with alternative sorbents for the recovery of Cd (II), MTC16900H resin is of the same order of magnitude than recently developed materials: Ha/Fe-Mn oxides-loaded biochar (i.e., 0.60 mmol Cd g^{-1}) (Guo et al. 2019), amino-functionalized core-shell magnetic mesoporous composites (i.e., 0.46 mmol Cd g^{-1}) (Tang et al. 2013) or higher than functionalized mineral resources (thiourea-zeolite-tuff, 0.103 mmol Cd g^{-1}) (Barragan et al. 2017) or earthworm manure-derived biochar (i.e., 0.27 mmol Cd g^{-1}) (Wang et al. 2017).

Metal desorption

Metal desorption is a critical parameter for the evaluation of process feasibility at industrial scale. Table 2 reports the tests performed on the desorption of cadmium and iron from metal-loaded resins using three types of acid eluents (i.e., nitric acid, hydrochloric acid, and sulfuric acid) at three levels of concentration (i.e., 0.1, 0.5, and 1 M). The two metals have very distinct behaviors in terms of desorption, and the resins show different efficiencies for desorption.

For cadmium, the efficiency of desorption increases with the concentration of the acidic eluent (especially for MTC1600H and MTS9570); in molar acidic solutions the desorption efficiency ranges between 86 and 100%. For MTC1600H and 1 M acid concentration, the desorption yields range between 98 and 100%; this is little better than MTS9570. For MTS9500, the concentration and the type of acid hardly change the desorption performance for cadmium (varying between 36 and 52%). For cadmium, the best

conditions for metal desorption correspond to 1 M H$_2$SO$_4$ eluent with MTC1600H resin: metal is completely eluted.

For iron desorption, the resins shows more difficulties for releasing the metal. Iron is almost not desorbed from loaded MTS9500 resin, whatever the concentration and the type of acid: maximum desorption does not exceed 3%. For MTS9570 resin, desorption is a little better but never exceeds 39%; HCl and H$_2$SO$_4$ solutions are much better than HNO$_3$ solutions. These conditions are highly unfavorable: the progressive saturation of the resin with iron will progressively poison and saturate the sorbents; this will limit the life cycle of the material. The sulfonic resin (MTC1600H) shows much more favorable desorption for iron. However, only sulfuric acid at the highest concentration (i.e., 1 M) succeeds in achieving the complete desorption of iron (i.e., desorption yield reaches 98.8%).

The difference in desorption of cadmium and iron may be associated to the probable effect of metal speciation. Cadmium does not form complexes with phosphate and the resin binds the metal ion under the form of free cadmium or cadmium chloride cation. On the opposite hand, the predominance of iron phosphate species (strongly stable), bound to the resins, makes iron desorption more complex.

Industrial phosphoric acid solutions

The complexity of the solution may strongly decrease sorption performances while compared with the levels of metal recovery from synthetic solutions (Prelot et al. 2014). Therefore, the resins are tested for the direct treatment of crude phosphoric acid (Table 3) and for pre-treated phosphoric acid solutions (Table 4). First, the comparison of the concentrations in the initial solutions shows the significant impact of solvent extraction on the content of hazardous elements. As expected, activated charcoal is less efficient than solvent extraction for removing heavy metals and fluoride (without cost analysis). The grade of phosphoric acid is of the same order of magnitude (around 21–23% w/w), regardless of the eventual pre-treatment.

Crude phosphoric acid

Crude phosphoric acid is loaded with very high levels of metal ions (but also probably some organic compounds, such as humic and fulvic acids, that may interact with the speciation of metal ions). This leads to strong saturation of the resins and the sorption efficiency is generally low. Table 3 shows that fluoride concentration is insignificantly changed after contact with resins. Iron content is reduced by 27% and 18% using MTC1600H and MTS9570, while Fe concentration remains unchanged after treatment with MTS9500. For Cr (hard metal according HSAB principle), sorption efficiency varies between 19 and 25%. Manganese (initially present the

Table 2 Effect of type and concentration of acids on metal desorption efficiency (%) from loaded resins (desorption experimental conditions: SD 5 g L^{-1}; contact time 24 h; T 20 ± 1 °C)

Resin		MTC1600H			MTS9500			MTS9570		
Metal	[Acid] (M)	1.0	0.5	0.1	1.0	0.5	0.1	1.0	0.5	0.1
Cd	Loading	31.9 mg Cd g^{-1}			4.3 mg Cd g^{-1}			22.1 mg Cd g^{-1}		
	HNO$_3$	97.9	76.4	6.4	47.6	36.0	39.0	95.9	86.6	38.8
	HCl	98.9	85.6	41.2	47.3	44.6	35.6	86.0	87.7	56.6
	H$_2$SO$_4$	100	82.6	18.0	52.2	49.8	37.7	96.7	86.0	43.6
Fe	Loading	32.8 mg Fe g^{-1}			18.3 mg Fe g^{-1}			23.9 mg Fe g^{-1}		
	HNO$_3$	49.0	21.1	9.7	0.6	2.3	2.5	1.5	1.8	6.0
	HCl	86.3	64.4	9.6	2.3	1.5	2.3	24.0	38.9	4.2
	H$_2$SO$_4$	98.8	82.8	22.0	2.5	2.9	2.3	28.8	29.2	10.0

concentration of 576 mg Mn L^{-1}) is poorly removed from phosphoric acid (less than 12%), whatever the resin. For Zn, sorption efficiency varies between 21 (with MTC1600H) and 30% (for both MTS9500 and MTS9570). For Pb (borderline metal, according HSAB principle), MTC1600 sulfonic resin shows poor efficiency; metal binding increases to 22% and 26% for MTS 9500 and MTS 9570, respectively. This is with cadmium (soft acid, HSAB) that the largest differences are observed; this can be also explained by much lower concentration in phosphoric acid. Consistently with the data obtained with synthetic solutions, for Cd the resins can be ranked according: MTC1600H (87%) >> MTS9570 (41%) >> MTS9500 (9%) (Table AM6). Under selected experimental conditions, the residual concentrations of heavy metals remain very high, making the acid inappropriate for food, pharmacy or electronic applications. However, crude phosphoric acid after contact with MTC1600H resin becomes suitable for the production of environmental friendly phosphate fertilizers: cadmium concentration (about 7 mg kg^{-1} P$_2$O$_5$) is acceptable with respect to the levels recommended by WHO, FAO, and European Food Safety Authority (Roberts 2014; Ulrich 2019).

Table 3 Specifications of crude phosphoric acid before and after contact with resins

Compound	Initial content	MTC1600H	MTS9500	MTS9570
	Concentration (%)			
P$_2$O$_5$	≈ 23.2	≈ 23.2	≈ 23.2	≈ 23.2
	Concentration (g L^{-1})			
Fe	9.5	6.9	9.5	7.7
F	8.6	8.6	8.6	8.6
	Concentration (mg L^{-1})			
Cr	120	96.2	90.5	90.3
Cd	16.7	2.2	14.7	9.9
Pb	55.0	50.5	43.1	35.1
Zn	271	215	189	190
Mn	576	506	520	539

Crude phosphoric acid pre-treated with activated charcoal

The pre-treatment with activated charcoal is supposed to remove essentially organic contaminants. This pre-treatment maintains high levels of metal ions (about 6.9 g Fe L^{-1}, 476 mg Mn L^{-1} or 241 mg Zn L^{-1}, for example) and up to 7.5 g L^{-1} for F. There is a large excess of this metal ions compared with cadmium concentration (i.e., 16.1 mg Cd L^{-1}). This high salinity means that the resin may be rapidly saturated. This is confirmed by the residual concentrations of target metals in the solution after being treated with the resins (Table 4). Compared to initial metal levels, the concentration abatements for Cr, Pb, Zn, and Mn are negligible and the three resins have very comparable sorption performances (Table AM7). For Fe and Cd, the resins show the expected ranking: MTC1600H > MTS9570 > MTS9500. However, even with the best resin (sulfonic-based MTC1600H) the residual concentrations (especially for Fe) are not appropriate for high-added value applications.

Crude phosphoric acid pre-treated by TBP solvent extraction

The solvent extraction process substantially reduces residual concentrations for the different metal ions (and fluoride that disappeared) (Table 4): lead and chromium are fully extracted by TBP and the levels of Fe, Zn and Mn are reduced by one order of magnitude.

After treatment by sorption on MTC1600H, the removals of Cd and Fe range between 93 and 96% (Table AM8). Residual concentrations decrease to 0.2 mg Cd L^{-1} and 31.8 mg Fe L^{-1} (Table 4). The combination of solvent extraction and sorption onto MTC1600H sulfonic resin drastically increases the purity of phosphoric acid. As expected, the other resins are less efficient in cadmium and iron removal. For MTS9570, the sorption efficiency ranges between 53 and 58%; residual concentration is rather limited for cadmium (about 2 mg Cd L^{-1}), but iron is still present at high concentration (i.e., 203 mg Fe L^{-1}). This means that the treatment is not sufficient for applications requiring high purity. The

Table 4 Specifications of pre-treated phosphoric acid before/after contact with resins

Compound	Pre-treatment							
	Activated charcoal (sorption)				TBP (solvent extraction)			
	Initial content	MTC1600H	MTS9500	MTS9570	Initial content	MTC1600H	MTS9500	MTS9570
P_2O_5	≈ 22.6%	≈ 22.6%	≈ 22.6%	≈ 22.6%	≈ 20.1%	≈ 20.1%	≈ 20.1%	≈ 20.1%
Fe	6.9 g L^{-1}	5.6	6.5	6.2	430 mg L^{-1}	31.8	244	203
F	7.4 g L^{-1}	7.4	7.4	7.4	–	–	–	–
Cr	101 mg L^{-1}	97.2	95.5	93.3	–	–	–	–
Cd	16.1 mg L^{-1}	2.0	14.4	9.3	4.8 mg L^{-1}	0.2	4.2	2.0
Pb	45.0 mg L^{-1}	44.5	40.2	37.6	–	–	–	–
Zn	241 mg L^{-1}	209	199	195	36.3 mg L^{-1}	22.7	28.7	25.0
Mn	476 mg L^{-1}	466	476	469	25.0 mg L^{-1}	18.4	22.5	20.8

results are even worst for MTS9500: sorption efficiency varies between 13 and 43%, with residual concentrations as high as 4.2 mg Cd L^{-1} and 244 mg Fe L^{-1}.

Recommendations

The high levels of heavy metals of crude phosphoric acid makes the resource inappropriate for manufacturing of fertilizers. The level of P_2O_5 remains unchanged after contact with the three resins. The treatment of crude phosphoric acid with MTC1600H sulfonic resin (at the sorbent dosage of 2.5 g L^{-1}) significantly decreases the residual concentrations of heavy metals, including cadmium and iron. However, their levels are not appropriate for food applications (for example). The presence of other contaminants, not extracted by the resin, may declass treated phosphoric acid for fertilizer application (and obviously other high added-value applications). The treatment of crude phosphoric acid with activated charcoal allows removing some inorganic contaminants but the impact on heavy metals is rather limited. The combination of sorption on activated charcoal and MTC1600H resin also meets the requirements for fertilizer manufacturing but the grade is not sufficient, at this stage, for food or pharmaceutical applications. The "cleaning" of crude phosphoric acid with TBP solvent extraction substantially remove metal impurities (and fluoride content); using MTC1600H sorption as polishing treatment allows reaching levels of contaminants much better than those required for fertilizer production. The optimization of this treatment (playing with sorbent dosage, etc.) would probably allow reaching concentrations levels compatible with food applications, providing the other contaminants to be also removed, such as sulfate, uranium, rare earth elements that may be also present in the crude phosphoric acid (depending on the origin of phosphate rocks).

Future work could consist of testing the resins in dynamic systems for the treatment of phosphoric acid pre-treated by sorption on activated charcoal and solvent extraction, using MTC1600H fixed-bed column as a polishing treatment. The desorption could be also tested with alternative acid eluents such as perchloric acid solutions (Kocjan 1999; Kushwaha et al. 2010; Montembault et al. 1999; Rivas et al. 2002); such an eluent brings both acidic and oxidizing effects that could contribute to enhanced desorption.

Conclusion

The purity of phosphoric acid controls its potential commercial uses. The removal of color and toxic metals is thus a critical step in the development of added-value products. Due to the high concentration of iron and the toxicity of cadmium, these two metals have been considered for purification of phosphoric acid using three resins bearing different functional groups (i.e., sulfonic, aminophosphonic, and bifunctional phosphonic/sulfonic groups). The study, performed on bi-component synthetic solutions, shows that the uptake kinetics are comparable for the two metals (difficulty to play on kinetics for separating cadmium and iron) with equilibrium time in the range 2–4 h. The uptake kinetics are fitted by the pseudo-first-order rate equation. The sorption efficiencies decrease with increasing phosphoric acid concentration and decreasing resin dosage. The sulfonic-based resin (i.e., MTC1600H) is much more efficient (higher sorption capacities and higher selectivity for Cd over Fe) than alternative resins. The selectivity for Cd over Fe increases with phosphoric acid concentration but decreases when the sorbent dosage exceeds 1 g L^{-1}. The superior properties of MTC1600H are also demonstrated by the much higher desorption efficiencies of Cd and Fe while using 1 M H_2SO_4 solutions: the desorption exceeds 99% contrary to other sorbents that show much lower desorption yield, especially for iron. Sulfonic acid resin appears the most efficient for the removal of iron and cadmium.

The comparison of these three resins demonstrate the critical impact of the type of functional groups: sulfonic resin (MTC1600H) > phosphonic/sulfonic bi-functional resin (MTS 9570) >> aminophosphonic resin (MTS9500).

The complex composition of crude industrial phosphoric acid solution (with huge concentrations of iron) does not allow efficient metal removal by direct sorption on the resin; a pre-treatment is required. Sorption on activated carbon does not allow reducing significantly iron concentration and a pre-treatment with TBP solvent extraction appears more appropriate for reducing residual concentrations to levels compatible with the regulations for fertilizer uses. After solvent extraction pre-treatment, the comparison of sorption efficiencies for the two metals and the tree resins confirms the conclusions raised with synthetic solutions: MTC1600H resin allows removing about 93% of iron and 96% of cadmium, i.e., much higher yields than for MTS9570 (53% and 58%, respectively) and even more for MTS9500 (43% and 13%, respectively). Combined with other treatments (for removal of other contaminants), the sorption of metal ions on MTC1600H offers promising perspectives for reaching the levels of decontamination compatible with food applications.

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