

Technical-economic comparison of chemical precipitation and ion exchange processes for the removal of phosphorus from wastewater

Agostina Chiavola , Simona Bongiolami and Giorgia Di Francesco

ABSTRACT

Chemical precipitation with the addition of ferric chloride is commonly used to remove phosphorus from wastewater. However, since its application also involves several disadvantages, alternative solutions are required. The present paper shows the results of a full-scale experimental work aimed at evaluating the efficiency of the ion exchange process using a polymeric anion exchange resin impregnated with aluminum ions in the removal of phosphorus from wastewater. The study compared the results obtained through this process with chemical precipitation, considering both technical and economic issues. At the same dosage of 6 L/hour and influent concentration (about 6 mg/L), total removal efficiency of 95% and 78% (including also that occurring in the mechanical and biological processes) was achieved by means of the anion exchange process and chemical precipitation, respectively. However, in the latter case, this value was insufficient to ensure consistent compliance with the limit of 2 mg/L P_{tot} set on the effluent; to achieve this goal, the ferric chloride dosage had to be raised to 12 L/hour, thus increasing the related costs. Furthermore, the anion exchange process generated a lower sludge production. Therefore, the ion exchange process represents a valid alternative to chemical precipitation for P removal from wastewater.

Key words | chemical precipitation, ion exchange, phosphorus, wastewater treatment plants

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INTRODUCTION

Increase of nutrient content, such as nitrogen (N) and phosphorus (P), in water bodies through untreated discharges is the main cause of eutrophication, which is the fast growth of algae and other plants which produces adverse effects on the balance of organisms and water quality (Beccari *et al.* 1993; Jarvie *et al.* 2006). It is therefore mandatory to reduce nutrient load in wastewater before its release into the receiving water body. In a wastewater treatment plant (WWTP), P removal occurs through mechanical (e.g. in the primary sedimentation tank) and biological (due to bacterial synthesis) processes. However, these systems are usually unable to comply with the more stringent limits of P set for effluents (EC 1998). An additional treatment unit specifically designed to enhance P removal must therefore be implemented and operated. For this the most common process is chemical precipitation through the addition of ferric chloride: in this way, orthophosphates react with iron to form iron phosphate, which is slightly

soluble and can be removed by sedimentation (Caravelli *et al.* 2010; Metcalf & Eddy 2013). Although widely used, there are several drawbacks to this process: the presence of competing reactions between PO_4^{3-} and HCO_3^- can increase chemical requirements; the pH must be carefully controlled in order to optimize process efficiency; a significant amount of chemical sludge is generated, which must be disposed of. Due to these issues, alternative solutions for reducing P content are strongly fostered (Genz *et al.* 2004; Nur *et al.* 2014; Acelas *et al.* 2015). Furthermore, due to the decreasing availability of natural resources worldwide, phosphorus recovery from wastewater is receiving increasing attention for its reuse in fertilizer production (Van Kauwenbergh 2010; Sengupta & Pandit 2011; Egle *et al.* 2015).

The ion exchange process may represent a possible alternative system for enhancing P removal from wastewater (Blaney *et al.* 2007; An *et al.* 2013; Nur *et al.* 2014). It is a

physical-chemical process in which ionic species present on an exchanger (the resin) are replaced by ionic species in solution and with the same type of charge (Helffferich 1995). The ion exchange resins are insoluble polymers containing highly basic or acidic functional groups, which are weakly bound to ions with the opposite charge. In particular, for the removal of phosphorus from wastewater, anionic resins that exploit the affinity between the orthophosphate and the polyvalent metals are used. The process can be highly efficient, mainly depending on the type of resins and liquid solution composition; for instance, competitive ions can be present in the solution which possess a higher affinity towards the resin than the pollutant ions and consequently are preferably removed in the exchange process. Therefore, the resin must be properly selected; furthermore, pilot tests with the real solution and the resin are strongly recommended to find the best operating parameters and also to evaluate the removal efficiency that can be achieved under real conditions.

The aim of the present study was to obtain a technical and economic comparison between the anion exchange process using a specifically designed resin and chemical precipitation with the addition of ferric chloride, for the removal of P from a real wastewater. The experimental work was carried out at two full-scale wastewater treatment plants (WWTP1 and WWTP2, respectively), located in central Italy and managed by Acqualatina S.p.A. A polymeric anion exchange resin impregnated with aluminum ions was used in the study to accomplish selective orthophosphate ion removal, exploiting the high affinity between these ions and polyvalent metals. Comparison was carried out taking into account removal efficiency as well as sludge production and costs of process operation.

METHODS

WWTP1 and WWTP2

Both wastewater treatment plants treat domestic sewage and have to adhere to the limit of 2 mg/L total phosphorus in the effluent, which is discharged into rivers. WWTP1 receives an average influent flow rate of 1,200 m³/day and includes the following main units: screening, degritting, biological reactors for denitrification-nitrification and carbon removal (Pasveer system), secondary settlement, chlorination, sludge aerobic digestion, drying beds. The anion exchange resin was applied in WWTP1 to the effluent of

the aerobic biological tank prior to treatment in the secondary sedimentation tank.

WWTP2 receives an influent flow rate of 6,000 m³/day on average. The lay-out of the water processing line consists mainly of: degritting, primary sedimentation, denitrification-nitrification and carbon removal tanks, secondary sedimentation and chlorination. Excess sludge is treated by thickening, aerobic digestion and centrifugation. Ferric chloride was added to the pre-denitrification tank of WWTP2.

The plants receive approximately the same total P load, 5 mg/L on average; however, the influent composition is very variable and phosphorus content ranges between 2 and 13 mg/L. In the absence of any additional treatment, both plants were unable to consistently adhere to the legal limit of 2 mg/L set for the effluent due to this wide variability.

Chemicals

The anion exchange resin (named CATFLOC 441), supplied by CATRA S.r.l., is made of insoluble organic polyamines containing the functional group Al(OH)₃ and also aluminum polychloride (PAC) as the coagulant. Three different dosages of CATFLOC 441 were tested: 1 L/hour, 3 L/hour and 6 L/hour. The resin operates in two steps: (1) PAC allows destabilization of the surface charges, hydrolysis of the aluminum salts and formation of the functional group Al(OH)₃; (2) polyamines act as the aggregation nucleus for particles, thus improving sludge sedimentation.

Ferric chloride was added as an aqueous solution at 40% FeCl₃, dosed initially at a flow rate of 6 L/hour and then at 12.6 L/hour.

Analyses

P removal at WWTP1 and WWTP2 was calculated based on P concentrations measured in samples collected from the influent and the effluent over a 4-month experimental period.

The following parameters were also determined for these samples: total phosphorus (P_{tot}), dissolved phosphorus (P_{dissolved}) and particulate phosphorus (P_{particulate}), chemical oxygen demand (COD), ammonia nitrogen (NH₃-N), nitrate nitrogen (NO₃-N), nitrous nitrogen (NO₂-N) and total suspended solids (TSS). These parameters were determined by following standard methods (APHA 2005). Analytical determinations were carried out in duplicate on each sample and the average was calculated. Furthermore,

during the experimental study, the collected data on the influent and effluent from the plants were statistically analyzed using logarithmic and normal distributions to find the most representative; the average values reported here were obtained using this procedure.

Automatic devices were used for sampling. For the effluent, the sampling system consisted of 24 fixed volume bottles, each one filled hourly per a total time interval of 24 hours, in order to provide a composite sample. For the influent, instantaneous sampling was used, applied prior to the pre-treatments in a section where the stream was completely mixed in order to obtain a representative sample. The volume used for the analytical determinations was always 500 mL. These procedures were used for both plants. Samples were collected every 4 days, on average, over the 4-month period of investigation and stored at 4 °C temperature before analysis.

The Imhoff cone tests were also conducted in order to determine the volume occupied by the sludge after 30 min. The results obtained were expressed as mL/g SS.

RESULTS AND DISCUSSION

Anion exchange process efficiency

Figure 1 shows the average removal of total P measured in WWTP1 prior to and after the anion exchange resin dosage. The removal includes the effect of mechanical and biological treatments alone prior to the addition and then the added contribution of the ion exchange process.

Based on the statistical analysis of the historical data of the influent and effluent phosphorus concentrations prior to the addition of the P removal process (average of 4.4 mg/L and 0.58 mg/L, respectively), an average removal efficiency

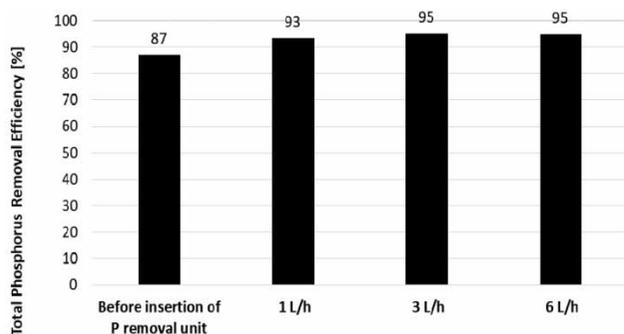


Figure 1 | Average removal efficiency of total P prior to and after the addition of the anion exchange process.

of 86.8% was calculated. Since the limit on the effluent is set at 2 mg/L total P, WWTP1 was capable of complying with the legal limits. However, beside the limit on the effluent, the WWTPs have also another limit to observe, i.e. the maximum number of excesses allowed per year in the effluent with respect to the limit. In the present case, the number is $(2/12) \times 100 = 17\%$, whereas before the addition of the P removal process it was 20%. Therefore, it was calculated that the goal for the maximum number of excesses could only be achieved by increasing the efficiency to 89.3%, which corresponded to an average P concentration in the effluent of 0.47 mg/L, using 4.4 mg/L as the average influent P concentration.

Figure 1 highlights that the addition of the anion exchange process enhanced P removal with respect to the previous period when it was due only to the mechanical and mainly biological (bacterial synthesis) processes; by increasing the dosage, the efficiency improved progressively from 93% to 95%. The beneficial effect obtained was far beyond the initial goal of 89.3%: this is likely to be attributed to the lower influent load entering the plant during the experimental period. Therefore, the dosage might be reduced to save the cost of the chemical; more generally, due to the wide variability of the influent characteristics, an automatic dosing system should be adopted, capable of adjusting the amount of resin to add based upon the required efficiency.

It is worth noting that during the experimental period, COD and ammonia nitrogen removal efficiency showed a decrease with respect to the average values measured in the past, as shown in Figures 2 and 3, respectively, due to lower influent concentrations; consequently, P removal due to only mechanical and biological processes decreased

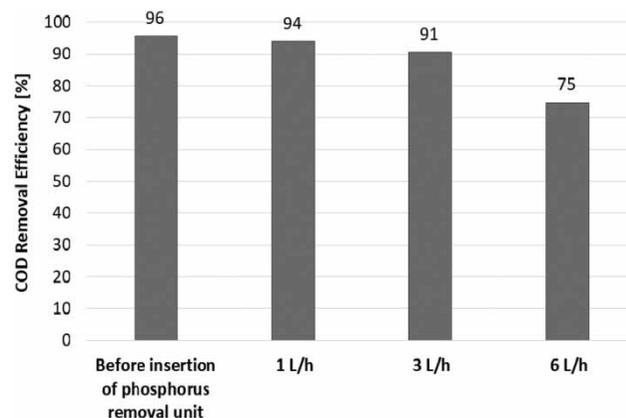


Figure 2 | Average COD removal efficiency prior to and after the addition of the anion exchange process.

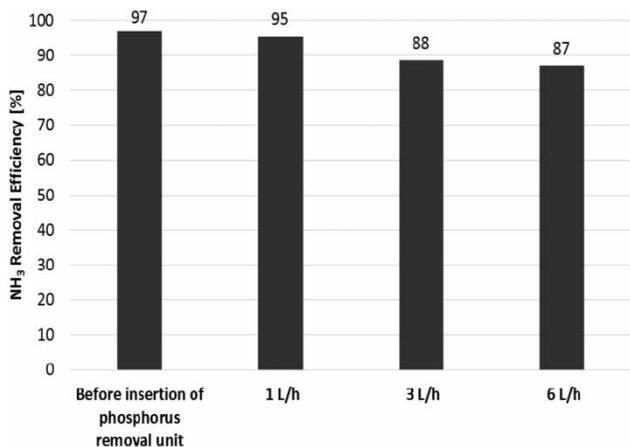


Figure 3 | Average NH₃ removal efficiency prior to and after the addition of the anion exchange process.

from 86.8% to 70%. Therefore, the real incremental improvement of P removal due to CATFLOC 441 addition accounted for a maximum of 25% (because $95 - 70 = 25\%$).

The phosphorus time-profile in the influent during the experimental period provided average concentrations of total and soluble fractions equal to 3.5 mg/L and 1.2 mg/L, respectively. These intervals are slightly lower than those recorded before the experimental period. In the effluent, total and dissolved phosphorus showed average values of 0.21 mg/L and 0.09 mg/L, respectively.

As mentioned above, during the experimental period the influent COD and ammonia nitrogen values were 195 mg/L and 23 mg/L, respectively, which are slightly below the historical data. The effluent concentrations of COD, ammonia, nitrate and nitrite nitrogen remained close to those recorded

before the addition of the resin and still far below the legal limits. Regarding TSS, the effluent concentration showed a slight increase after the resin addition, but the standard of 35 mg/L TSS was still always met.

By exploring the effect on the different phosphorus fractions, it was observed that a decrease of TSS removal efficiency in the secondary sedimentation led to a reduction of dissolved phosphorus removal: this is likely to have occurred because the larger amount of solids hindered contact between the orthophosphate ions and the ion exchange sites on the resin, thus reducing the efficiency of the process.

The Imhoff cone tests conducted with sludge samples collected at WWTP1 showed that the resin addition produced an improvement of sedimentation characteristics, as shown in Figure 4; in particular, the sludge volume measured after 30 min settling time decreased from an average of 187 mL/g SS prior to the addition of CATFLOC 441 to about 126 mL/g SS and then to 116 mL/g SS as the dosage was increased.

In terms of the effect on sludge production, an increase of about 25 kg/day was measured during the experimental period, which represents an extra of about 13% with respect to the average value recorded before. This additional amount of sludge was calculated to be approximately equal to the resin weight applied during the experimental work. It is worth noting that, based on the resin's technical data sheet, the removal process is carried out only through a transfer of ions between the bulk solution and the resin. Therefore, any extra sludge being produced represents the weight of the resin. These results suggest that for the future applications of the resin to WWTPs, additional

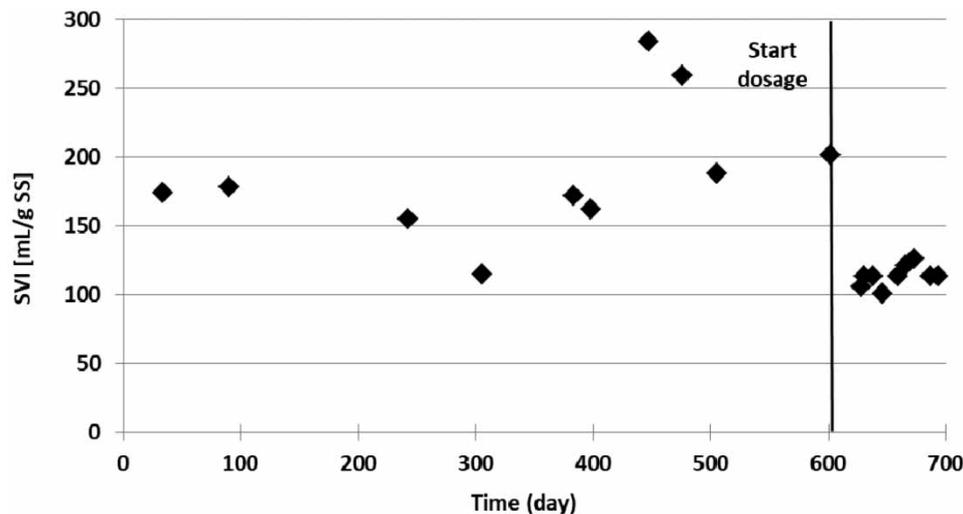


Figure 4 | Time-profile of sludge volume index (SVI) prior to and after the addition of the ion exchange process.

sludge production can be approximately predicted based upon the amount of resin added.

Chemical precipitation efficiency

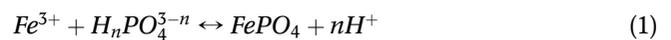
The average influent and effluent P concentrations in WWTP2 were statistically determined to be 6.2 mg/L and 1.4 mg/L, respectively, an average removal efficiency of 77.7%. The maximum number of excesses allowable with respect to the limit of 2 mg/L set for the effluent is still $(2/12) \times 100 = 17\%$, which requires the concentration to be reduced to 0.72 mg/L. As a consequence, the removal efficiency should be raised to 88% at least.

Different dosages of ferric chloride solution were tested in WWTP2 with the aim of finding the one that consistently helped to achieve this goal. The same dosage used for the resin in WWTP1, i.e. 6 L/hour, gave a total P removal efficiency of 78%, which was not enough. Therefore, the dosage was progressively increased to 12.6 L/hour, which was found to be the lowest leading to consistent compliance with the legal limits on the plant effluent. Figure 5 shows the effect of this addition on P removal. It can be observed that phosphorus content in the effluent was consistently lower than the limit. Furthermore, this value also guarantees to maintain the required efficiency even in the event of any change in the phosphorus content in the influent, as frequently observed in the past.

In terms of the main influent parameters monitored during the experimental period, total P, COD and ammonia-nitrogen showed average values of 6.2 mg/L, 303 mg/L and 38 mg/L, respectively, which were slightly lower than

the historical data recorded before; the effluent concentrations of COD, NH_3 , NO_2 and NO_3 did not change appreciably, remaining below the legal limits. In terms of TSS, a slight increase was observed, but the limit was still met. Therefore, the presence of chemical precipitation in WWTP2 did not produce any significant change in the removal of COD, NH_3 , NO_2 and NO_3 , as also observed in the case of WWTP1.

An increase of sludge production was recorded in WWTP2 during the experimental period, as in WWTP1. However, it was higher than in the previous case: indeed, at the optimal dosage of 12.6 L/hour it accounted for about 105 kg/day, which corresponds to an extra 17% with respect to the average historical data of plant operation. This value was ascribed to chemical sludge production and therefore corresponding to the following stoichiometric relationship:



Operating cost evaluation

The WWTPs investigated have similar lay-outs and received the same influent concentration of P on average. The influent was likely to have the same composition since they came from domestic sewage in both cases. Besides, the plants had to meet the same limit set for the effluent for P and encountered difficulties in complying with it consistently. Therefore, due to these similarities, it is likely that a similar dosage of either resin or ferric chloride would be required by both plants to achieve the same goal.

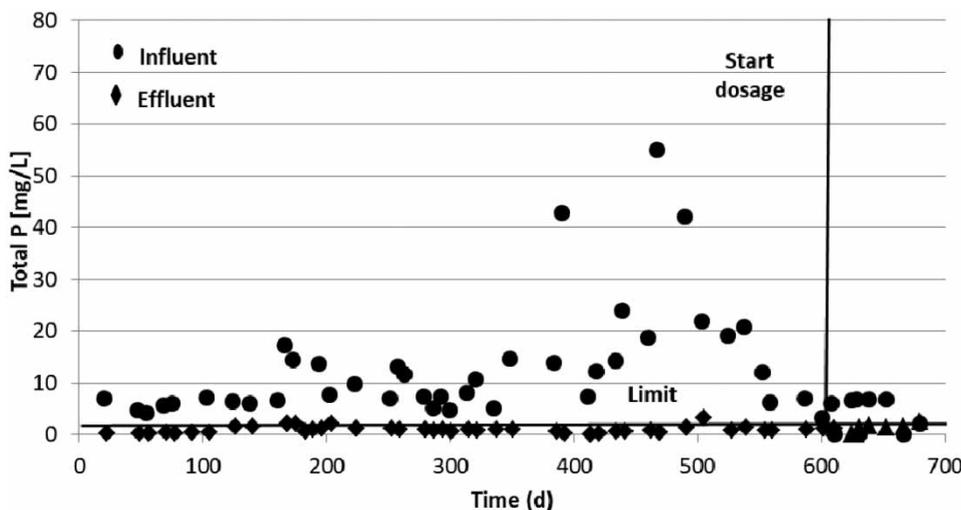
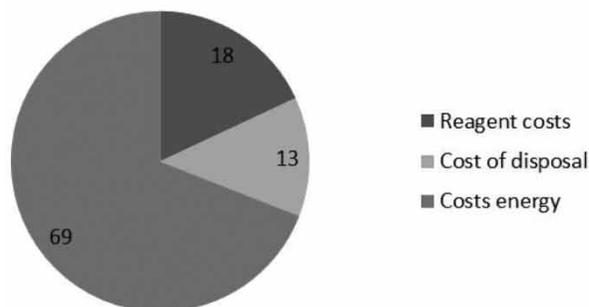


Figure 5 | Effect of ferric chloride addition on total P removal in WWTP2.

WWTP1: anion exchange process



WWTP2: chemical precipitation

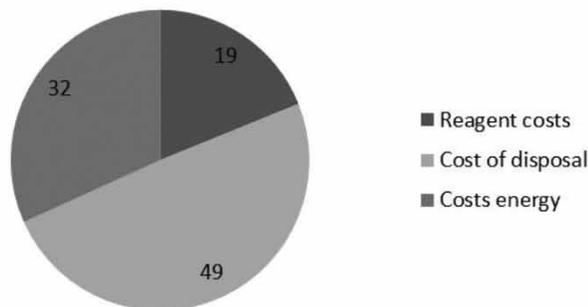


Figure 6 | Effect of cost items [%] for the two P removal technologies on the overall operating costs.

Comparison of operating costs of anion exchange and chemical precipitation processes was carried out for the following items: chemical purchase, energy consumption, sludge disposal. Personnel was not considered as it was deemed comparable.

The unit cost of reagent purchase was significantly different: 0.75 €/kg and 0.19 €/kg, for the resin and ferric chloride solution, respectively. However, due to the low dosage required for achieving the goal of removal, the effect of reagent cost in WWTP1 on the overall operating costs of the plant increased only by about 3%, whereas in WWTP2 it did not change significantly. It is worth noting that the treatment capacity of WWTP2 was much higher than that of WWTP1. As a consequence, in WWTP2 the unit cost of reagent per treated flow rate was not significantly affected and remained at approximately 11.5 €/m³ · day, whereas it increased from 6.2 €/m³ · day to 9 €/m³ · day in WWTP1. Energy consumption in both plants did not change significantly due to the addition of the pumps used for chemical dosage. Cost of energy consumption per unit of flow rate remained higher in WWTP1 than in WWTP2 due to the different treatment capacity.

In terms of sludge disposal costs, as mentioned above, implementation of the P removal processes led to additional sludge production in the plants. Due to the lower influent organic load recorded during the experimental period, sludge produced in the biological process and primary settlement (the latter in WWTP2 only) decreased slightly. Therefore, the total amount of sludge did not change significantly so the disposal costs remained at about 30 €/m³ · day in WWTP2 versus 7 €/m³ · day in WWTP1. It has to be highlighted that extra sludge has more impact in a plant such as WWTP2, where the cost of disposal is already high; besides, chemical precipitation led to greater sludge production than removal through the resin.

Figure 6 shows the percentage effect of each cost item on the overall operating costs for the two systems, calculated during the experimental period at the optimal dosage.

CONCLUSIONS

The experimental study conducted at full-scale WWTPs showed that at the same dosage and influent P concentration, the anion exchange process allowed the required removal efficiency to be achieved, whereas chemical precipitation was unable to ensure consistent compliance with the limit set on the effluent; to achieve this goal, a higher ferric chloride dosage had to be applied, which implied increased costs.

In terms of additional sludge production, the anion exchange process led to a significantly lower quantity than chemical precipitation. Furthermore, the resin addition also provided the advantage of an improvement in sludge settleability.

These results show that excess phosphorus can be efficiently removed from wastewater by means of the anion exchange resin tested in the present study. This process can be considered to be a valid alternative from the technical and economic points of view to the more common and well known chemical precipitation. Furthermore, the ion exchange process offers also the opportunity to recover P from the exhausted resin.

REFERENCES

- Acelas, N. Y., Martin, B. D., López, D. & Jefferson, B. 2015 Selective removal of phosphate from wastewater using hydrated metal oxides dispersed within anionic exchange media. *Chemosphere* **119**, 1353–1360.
- An, B., Nam, J., Choi, J. W., Hong, S. W. & Lee, S. H. 2013 Enhanced phosphate selectivity from wastewater using copper-loaded

- chelating resin functionalized with polyethylenimine. *Journal of Colloid Interface Science* **409**, 129–134.
- APHA 2005 *Standard Methods for the Examination of Water and Wastewater*, 21st edn. American Public Health Association, Washington, DC.
- Beccari, M., Passino, R., Ramadori, R. & Vismara, R. 1995 *Rimozione di azoto e fosforo dai liquami*. Hoepli, Milan, Italy.
- Blaney, L. M., Cinar, S. & SenGupta, A. K. 2007 Hybrid anion exchanger for trace phosphate removal from water and wastewater. *Water Research* **41**, 1603–1613.
- Caravelli, A. H., Contreras, E. M. & Zaritzky, N. E. 2010 Phosphorous removal in batch systems using ferric chloride in the presence of activated sludges. *Journal of Hazardous Materials* **177** (1–3), 199–208.
- EC 1998 *European Commission Directive 98/15/EC of 27 February 1998, Amending Council Directive 91/271/EEC on Urban Wastewater treatment*. Official Journal of the European Communities L67/29.
- Egle, L., Rechberger, H. & Zessner, M. 2015 Overview and description of technologies for recovering phosphorus from municipal wastewater. *Resources, Conservation and Recycling* **105** (Part B), 325–346.
- Genz, A., Kornmüller, A. & Jekel, M. 2004 Advanced phosphorus removal from membrane filtrates by adsorption on activated aluminium oxide and granulated ferric hydroxide. *Water Research* **38**, 3523–3530.
- Helferich, F. 1995 *Ion Exchange*. Dover Publications, Inc., New York, USA.
- Jarvie, H. P., Neal, C. & Withers, P. J. A. 2006 Sewage-effluent phosphorus: a greater risk to river eutrophication than agricultural phosphorus? *Science of the Total Environment* **360** (1–3), 246–253.
- Metcalf & Eddy, Tchobanoglous, G., Stensel, H. D., Tsuchihashi, R., Burton, F. L. 2013 *Wastewater Engineering: Treatment and Resource Recovery*. McGraw-Hill Education, USA.
- Nur, T., Johir, M. A. H., Loganathan, P., Nguyen, T., Vigneswaran, S. & Kandasamy, J. 2014 Phosphate removal from water using an iron oxide impregnated strong base anion exchange resin. *Journal of Industrial and Engineering Chemistry* **20** (4), 1301–1307.
- Sengupta, S. & Pandit, A. 2011 Selective removal of phosphorus from wastewater combined with its recovery as a solid-phase fertilizer. *Water Research* **45**, 3318–3330.
- Van Kauwenbergh, S. J. 2010 'The Manufacture of Phosphate Fertilizers' in *World Phosphate Rock Reserves and Resources*. International Fertilizer Development Center (IFDC), Muscle Shoals, AL, USA.

First received 13 May 2019; accepted in revised form 15 January 2020. Available online 24 January 2020