
**Phosphorus recovery from phosphonate-contaminated
wastewater by nonthermal plasma treatment prior to adsorption
on granular iron-coated sand**

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Abstract

Phosphonate contamination of water resources has drawn much attention.
Advanced oxidation combined with phosphorus recovery is considered as a promising

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solution, but the development of a cost-efficient process remains challenging. This work demonstrates an effective two-step process including a plasma-based oxidation of phosphonate, followed by phosphate adsorption on granular iron-coated sand (ICS). In the first step, a tandem reactor configuration, which consists of a dielectric barrier discharge (DBD) plasma chamber and an ozonation chamber, was used to transform 1-hydroxyethane-1,1-diphosphonic acid (HEDP) to Ortho-phosphate (Ortho-P). When lava rock was added as a packing material in the ozonation chamber, the Ortho-P production was enhanced by 10-35%, due to an increased exposure of reactive species (O_3 , $\bullet OH$ and $O_2\bullet^-$) by 120%, 20% and 30%, respectively. The use of O_2 as carrier gas in the plasma reactor resulted in the highest Ortho-P production efficiency (86%), followed by Ar (48%), N_2 (21%) and air (13%). Humic acids present in the wastewater can compete with phosphonates for reactive species, decreasing the Ortho-P production efficiency by 30%. In the second step, ICS granules were used to adsorb the produced Ortho-P. The final recovery efficiency of Ortho-P from synthetic and real textile wastewater was 85% and 53%, respectively. The treatment performance of this novel two-step process is better compared to that of ozone-based AOPs, while the associated operational treatment costs are still somewhat higher. This indicates that optimizing energy consumption is still the biggest challenge for further industrial applications of nonthermal plasma-based AOPs.

Keywords

Adsorption, Advanced oxidation, Lava rock, Nonthermal plasma, Ozonation, Phosphonate

1. Introduction

Phosphorus is an essential yet non-renewable element for plant growth. However, excess phosphorus content in water bodies can lead to aquatic plant flourishing and eutrophication [1-3]. At present, the production of phosphorus is mainly obtained by decomposing phosphate ore, but this process is energy-intensive, environmentally harmful, and costly [4]. Removal and/or recovery of phosphorus from wastewater is regarded as a promising strategy to lower the burden of phosphorus production and prevent aquatic eutrophication.

As dissolved organic phosphorus in wastewater, phosphonate is toxic and low-biodegradable [5]. Phosphonate is widely used in industrial production and domestic life, which leads to the presence of phosphonates in industrial (such as papermaking wastewater, textile wastewater) and municipal wastewater [6]. Traditional processes (such as adsorption, coagulation/flocculation, biological treatment) cannot effectively remove phosphonate [2, 7]. The conversion of phosphonate to Ortho-P is therefore advisable to achieve a good total phosphorus (phosphonate + Ortho-P) removal.

In recent years, advanced oxidation processes (AOPs) and their derivatives have

attracted significant attentions in the conversion of phosphonates to Ortho-P. Examples include electrochemical processes, ozonation, UV/Fe(II)/H₂O₂, UV/peroxydisulfate (PDS) and UV/chlorine processes [8-12]. The C-P bond in phosphonate is very stable and not easily to be broken by AOPs [13, 14]. The Ortho-P production efficiency is limited (< 60%). UV can promote the degradation of phosphonates, but the use of UV usually leads to an increase in the associated costs of wastewater treatment. The production and accumulation of iron-containing sludge in Fe-based process also causes an increase in sludge disposal costs [15]. Ozonation was already used to degrade 1-hydroxyethane-1,1-diphosphonic acid (HEDP) [11]. However, the reaction rate constant of HEDP with ozone (O₃) is low (approximately 0.58 M⁻¹s⁻¹) [16], and a long treatment time (> 90 min) and high O₃ dosages (> 18 mg/(min L_{water})) are accordingly required [11]. As such, there is a need to develop a more effective process to facilitate the conversion of phosphonate to Ortho-P.

Different from all the above-mentioned technologies, nonthermal plasma-based advanced oxidation processes (AOPs) are an innovative technology for wastewater remediation [17-19]. Nonthermal plasma-based AOPs have the advantages of strong oxidation ability, short treatment time, no external additives, and no secondary pollution [20, 21]. It is considered to be a composite of various oxidation processes such as ozone oxidation, photocatalysis and ultrasonic degradation. Both short living radicals ($\bullet$ OH, O₂ $\bullet^-$, ¹O₂) as well as longer-life oxidants (H₂O₂ and O₃) are produced in the nonthermal plasma reactor. Their lifetimes are shown in Table S1 (SI).

When applying the nonthermal plasma-based technology to treat textile wastewater containing phosphonates, enhancing the mass transfer of reactive species from the gas phase to the liquid phase might be an effective solution to lower energy consumption and increase Ortho-P production efficiency. Lava rock generated by the cooling of magma is a ubiquitous mineral on Earth [22]. It is a low-cost mineral and consists of different minerals including bentorite ($\text{Ca}_6\text{Cr}_2(\text{SO}_4)_3(\text{OH})_{12.26}\text{H}_2\text{O}$), halloysite ($\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 \cdot 2\text{H}_2\text{O}$), maghemite (Fe_2O_3) and diopside ($\text{Ca}(\text{Mg},\text{Al})(\text{Si},\text{Al})_2\text{O}_6$) [22]. Its notable characteristics include high porosity, mechanical strength, and adsorption capacity, as well as containing various metal oxides. Lava rock with porous properties and uneven surface can effectively enhance the gas/liquid mass transfer efficiency. Indeed, the presence of lava rock in an ozone reactor prolongs the residence time of O_3 , which is helpful to enhance the O_3 exposure. Metal oxides are important compounds in lava rock, which can work as Lewis centers and accelerate ozone decomposition into free radicals (i.e. $\cdot\text{OH}$, $\text{O}_2\cdot^-$, $^1\text{O}_2$) [23]. Based on this, it can be assumed that the addition of lava rock might increase the O_3 mass transfer and improve the Ortho-P production efficiency correspondingly.

Iron-coated sand (ICS) granules are a solid waste material produced when iron is removed during drinking water production from ground water [24]. A previous work reported that 99% of Ortho-P removal efficiency was achieved and maintained when ICS granules were used as adsorbents in a full-scale test after nearly 400 days of operation [24]. Adsorption on ICS granules has many advantages for the recovery of

Ortho-P, including high adsorption capacity, no sludge generation, ease of operation, and low cost [25]. Therefore, the use of ICS granules in a second step is proposed to adsorb and sequentially recover the produced Ortho-P.

Different from previous studies, this work demonstrates a two-step process aimed at recovering phosphorus resources from textile wastewater rather than simply degrading phosphonates. In the first step, a tandem reactor configuration which consists of a dielectric barrier discharge (DBD) plasma chamber and an ozonation chamber packed with lava rock connected in series is used to degrade phosphonate and produce Ortho-P. Compared with previous plasma reactor, the tandem reactor configuration has a high utilization of reactive species due to the presence of ozonation chamber. This is due to the longer-life oxidants (H_2O_2 and O_3) that degrades the pollutants in the ozonation chamber. In the second step, the goal is to investigate the adsorption of the Ortho-P obtained after the degradation of phosphonates on ICS granules in view of phosphorus recovery.

2. Materials and Methods

2.1 Textile wastewater and chemicals

Textile wastewater was collected from a textile company in Ronse (Belgium) and stored at 4 °C before use. Properties of the textile wastewater used in this work are shown in Table 1. Textile and synthetic wastewater were spiked 333 mg L⁻¹ HEDP (i.e.,

the P content is 100 mg L⁻¹), respectively. The concentration (100 mg L⁻¹) is similar to other studies and in line with industrial waste water concentration [11].

Table 1. Here.

Lava rocks were provided by the Disaghor Group (Belgium), and their diameter and density are 8-16 mm and 1.10 g cm⁻³, respectively. The ICS granules were obtained from the Provincial and Intercommunal Drinking Water Company (Pidpa, Belgium), and their diameter and density are 2-5 mm and 1.23 g cm⁻³, respectively. Detailed descriptions of the lava rocks and ICS granules used in this study, such as data from Fourier Transform infrared spectroscopy (FTIR) and X-ray diffraction (XRD), can be found in our previous work [11].

2.2 Setup and experimental procedures

2.2.1 Plasma degradation

A schematic of the reactor is shown in Figure. 1. The reactor consists of a plasma chamber (see the right part of Figure. 1) and an ozonation chamber that can be packed with lava rock (see the left part of Figure. 1). For the plasma chamber, a stainless-steel tube was used as the ground inner electrode, and was set inside of a quartz tube. The surface of the grounded electrode was coated with a porous Cr₂O₃ layer of about 300 μm coated by Aalberts Surface Technologies Beuningen B.V. Additional details of the experimental set-up can be found in our previous work [26-30]. For the ozonation

chamber, 1 kg lava rock was randomly packed in the ozonation chamber, and the height of the packing material was approximately 50 cm.

Figure 1. Here.

Since the pH of textile wastewater containing HEDP was close to neutral (See Table 1), also the initial pH of the synthetic wastewater was adjusted to 7.0. Wastewater (500 mL) was added into the ozonation chamber, ensuring that all the lava rock was submerged. Prior to addition, the lava rock used in this study was saturated with Ortho-P, as described in Text S1 of Supporting Information, SI. Wastewater flowed from the ozonation chamber entering the plasma chamber through the inner channel of the stainless-steel tube at a liquid flow rate of 100 mL min⁻¹. Then, the liquid flowed out on the top of the stainless-steel tube, forming a water-falling film on the porous Cr₂O₃ layer. The wastewater was cycled over the ozonation and plasma chambers. The carrier gas entered the reactor from the bottom of the plasma chamber at a gas flow rate of 0.6 standard liter per minute (SLM), and reactive species were generated in the plasma zone. The gas containing reactive species entered the ozonation chamber through an aeration device. The discharge power and duty cycle were set at 80 W and 12.5%, respectively, and their definition and calculation were given in Text S2, SI. The wastewater was sampled at a pre-set reaction time (8, 16, 24, 32 and 40 min). The Ortho-P production efficiency (R) was defined as follows:

$$R = \frac{c_t}{c_0} * 100\% \quad (1.)$$

where c_0 is the initial Total-phosphorus (Total-P) concentration in synthetic and

real textile wastewater (100 mg L⁻¹) and c_t (mg L⁻¹) is the concentration of Ortho-P in synthetic and real textile wastewater.

Control experiments were performed at the same operational parameters without lave rocks. All experiments were performed in triplicate, and error bars represent the standard deviation on the average of triplicate experiments.

2.2.2 ICS granules adsorption

After the textile and synthetic wastewater was treated in the plasma reactor, the generated Ortho-P was adsorbed by ICS granules. A volume of 200 mL synthetic HEDP wastewater or real textile wastewater containing HEDP were filled into a 500 mL flask containing 2.0 g ICS granules after the plasma treatment. Next, the flask was shaken at a stirring rate of 150 rpm for 48 h. At the designed time, the concentration of Ortho-P and Total-P in wastewater were analyzed. The Ortho-P recovery efficiency (%) of the wastewater containing HEDP was calculated by Eq. (3):

$$\text{Ortho-P recovery efficiency} = \frac{c_{0, \text{phosphate}} - c_{t, \text{phosphate}}}{c_{0, \text{HEDP}}} \times 100\% \quad (3)$$

where $c_{0, \text{phosphate}}$ (mg L⁻¹) is the initial concentration of Ortho-P. $c_{t, \text{phosphate}}$ (mg L⁻¹) is the concentration of Ortho-P at a given adsorption time. $c_{0, \text{HEDP}}$ (mg L⁻¹) is the initial HEDP concentration before plasma treatment.

2.3 Analytical methods

The titaniumoxysulphate method was used to determine the concentration of H₂O₂

in the liquid phase [31]. The ozone in liquid phase was determined by the indigo method [32]. $\int [\text{O}_3]dt$ and $\int [\text{H}_2\text{O}_2]dt$ represent the exposures of O_3 and H_2O_2 respectively, and are measured from the time-integrated concentration of O_3 and H_2O_2 over the reaction time [33]. The exposures of free radicals (e.g. $\cdot\text{OH}$, $\text{O}_2\cdot^-$ and $^1\text{O}_2$) were determined by probe-based kinetic models, and the detailed procedures can be found in Text S3, SI [34-36]. In a preliminary experiment, wastewater with and without probe chemicals was treated by plasma alone in order to study the effect of probe chemicals on the phosphate production efficiency. The presence of the probes did not make a significant difference in the production efficiency of phosphate, as shown in Figure S3. It indicates that probes do not compete for reactive species with phosphonates because the concentration of probe chemicals is very low.

The commercial Hach test kits were used together with an UV-vis spectrophotometer (DR2800, Hach, Belgium) to measure the concentration of Ortho-P (P-PO_4^{3-}), total phosphorus (TP), nitrite (NO_2^-), nitrate (NO_3^-), sulfate (SO_4^{2-}), and Chemical Oxygen Demand (COD), according to standard methods. The pH of the wastewater was measured using a portable pH meter (HQ30d, HACH, US).

3. Results and Discussion

3.1 Production of Ortho-P in the plasma system

3.1.1 Effect of the carrier gas composition

The effect of using different carrier gasses (Ar, N₂, Air, O₂) on the Ortho-P production efficiency was studied. The use of different carrier gases affects the discharge mode and strength. As such, the input voltage was changed to keep the discharge power stable. Figure 2 shows that the Ortho-P production efficiency in O₂ atmosphere was the highest after 40-min reaction (86%), followed by Ar (48%), N₂ (21%) and air (13%).

According to previous studies, different carrier gases in a plasma system can result in generating different reactive species [37-40]. Reactive oxygen species (ROS) are considered as the main working species for the degradation of pollutants. An O₂ plasma promotes the generation of ROS, yielding higher ROS content in an O₂ plasma than in an Ar, air and N₂ plasma. Despite use of Ar or N₂ as the feed gas, the plasma gas also contains considerable amount of water vapour (due to water evaporation and sputtering) that results in generation of ROS in Ar and N₂ atmosphere. Highest ROS production is expected in oxygen environment, this explains why the Ortho-P production efficiency after treatment with an O₂ plasma is the highest. Shang et al. studied the degradation mechanisms of Acid Orange 7 treated by an Ar plasma, and they found that Ar*, Ar⁺

and $\bullet\text{OH}$ are the main reactive species in Ar plasma reactors, but also O_3 , H_2O_2 , and other reactive species can be generated, which is beneficial to degrade pollutants [41]. Generally, the amount of O_3 produced is very small in an Ar plasma, which may be an important reason why the ability of an Ar plasma to degrade pollutants is not as good as that of an O_2 plasma. When using N_2 as plasma carrier gas, such ROS can be produced due to the reaction of high-energy electrons and water molecules [41]. Shen et al. observed that the $\bullet\text{OH}$ generation efficiency of an O_2 plasma system was about 45% higher than that of air plasma [37]. Lukes et al. found that the efficiency of O_3 generation was reduced by 25% when the carrier gas was switched from O_2 to air [38]. Wang et al. reported that O_2 plasma treatment has 40-70% higher H_2O_2 generation efficiency than Ar, N_2 and air plasma treatment [39]. Chandana et al. found that a liquid H_2O_2 concentration of 50, 16 and 7 mg L^{-1} during Ar, N_2 and air plasma treatment, respectively [40]. Therefore, the low Ortho-P production efficiency in the Ar, N_2 and air plasma system might be because the amount of ROS (e.g., O_3 , H_2O_2 and $\bullet\text{OH}$) is reduced. When the gas atmosphere contains nitrogen, reactive nitrogen species (RNS) are produced. As shown in Table S3, ROS normally have a higher oxidation potential than RNS. The decrease of ROS and generation of RNS is thus limiting the Ortho-P production. To understand the lowest Ortho-P production efficiency in an air plasma, the pH of the treated wastewater should be considered. The pH changed to 5.33, 4.77, 4.44 and 4.07 in the O_2 , Ar, N_2 and air plasma treatment system, respectively, indicating that the highest level of H^+ was produced in the air atmosphere. The presence of

nitrogen results in the generation of H^+ , as shown in Eq. (2) - (3), and H^+ consumes ROS (as shown in Eq. (4) - (6)). The conductivity of wastewater treated by O_2 , Ar, N_2 and air plasma was increased from 4.40 to 4.81, 4.75, 4.75 and 4.80 $mS\ cm^{-1}$, respectively, which confirms the generation of Ortho-P and RNS.



It is worth to mention that the generation of RNS not only has a negative effect on the Ortho-P production, but also increases the wastewater treatment challenges. The total concentration of nitrate and nitrite in the liquid phase after N_2 and air plasma treatment was 271 and 285 $mg\ L^{-1}$, respectively (See Figure S1, SI). The EU Nitrate Directive (91/676/EEC) stipulates that the maximum allowable concentration of NO_X^- in surface water and groundwater is 50 $mg\ L^{-1}$ [29]. Therefore, additional treatment costs will be required to remove these nitrogen components before N_2 and air plasma treated wastewater is discharged into the receiving water.

Overall, based on the above observations, O_2 was selected as the carrier gas for the rest of the experiments.

Figure 2. Here.

3.1.2 Role of lava rock packing on Ortho-P production

Real textile and synthetic wastewater were fed to the combined plasma-ozonation system with/without the addition of lava rock, and the Ortho-P production efficiency was measured as shown in Figure 3. Compared with synthetic wastewater, real textile wastewater has a more complex inorganic and organic composition. Inorganic ions can quench free radicals, and organic matter can compete with HEDP for reactive species. Hence, the Ortho-P production efficiency was 10-30% lower (after e.g. 40-min reaction time) in real textile wastewater than that in synthetic HEDP wastewater.

When the lava rock was added into the ozonation chamber, the Ortho-P production efficiency in synthetic wastewater rapidly reached up to 86% after 40-min treatment, and gradually further increased to 93% after 90-min treatment. HEDP can be oxidized by reactive species (such as $\cdot\text{OH}$, $\text{O}_2\cdot^-$, $^1\text{O}_2$, H_2O_2 , O_3), and most of the Ortho-P could be generated within 40-min of reaction. Longer reaction times cause a higher energy consumption. The Ortho-P production efficiency in the plasma reactor with lava rock was 10-35% (after e.g. 40-min reaction time) higher than without lava rock. This difference is valid for both synthetic and real textile wastewater. This might be because the presence of lava rock promoted the mass transfer of reactive species, and thus the reaction rate was enhanced.

Figure 3. Here.

3.1.3 Role of lava rock packing on reactive species exposure

To investigate the occurring enhancement mechanisms, the exposure of reactive species in the plasma reactor with and without lava rock packing in the ozonation chamber was measured for 40 min of reaction with HEDP-containing synthetic wastewater. As shown in Figure 4 (A), the presence of lava rock increased the O_3 exposure from 7.7×10^{-2} to 16.7×10^{-2} (M s). According to previous studies, the O_3 mass transfer from gas phase to liquid phase is limited in a conventional bubble reactor, while the addition of lava rock packing can promote O_3 gas dissolving into water and thus increasing the O_3 exposure in the water phase [42]. As such, the presence of lava rock with porous properties and uneven surface can effectively prolong the residence time of O_3 in the reactor, which is helpful to enhance the O_3 exposure. The increase of O_3 exposure is conducive to form $\bullet OH$ and $O_2\bullet^-$, as the exposures of $\bullet OH$ and $O_2\bullet^-$ increase from 4.4×10^{-11} and 3.0×10^{-10} to respectively 5.3×10^{-11} and 4.0×10^{-10} (M s) (See Figure 4 (C, D)). The overall enhancement of the free radical exposure is mainly attributed to the catalytic activity of lava rock. Metal oxides are important compounds in lava rock, which can work as Lewis centers and accelerate ozone decomposition into free radicals (i.e. $\bullet OH$, $O_2\bullet^-$, 1O_2) [23]. In previous research, we found that the valence state of Fe varies after ozonation, and the content of Fe (II) was reduced and that of Fe (III) obviously increased after ozonation [43]. It confirms that Fe elements in lava rock are involved in the catalytic ozonation reactions. In addition, lava rock can catalyze the

decomposition of H_2O_2 and promote the formation of $\cdot\text{OH}$ [44, 45]. In contrast, the addition of lava rock reduced the H_2O_2 exposure from 36.2×10^{-2} to 10.5×10^{-2} (M s) (See Figure 4 (B)). It can be hypothesized that, due to the high solubility of H_2O_2 , the presence of lava rock showed no significant influence on the H_2O_2 mass transfer, while the iron oxide-based catalysts can promote the decomposition of H_2O_2 to form $\text{O}_2\cdot^-$ [46]. This can explain the decrease in H_2O_2 exposure while the $\cdot\text{OH}$ and $\text{O}_2\cdot^-$ exposures were increased by lava rock. The $^1\text{O}_2$ exposure was slightly reduced from 13.9×10^{-9} to 12.3×10^{-9} (M s) (See Figure 4 (E)). It is possible that $^1\text{O}_2$ in the liquid phase reacts with some components in the lava rock. However, this assumption requires further investigation.

Lava rock can catalyze the ozonation processes repeatedly. Our previous works have proven that the Fe elements in lava rock that has been reused for five times still have an excellent catalytic effect on the ozonation process [43]. The catalytic activity of the lava rock stops when all Fe (II) is oxidized to Fe (III).

Figure 4. Here.

3.1.4 Comparison of different operational modes

Synthetic wastewater containing HEDP was treated by 5 different operational modes using the same reactor setup, i.e. (i) plasma & packed ozonation chamber, (ii) plasma & ozonation chamber without packing, (iii) plasma alone, (iv) packed ozonation chamber alone, and (v) ozonation chamber without packing. The detailed procedures

for these 5 operational modes of the reactor are given in Text S4, SI.

When the wastewater was treated only by the ozonation chamber without packing, the Ortho-P production efficiency was the lowest (18%). There are mainly long-lived oxidants such as H_2O_2 and O_3 in the ozonation chamber, and a small amount of short-lived free radicals are mainly formed by the decomposition of H_2O_2 and O_3 . H_2O_2 has a low reactivity towards different pollutants [47] and O_3 has also been shown to be very low reactive towards HEDP [16]. As such, the Ortho-P production in the ozonation chamber mainly resulted from the $\bullet\text{OH}$ that were generated from the decomposition of H_2O_2 or O_3 . However, the decomposition of H_2O_2 or O_3 in a conventional bubble column is limited. When adding lava rock in the ozonation chamber, the exposure of O_3 increased from 4.1×10^{-2} to 14.1×10^{-2} (M s) (See Figure 5 (B)). This favored the generation of $\bullet\text{OH}$ and ultimately resulted in a higher Ortho-P production efficiency (39%).

When the wastewater was treated by plasma alone, the production of Ortho-P was closely attributed to the reactive species $\bullet\text{OH}$, $\text{O}_2\bullet^-$ and $^1\text{O}_2$. These ROS have a strong oxidation potential and can directly attack the molecular structure of HEDP. In addition, the exposure of O_3 in wastewater treated by plasma alone reached 7.7×10^{-2} (M s), which was higher than that treated by ozonation alone. The Ortho-P production efficiency was similar as in case of using only the packed ozonation chamber (39%).

When the wastewater was treated by plasma & ozonation system without packing, HEDP could react with different reactive species, including $\bullet\text{OH}$, $\text{O}_2\bullet^-$, $^1\text{O}_2$, H_2O_2 and

O₃ in the plasma and ozonation chamber. As such, the Ortho-P production efficiency reached 51%, which is higher than operated by plasma alone. This is because the utilization of ROS when using plasma alone is lower. For some long-living ROS (H₂O₂ and O₃) the reaction time in the plasma chamber is too short to participate in HDEP degradation. These long-living ROS were released with the gas phase and are introduced in the ozonation chamber. The highest Ortho-P production efficiency (86%) was achieved in the plasma & packed ozonation chamber. As described in Section 3.1.1, when using this reactor configuration, the O₃, •OH and O₂^{•-} exposures were respectively increased by 120%, 20% and 30% compared to the plasma & ozonation configuration without packing, which explains the higher efficiency.

The production kinetics of Ortho-P for the 3 different processes are shown in Figure S4. The synergistic index of Ortho-P production between plasma and ozonation was calculated to be 1.88. Therefore, the plasma & packed ozonation system have a strong synergistic effect on the conversion of phosphonate to Ortho-P.

Figure 5. Here.

3.1.5 Effect of wastewater composition on Ortho-P production

The composition of real textile wastewater is complex, and wastewater from different sources often exhibit different pH and different composition [48]. Therefore, synthetic wastewater was treated at different initial pH, and the results are shown in Figure 6 (A). In comparison to acidic wastewater, the Ortho-P production efficiency in

the alkaline wastewater treated by plasma-ozonation reactor increased by about 15%. Liu et al. observed that when the initial pH of the wastewater increased from 2.0 to 10.0, the degradation efficiency of acid orange 7 increased by 40% after treatment with non-thermal plasma-based AOPs [49]. Protons consume a lot of high-energy electrons under acidic conditions, which prevents the formation of $\bullet\text{OH}$ and O_3 . The generation of $\bullet\text{OH}$ in an alkaline environment is promoted, which is conducive to degrade contaminants [50]. The pH value of wastewater decreased with the reaction time (See Figure S5), indicating that acidic substances (H^+) were generated during Ortho-P production which lowers its efficiency. Therefore, controlling the pH of wastewater during the reaction may be an effective way to increase the Ortho-P production efficiency in full-scale applications.

Figure 6. Here.

Additionally, the effect of co-existing components (i.e., humic acids, nitrate, sulfate, carbonate) on the Ortho-P production efficiency was studied. After 40-min reaction, the Ortho-P production efficiency was reduced from 86% to 57% when the synthetic wastewater contained 100 mg L^{-1} humic acids. Humic acids, ubiquitously present in real wastewaters, can thus compete with phosphonates for reactive species, thereby reducing the Ortho-P production efficiency. When the wastewater containing humic acids was treated by lava rock adsorption, approximately 20% of the humic acids was removed (See Figure S6). The adsorption capability of lava rock for humic acids was limited. When treating wastewater containing only humic acids by plasma &

ozonation system, their removal efficiency can reach 85%. In case wastewater containing both humic acids and HEDP was treated at the same operational conditions, the removal efficiency of humic acids reduced by 10%, which indicates that the competitive degradation behavior of humic acids and phosphonates not only affects the Ortho-P production efficiency but also the humic acids removal efficiency. When high concentrations of co-existing ions (i.e., nitrate, sulfate, carbonate, 100 mg L⁻¹) were added to the synthetic wastewater, the Ortho-P production efficiency was reduced by about 10% (See Figure 6 (B)). Also, co-existing ions thus consume reactive species, restricting the degradation of phosphonates, although the effect is less significant than that caused by humic acids.

3.1.6 Economic analysis

The cost of the treatment depends on the treatment time and the discharge power of the plasma reactor (80 W). The electricity cost is assumed to be 0.18 € per kWh. When the treatment time was 40 and 90 min, the Ortho-phosphate (Ortho-P) production efficiencies were 86% and 92%, respectively. Thus, the costs for producing 1 ton of Ortho-P were € 450 and € 220, respectively. These values are compared with the operational costs of other AOPs – as reported in literature – in Table 2 [8, 10, 11]. Compared with UV and ozone-based AOPs, a clearly higher efficiency and a shorter treatment time were obtained in the plasma-ozonation reactor with lava rock packing used in this study, showing its great potential in promoting the conversion of HEDP

into Ortho-P. However, the treatment cost in this work is still somewhat higher than that of ozone-based AOPs. It indicates that the high energy consumption is still the biggest barrier to implement nonthermal plasma-based AOPs in industrial applications.

Table 2. Here.

3.2 Adsorption of Ortho-P on ICS granules

To recover phosphorus from phosphonate-containing wastewater, ICS granules were used to adsorb the generated Ortho-P from both real textile and synthetic wastewater after plasma-ozonation treatment. After 48-h of ICS adsorption, the Ortho-P adsorption efficiency from real textile and synthetic wastewater reached up to 79% and 92%, respectively (See Figure S7). It has been reported that ICS granules have a strong adsorption capacity for Ortho-P [11, 24]. The inorganic ions and organic matter present in real textile wastewater may occupy, however, adsorption sites of ICS granules, leading to a decreased Ortho-P adsorption efficiency by 10%.

Overall, after treatment the phosphonate-containing wastewater with the proposed two-step process of plasma-ozonation and ICS adsorption, an effective phosphorus removal and recovery strategy was achieved. The final recovery efficiency of Ortho-P from real textile and synthetic wastewater was calculated by multiplying the Ortho-P production efficiency and adsorption efficiency, and reached up to 53% and 85%, respectively. Yang et al. developed a similar two-steps process including an ozone degradation step (using a packed ozone reactor) followed by adsorption on granular

iron-coated sand (ICS) to recover Ortho-P from synthetic phosphonate-contaminated wastewater. The Ortho-P recovery efficiency when using synthetic wastewater was 60-65% [11]. The higher recovery efficiency of Ortho-P obtained in this work can be attributed to the effective plasma reactor and the enhanced mass transfer of reactive species in the ozonation chamber. However, the complexity of the real textile wastewater composition (including humic acids, coexisting ions, etc.) reduces both the Ortho-P production and adsorption, making future research necessary focusing on how to tackle this issue. For example, some additional oxidants such as hydrogen peroxide and persulfate may be combined with nonthermal plasma-based AOPs, which could further enhance the treatment of complex textile wastewater.

4. Conclusions

A two-step process combining a non-thermal plasma and ozonation treatment followed by adsorption on ICS granules was developed to recover Ortho-P from phosphonate-contaminated wastewater. The carrier gas composition has a significant impact on the generation of reactive species (ROS), and a O₂ plasma provides the highest Ortho-P production efficiency, followed by Ar plasma, N₂ plasma, and air plasma. During plasma-ozonation treatment, the Ortho-P production efficiency in both synthetic and real textile wastewater increased by 15-35% when lava rock packing is added in the ozonation chamber, which could be explained by a 120%, 20% and 30%

higher exposures of respectively O_3 , $\bullet OH$ and $O_2\bullet^-$. Compared to a conventional plasma reactor, the coupling with an ozonation chamber and the use of lava rock packing herein increase the utilization efficiency of the formed reactive species. Therefore, the Ortho-P production efficiency was clearly the highest (86%) when a non-thermal plasma reactor and packed ozonation chamber was used, as compared to a plasma & ozonation chamber without packing (51%), plasma alone (39 %) $\approx$ packed ozonation chamber alone (39%), and only an ozonation chamber without packing (18%). Maintaining a high pH during the degradation process is helpful to promote the conversion of phosphonate to Ortho-P. The presence of humic acids resulted in about 20% reduction in phosphate production efficiency compared to other coexisting ions. ICS granules show a good potential to recover the produced Ortho-P after plasma-ozonation treatment, as exemplified by an overall recovery efficiency of Ortho-P of 53% and 85% from HEDP-containing real textile and synthetic wastewater, respectively.

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