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Using aluminum-doped magnetic nanoparticles for total phosphorus removal in poultry processing wastewater

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ABSTRACT

Poultry processing wastewaters contain high levels of contaminants and need to be treated before being discharged. In this study, wastewater samples from a poultry processing plant were collected, characterized, and treated with aluminum-doped magnetic nanoparticle to remove phosphorus species. Each sample was taken from different points along the treatment process so that the efficacy of each operation could be assessed. This assessment was mainly focused on phosphorus (P) speciation analyses to monitor the changes and removal of P species after each treatment step. It was observed that the distribution of P species changed significantly along the wastewater treatment process. Total phosphorus (TP) ranged from 4 to 56 ppm and the percentages of total soluble phosphorus species varied from 40% to 94% of TP depending on the stage of the wastewater treatment process. Particularly, the bioavailable, soluble reactive phosphorus (sRP) varied from 0% to 42% of TP along the process. Treatment of wastewater samples with aluminum-doped magnetic nanoparticles (Al-MNP) reduced TP by over 90% in all samples. Al-MNP removed sRP preferably but also removed other P species effectively. In addition, the levels of other contaminates were removed by Al-MNP including chemical oxygen demand (COD) by 20%–87%, total suspended solids (TSS) by 50%–97%, and fat oil grease (FOG) by 78%–99%. Based on these removal efficiencies, the suggested application point of Al-MNP in the poultry wastewater treatment process will be to treat the effluent of dissolved air flotation, where the COD, FOG, and TSS have been removed significantly. The low cost of Al-MNP as well as their ease of application makes them promising materials for wastewater treatment.

Keywords: Phosphorus speciation; Adsorption; Magnetic nanoparticle; Wastewater treatment

1. Introduction

The meat and poultry industry is one of the largest segments of U.S. agriculture. Total meat and poultry production in 2011 reached more than 92.3 billion pounds, and the meat and poultry industry's economic ripple effect generates $864.2 billion annually to the U.S. economy, which is roughly 6% of the entire GDP [1]. The production of meat requires and pollutes large amounts of water. The amount of wastewater generated from meat processing plants is significant. On average, a typical broiler facility uses 6–9 gallons of water to process one bird. Total wastewater generation by U.S. slaughter plants is now between 45 and 90 billion gallons annually with over 9 billion birds processed each year [2]. Water is consumed for scalding in the feather removal process, bird washing before and after evisceration, chilling, cleaning, and sanitizing of equipment and facilities, and for cooling of mechanical equipment such as compressors and pumps [3]. The highest cost driver for water usage is the subsequent expenditure for facility processing effluents (e.g., wastewater pre-treatment or treatment for direct discharge). The poultry wastewater is

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contaminated with feathers and offal, blood, viscera, fecal material, etc. The contaminated constituents are expressed in terms of biochemical oxygen demand (BOD), COD, TSS, total Kjeldahl nitrogen (TKN), FOG, and TP. The characteristics of wastewater generated from a poultry slaughter facility were listed in Table 1. Before being discharged this wastewater would need additional treatment to reduce concentrations of regulated components by 10 to 100 times depending on wastewater disposal methods.

The treatment methods for poultry processing wastewater vary greatly depending on the discharge methods; either by indirect discharge (the treated wastewater is sent to a publicly owned treatment work [POTW]) or by direct discharge (treated wastewater is discharged into navigable waters). Almost 94% of poultry processing plants are indirect dischargers and the discharge limits are regulated by Pretreatment Standards for Existing Sources [4].

The nutrient components of meat processing effluents (phosphorus and nitrogen) are the major concerns. Excess nitrogen and phosphorus stimulate algae blooms in receiving waters (eutrophication) which produce harmful toxins to humans [5,6] and threaten aquatic life by reducing oxygen levels. Eutrophication occurs when the concentration of inorganic nitrogen and phosphorus exceeds 0.3 and 0.01 mg/L [7], respectively. To control algal growth, the EPA water quality criteria state that phosphorus should not exceed 0.05 mg/L for streams discharge into lakes or reservoirs and 0.1 mg/L for treated water discharge in streams or flowing waters not discharging into lakes or reservoirs [8]. Indirect dischargers are required to pretreat wastewater to a level acceptable to the local POTW. The discharge of TP for local poultry wastewater treatment plant should not exceed 7 ppm [9], which is a typical level for TP in raw sewage [10].

Conventional phosphorus removal method employs biological, chemical, or combined biological and chemical based technologies. In the chemical processes, P is removed by adding aluminum, iron, or calcium-based coagulants to precipitate it from the wastewater and allowing it to settle out. The high cost associated with the use of metal salts, a large amount of sludge generation to be disposed, alkalinity depletion, and an increase in total dissolved solids are handful drawbacks of the chemical precipitation–based processes. In the biological processes, phosphorus is removed by using a specific group of polyphosphate-accumulating microorganisms that are capable of consuming excess phosphorus as intracellular storage. Biological processes are prone to apparent instability and unreliability. The performance of biological processes can be reduced dramatically due to several environmental and operating factors [11]. In addition, these approaches do not recycle phosphorus as a truly sustainable product because it is removed with various other waste products, some of which are toxic [12]. The nonsolubilized P compounds are typically buried at landfills after incineration of the organic matter. They could be reused as sludge fertilizer if the treatment facility eliminates human pathogens and toxic compounds. However, the high cost of the sludge treatment and the risk of secondary pollution discourage the use of these processes for the treatment of sludge [13]. We have recently demonstrated a unique aluminum-doped magnetic nanoparticle (Al-MNP) based adsorbent for P removal [14]. Structure analysis of the prepared magnetic nanoparticles indicated an inverse spinal structure. They showed great affinity to phosphate with a maximum adsorption capacity of 102 mg/g. The adsorption was selective, and the presence of other common anions and organic matters did not interfere with the phosphate adsorption efficacy. In addition, the removal is fast and solid–liquid separation can be achieved easily under an applied magnetic field. In this study, the removals of P species in poultry wastewater were examined using these Al-MNP. Wastewater samples collected at the different stages of treatment were characterized and treated with Al-MNP. P speciation was performed before and after the treatment to understand the removal efficacies of Al-MNP toward various types of P species. Great reduction on total P was observed for the examined wastewater in this study, demonstrating that Al-MNP has a promising potential for P removal in meat processing wastewater.

2. Materials and methods

2.1. Chemicals and materials

2.1.1. Materials

Ferrous chloride ($FeCl_2$), ferric chloride ($FeCl_3$), hydrochloric acid (HCl), nitric acid (HNO_3), aluminum sulfate ($Al_2(SO_4)_3$), monopotassium phosphate (KH_2PO_4), potassium antimonyl tartrate, ammonium molybdate, ascorbic acid, and sodium hydroxide (NaOH) were obtained from Sigma-Aldrich (St. Louis, MO, USA) and used as received. ICP standards for Fe, Al, and P were purchased from High-Purity Standards (Charleston, SC, USA).

2.2. MNP synthesis and characterization

2.2.1. Preparation of aluminum-doped magnetic nanoparticles

Al-MNP was prepared by first dissolving stoichiometric amounts of $Al_2(SO_4)_3$, $FeCl_3$, and $FeCl_2$ in 300 mL of deionized water. The solution was heated to 80°C, then 100 mL of 1.5 M NaOH were added and maintained at a temperature between 80°C and 100°C for 10 min. A black precipitate was produced

Table 1
Compiled profile of wastewater from poultry slaughter plant [2]

Parameter	Flow Gal/animal	pH	TSS (mg/L)	FOG (mg/L)	BOD_5 (mg/L)	COD (mg/L)	TKN (mg/L)	Total P (mg/L)
Range	(Broiler) 5.5–17	4.9–7.2	213–365	192–500	500–2,000	1,180–3,000	90–700	0–80

upon addition of NaOH. Finally, the cooled black suspension was placed on a magnetic separator (DynaMag-50, Life Technology) and washed five times with deionized (DI) water. The final Al-MNP suspension was stored in DI water at room temperature.

2.2.2. Material characterization

X-ray diffraction (XRD) data was collected with a Bruker D8 Advanced X-Ray Diffractometer with a copper Kα source over a 15°–85° 2θ range. Magnetic measurements were performed using a Quantum Design MPMS-5S SQUID magnetometer. Particles were immobilized in icosane ($C_{20}H_{42}$, Sigma-Aldrich) for hysteresis measurements. The composition of the Al-MNP was determined by inductively coupled plasma optical emission spectrometry (ICP-OES). For this procedure, a known amount of nanoparticles were digested by concentrated HNO_3 in a Parr bomb at 200°C for 2 h. Serial dilutions were performed in 2% HNO_3. Elemental analysis for Fe, Al, and P was performed on Perkin Elmer Optima 8000 ICP-OES.

2.3. Wastewater collection

Poultry processing wastewater samples were collected at a local poultry processing plant. The wastewater treatment system contains screening to remove the large particulates; dissolved air flotation (DAF) system to remove suspended solids, oil, and grease; an activated sludge system to reduce BOD and COD; a chemical DAF to remove excess TP; and an equalization pond. Final effluent of pond is discharged to public municipal system, as shown in Fig. 1. Wastewater samples were collected from the effluent of physical screening (Raw), effluent of DAF (DAF), effluent of biological treatment (Bio), effluent of chemical DAF (chemical DAF), and the final effluent (pond) following the standard wastewater sampling procedures developed by EPA [15,16]. One gallon of each wastewater sample was manually collected in acid cleaned glass bottles, stored at 4°C and transported to the lab for analysis. Samples were analyzed as soon as possible after collection. Portions of samples were preserved with H_2SO_4 and stored at 4°C for COD, TKN, and FOG tests if the analyses cannot be finished in 24 h.

2.4. Wastewater characterization

Parameters including COD, TSS, TDS, FOG, TKN, and TP were measured for wastewater characterizations. COD was measured using Hach method 8000 wherein 2 mL of wastewater samples were digested with a COD digestion reagent (Hach, Loveland, CO, USA) in a Hach DRB200 reactor for 2 h. Then a Hach DR 3900 colorimeter was used to read the COD level. TKN was measured using the Hach method 10242 in which inorganic and organic nitrogen are oxidized to nitrate by digestion with peroxodisulfate. The difference of nitrate before and after the digestion was calculated as TKN. TSS and TDS were measured gravimetrically by filtering a known volume of wastewater (from 2 to 40 mL depending on the level of contamination) and measuring the weight of the residue on the filter after thorough drying (TSS). The filtrate was evaporated and the remaining residue was weighted (TDS). Hexane extractable FOG was measured gravimetrically by extracting 350 mL of water sample with multiple aliquots of 25 mL hexane followed by the evaporation of all of the solvent. The residue was weighted. Each measurement was duplicated and the averaged results were reported.

2.5. P speciation

P species in poultry wastewater samples were differentiated using EPA 365.2 method [17,18]. In bodies of water, phosphorus is present in several soluble and particulate forms such as organically bound phosphorus, and inorganic orthophosphates. Fig. 2 summarizes the testing methods to be used to characterize these P species in liquid streams. Basically, wastewater samples were split into two portions. One portion was filtered through a 0.45 µm filter and the second portion was analyzed without any filtration. The unfiltered water sample was treated by three methods independently to obtain total reactive phosphorus (mainly orthophosphate A), total acid hydrolysable phosphorus (combination of orthophosphate A and polyphosphate B), total phosphorus (TP) C (orthophosphate A, polyphosphate B, and organo P species D). Similar approaches were conducted on the filtered water samples to get soluble reactive phosphorus (E), total soluble acid hydrolysable phosphorus (combination of soluble orthophosphate E and soluble acid hydrolysable phosphorus F), and total soluble phosphorus G (E, F and organo P species H). The differences between C and G, A and E, B and F, and D and H generate the levels of P species in the particulate forms. Alternatively, TP in the filtered and unfiltered water samples can be measured by ICP-OES method after acid digestion.

2.5.1. Ascorbic acid colorimetric method

4 mM potassium antimonyl tartrate solution, 0.03 M ammonium molybdate, and 0.1 M ascorbic acid were prepared in DI water. A combined reagent mixture was created by mixing 50 mL of 2.5 M sulfuric acid, 5 mL potassium antimonyl tartrate solution, 15 mL ammonium molybdate solution, and 30 mL ascorbic acid solution in order at room temperature. Next, 1.6 mL of the reagent mix were added to 10 mL of each sample. After 10 min, each sample had its absorbance measured at 880 nm by UV–Vis.

Fig. 1. Poultry wastewater treatment process.

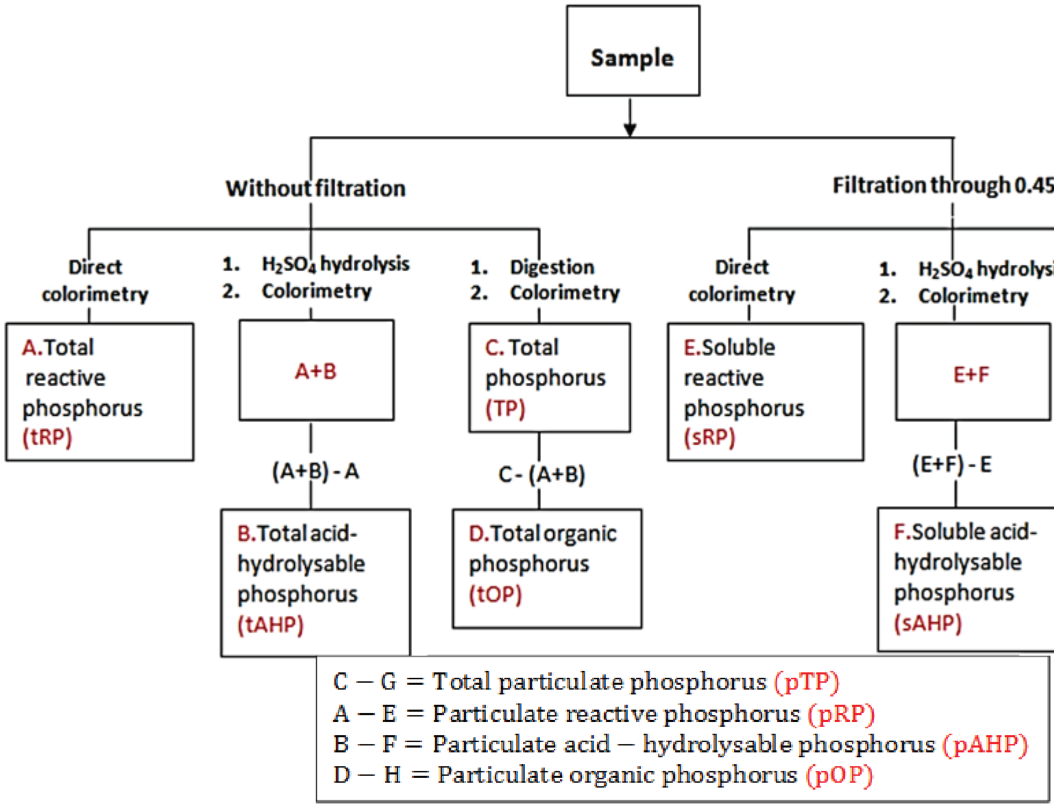

Fig. 2. Analytical methods for the determination of various P fractions.

2.5.2. Acid hydrolysis for total acid hydrolysable phosphorus analysis

An acid mixture containing 5.4 M H_2SO_4 and 0.06 M HNO_3 solution was prepared in DI water. 100 µL of the acid solution were added to 10 mL of each of the wastewater samples. The samples were then placed in an autoclave for 30 min at 121°C. The samples were allowed to cool to room temperature, and had the ascorbic acid test performed on each sample, then had the absorbencies measured by UV–Vis.

2.5.3. Acid digestion for total phosphorus analysis

200 µL of 5.4 M sulfuric acid and 80 mg of ammonia persulfate were added to 10 mL of each wastewater sample. The samples were then placed in an autoclave for 30 min at 121°C. The samples were allowed to cool to room temperature, and had the ascorbic acid test performed on each sample, then had the absorbencies measured by UV–Vis.

2.6. Phosphate adsorption experiment

2.6.1. Phosphate removal studies

Each wastewater sample had its total phosphorous concentration measured by ICP. The mass ratio of Al-MNP to TP in 50:1 was used for wastewater treatment. Al-MNPs were added to 50 mL centrifuge tubes containing 40 mL of each wastewater sample and the tubes were placed on a wrist action shaker for about 1 h, then placed in a magnetic separator. The supernatants were drawn from the tubes after 10 min on the separator, then had their new phosphorous concentrations measured by ICP. Phosphorus removal efficiency at time t was calculated as:

$$\% \text{ Removal} = \frac{C_o - C_t}{C_o} \times 100\% \qquad (1)$$

where C_o and C_t are the concentrations of P before and after 1 h of the Al-MNP treatment.

3. Results and discussion

3.1. Nanomaterial characterization

Prepared magnetic materials were characterized using XRD, SEM, and magnetometer to measure the crystalline structure, particle size and magnetic properties, respectively. The locations and intensities of peaks in the XRD pattern (Fig. 3) of the Al-MNP are in agreement with the standard magnetite (red lines) JCPDS card (card no. 19-0629), indicating a magnetite structure with aluminum fully incorporated in the cubic inverse spinel lattice. The formation of solid solution Fe_3O_4–$FeAl_2O_4$ was confirmed previously and the lattice constant of the doped Fe_3O_4–$FeAl_2O_4$ solid solution was reduced, compared with the pure Fe_3O_4 [14]. The averaged crystallite size was estimated using XRD, and the results indicated that the averaged grain size was about 9.9 nm in Al-MNP.

The saturation magnetization of the prepared Al-MNP displayed superparamagnetism without hysteresis and remnant magnetization at room temperature. The saturation magnetizations of Al-MNP are negative correlated with the doping level of Al. They are 77, 46, 34, and 18 emu/g for 0%, 10%, 15%, and 20% of Al doping, respectively, as shown in Fig. 4. The linear reduced magnetization for Al-MNP could be explained by the replacement of Fe^{3+} by nonmagnetic Al^{3+} in octahedral sites in a face-centered cubic lattice structure [19]. Al-MNP with 20% of Al doping was used in this study due to the higher adsorption capacity toward P species.

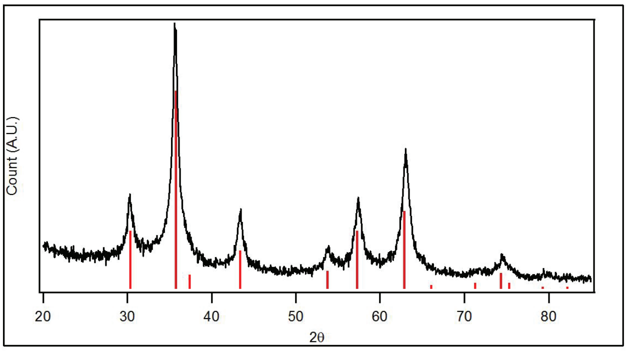

Fig. 3. X-ray diffraction patterns of pure and Al-doped magnetite. The locations and intensities of peaks are in agreement with the standard magnetite (red lines) JCPDS card (card no. 19-0629).

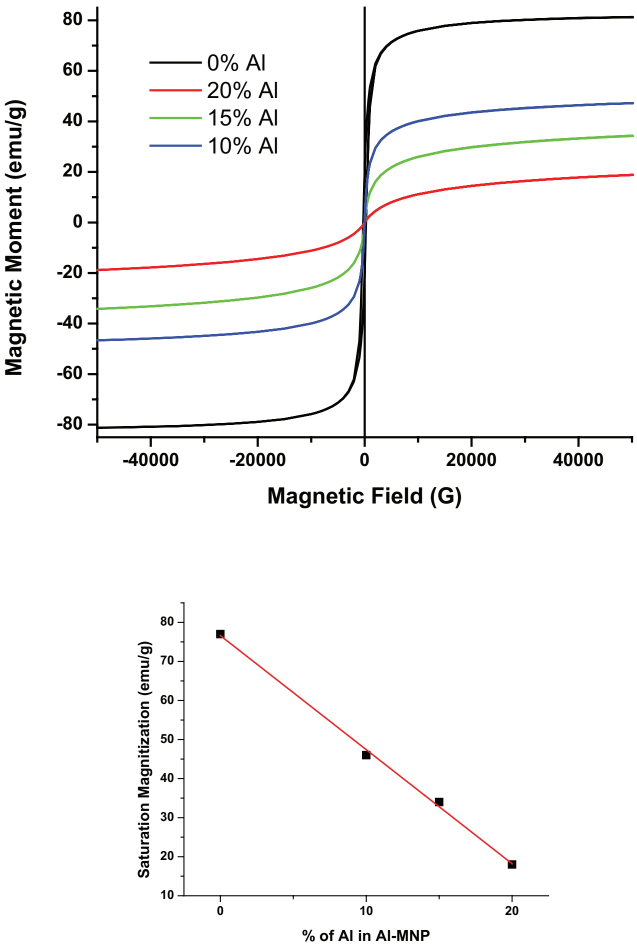

Fig. 4. Magnetic moment measurements for pure and Al-doped MNP.

3.2. Wastewater characterization

The treatment methods for poultry processing wastewater vary greatly depending on the discharge methods; either by indirect discharge (the treated wastewater is sent to a publicly owned treatment plant) or by direct discharge (treated wastewater is discharged into a stream or other receiving water body). Almost 94% of poultry processing plants are indirect dischargers [4]. Wastewater samples were collected from a poultry processing plant where the wastewater is indirectly discharged. The plant processes about 200,000 birds/d with average wastewater flow of 1.7 million gallon per day. A series of wastewater treatment steps including DAF systems and aerobic system, as shown in Fig. 1, are followed to reduce the contamination levels. Polymer-based coagulants are added in the DAF system to assist the removal of suspended particles. The effluent of DAF is then transferred to a completely mixed, activated sludge tank designed to address soluble COD and BOD. The effluent from the biological treatment is further treated in chemical DAF, where ferric salt and polymers are added to reduce TP. The effluent from chemical DAF and the stormwater runoffs are sent to an equalization pond before they are discharged to a POTW.

Changes in contamination levels were monitored by collecting wastewater samples after each step of the treatment process. Parameters including pH, COD, TSS, TDS, FOG, TKN, and TP were characterized. The results were listed in Table 2. The post screening effluent (Raw) contains high levels of COD, TSS, FOG, TKN, and TP. The level of contaminants in Raw is in good agreements with the reported literature values [20–22]. After the chemically enhanced DAF treatment, more than 98% of TSS and 90% of FOG were removed. Moderate removals of other contaminants were achieved including reductions of COD by 67%, TKN by 52%, and TP by 36%. These removed contaminants were likely associated with the suspended solids. It has been reported that 40%–50% of COD in screened (1 mm mesh) effluent of meat processing wastewater was in coarse suspended form [23]. This varies considerably from domestic wastewater, in which the COD is present mainly in the soluble and colloidal forms [24].

DAF is applied widely in the pretreatment of industrial wastewater [25–27]. Air in the DAF system is usually dissolved in water under pressure (400–600 kPa) in a saturator, and microbubbles are released through nozzles or special valves at the bottom entrance to the contact zone [28]. In the contact zone, microbubbles attach to flocs to produce bubble−floc aggregates. Then the bubble−floc aggregates are separated from water due to the density difference in the separation zone. Flocculants and/or coagulants may be added in the removal of targeted contaminants such as solids/fats to enhance the performance of DAF. Typical reductions of COD, TSS, and FOG are in the range of 50%–80% depending on the air pressure [26] and the type of flocculants [21,25,29] inside the DAF. DAF has also been used to remove TP in the meat processing wastewater [30,31].

Table 2
Wastewater characterization before and after MNP treatment

Type	pH	COD (ppm)	FOG (ppm)	TSS (ppm)	TDS (ppm)	Total N (ppm)		TP (ppm)
						$NO_3 + NO_2$	TKN	
Raw	5.4	3,495 ± 49	517 ± 21	1,195 ± 21	865 ± 64	6.59 ± 1.33	140 ± 9.89	51.2 ± 3.89
Treated		439 ± 0.71	3 ± 2	41 ± 14	670 ± 14	4.52 ± 2.43	62.6 ± 13.5	3 ± 0.07
Reduction %		87.4	99.4	96.6	22.5	31.4	55.3	94.1
DAF	5.1	715 ± 7	18 ± 12	17 ± 5	852 ± 24	3.62 ± 0.32	66.8 ± 1.48	39.58 ± 0.32
Treated		401 ± 4.24	4 ± 3	36 ± 18	680 ± 12	4.46 ± 0.97	57.6 ± 9.05	1.66 ± 0.06
Reduction %		43.9	77.8	-118	20.2	NA	13.8	95.8
Biological	6.8	1,160 ± 71	107 ± 10	600 ± 0	625 ± 0	3.14 ± 0.62	110.3 ± 15.13	55.77 ± 1.48
Treated		192 ± 0.71	18 ± 10	148 ± 68	658 ± 3	2.95 ± 0.73	66.5 ± 3.61	2.86 ± 0.006
Reduction %		83.4	83.2	75.3	NA	6.05	39.5	94.9
Chemical DAF	6.5	226 ± 4	BD	70 ± 38	657 ± 9	1.96 ± 0.09	88.85 ± 29.9	4.7 ± 0.19
Treated		187 ± 2.12	NA	36 ± 18	698 ± 6	2.58 ± 0.41	72.2 ± 4.81	0.59 ± 0.03
Reduction %		17.3	NA	48.6	NA	NA	18.4	87.4
Pond	6.7	111 ± 4	BD	127 ± 47	623 ± 5	2.23 ± 1.69	88.25 ± 0.78	12.18 ± 0.41
Treated		77.5 ± 3.53	NA	48 ± 4	641 ± 14	2.84 ± 0.19	73.6 ± 0.78	1.19 ± 0.03
Reduction %		30.2	NA	62.2	NA	NA	16.6	90.2

Note: BD, below detection limit; NA, not available.

The DAF effluent was delivered to an activated sludge treatment system to remove organic matters. However, it only reduced COD by 13%. In addition, the amount of TSS increased from 17 to 600 ppm, FOG from 18 to 107 ppm, TKN increased from 66.8 to 110 ppm, and TP increased from 18.6 to 50.6 ppm. These increases could be attributed to the presence of unsettled sludge in the effluent.

Activated sludge system is used to reduce BOD and COD, and to convert ammonia to nitrate [23]. The typical removal rate for COD [32], TP, and TKN is in the range of 80%–90% [33]. However, we only observed a 13% reduction of COD while levels of TP, suspended solids, and TKN were increased, indicating the biological treatment was not working properly. The performance of the aerated biological treatment is dependent on many factors including hydraulic retention time [34], the age and health of the sludge. A sludge age of 5–20 days is recommended for treating slaughterhouse wastewater [23] as proteins are less readily biodegradable than simple molecules. In addition, one limitation of this technology is the poor settling floc in activated sludge systems while treating slaughterhouse wastewater. This was due to a combination of the high fat content of the influent and a low dissolved oxygen concentration in the activated sludge reactor [35]. The increased TSS, TP, and TKN in the effluent are likely remnants from the unsettled floc.

The effluent of activated sludge was sent to another DAF system to remove TP, where the level of TP was reduced TP from 50.6 to 4.14 ppm with additional removals of COD and TSS. The level of FOG was below the detection limit after this step of treatment. The effluent of chemical DAF was sent to an equalization pond where the stormwater runoffs were also collected. The final effluent was then discharged to POTW. It is interesting to note, compared with the effluent of chemical DAF, that the level of COD was 50% reduced in the final effluent of equalization pond while the levels of TSS, TKN, and TP were all increased. The level of TDS remains relative unchanged along the treatment process. It is speculated that the increased TSS, TKN, and TP were from inorganic sources in the equalization pond or stormwater runoffs in the processing facility.

Chemical-based P removal processes convert the soluble P species into the particulate forms which are then separated from the liquid using DAF treatment (chemical DAF). Chemical DAF was typically applied after the biological treatment as the effluent of biological treatment has better quality and is more stable [36]. The local poultry processing plant uses both ferric salts and cationic polymers in chemical DAF to remove TP. It was observed that above 90% of TP was removed in the chemical DAF, which was in good agreement with the reported performance [36,37].

3.3. P speciation in poultry wastewater

For phosphorus, most permit limits are based on TP, so all forms of P in the final effluent need to be considered for P reduction. The forms of P are classified based on their solubility (pass 0.45 μm filter) and reactivity in acid [38]. Both particulate and soluble form of phosphorus can be fractionized into reactive phosphorus (normally assumed as ortho-P), acid hydrolysable phosphorus (e.g., polyphosphate and condensed P), and organic phosphorus (e.g., intracellular molecules that contain phosphorus) [39].

P speciation analyses on wastewater samples collected at different treatment stages were conducted to understand the effects of each treatment stage on the distribution and variation of P species. As Figs. 5 and 6 show, the TP in the raw influent is composed of 35% soluble reactive phosphate (sRP), 19% soluble acid-hydrolysable phosphorus (sAHP), 20% soluble organic phosphorus (sOP), 16% particulate reactive phosphate (pRP) and 10% particulate organic phosphorus (pOP). A study indicated that the TP in municipal effluent from primary clarifiers contains roughly 60% sRP, 17% pRP, 20% acid hydrolysable phosphorus in the particulate form (pAHP), 3% of organic phosphorus in both soluble and particulate forms [38]. And the wastewater from the dairy processing industry contained 23.14% sRP, 15.3% sAHP, 50.9% sOP, 8.5% pRP, 1% of pAHP, and 1.2% pOP of the TP [40]. Compared with the composition of P species in the effluent of a primary clarifier in a sewage treatment plant, the percentages of sRP and sAHP in food processing wastewater are lower while the percentages of sOP and pOP are higher [38,41]. Acid hydrolysable phosphorus are mainly condensed phosphate and they are used in water treatment to prevent scale formation and corrosion control.

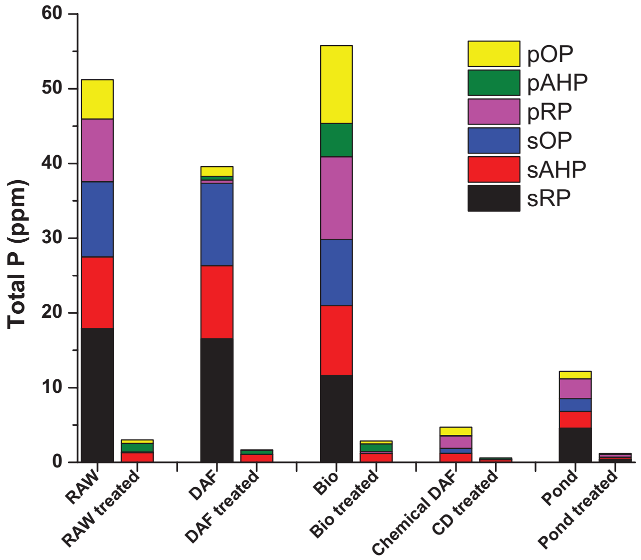

Fig. 5. Distribution and comparison of P species in wastewaters before and after Al-MNP treatment for the samples collected at the different stages of wastewater treatment.

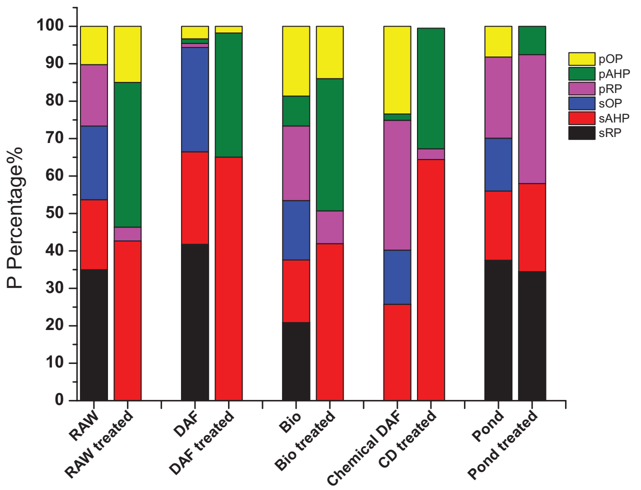

Fig. 6. Percentage distribution of each P species in wastewaters before and after Al-MNP treatment for the samples collected at the different stages of wastewater treatment.

After the first DAF treatment, all the P species in particulate forms were reduced significantly while the soluble P species remained at similar levels. Aerobic biological treatment reduced some soluble forms of P (29.6% reduction of sRP and 20% reduction of sOP), which is low compared with a step-feed biological nutrient removal system where over 95% of sRP was removed [38]. In addition, total particulate phosphorus (TPP) was increased dramatically due to the unsettled sludge in the effluent. The distribution of P species can be found in Table 3. Almost half of TP were from TPP.

Chemical DAF not only removed all the sRP but also reduced other P species dramatically with combined precipitation and adsorption processes [42]. TPP in the effluent of chemical DAF are about 60% of TP, where pRP is the major form of TPP (60%) and followed by pOP (~40%). It has been reported that P was predominantly bound to iron in the suspended solids (particulates greater than 0.45 μm) when ferric chloride was used in wastewater treatment [42]. $FeCl_3$ reacted not only with dissolved orthophosphate but also with organic compounds containing P. The primary pOP might be orthophosphate monoester and orthophosphate diester species [42].

The composition of TP in the final effluent consisted of 37.5% sRP, 18.5% sAHP, 14% sOP, 21.5% pRP, and 8.5% pOP. The composition of sRP was low compared with the discharge of a typical sewage treatment plant, where the percentage of sRP is in the range of 75%–90% [43]. The higher percentage of sRP in the discharge of sewage treatment posed a greater risk for similar amounts of total P released to water body [44].

3.4. Wastewater characterization after MNP treatment

Wastewater parameters were characterized after Al-MNP treatment to understand the impacts of the treatment on TP and other pollutants in wastewater. To compare the removal efficiencies of Al-MNP on TP in different types of wastewater, the mass ratio of Al-MNP to TP was kept constant at 50:1 (Al-MNP:TP), which was selected based on the maximum adsorption capacity and contact time [14]. Treated wastewaters were characterized to determine the removal efficiencies on the wastewater parameters including COD, TSS, TDS, FOG, TKN, and TP. The results can be found in Table 2. The removal efficiencies on TP ranged from 87.4% in the effluent of chemical DAF to 95.8% in the effluent of DAF. The relative lower removal efficiencies in effluents of chemical DAF could be caused by the presence of excess ferric chloride in chemical DAF, which may interfere for the availability of phosphate. About 95% of TP were removed from the influents of DAF, biological treatment and chemical DAF, indicating high removal efficiency on TP regardless the compositions of P species.

In addition to TP removal, significant reductions on COD, FOG, and TSS were also observed in the Al-MNP treated raw

Table 3
P Speciation in wastewater before and after the MNP treatment

	TP	TsP	sRP	sAHP	sOP	TpP	pRP	pAHP	pOP
RAW	51.2	37.55	17.9	9.59	10.06	13.65	8.4	0	5.25
Treated	3	1.28	0	1.28	0	1.72	0.11	1.16	0.45
Reduction %	94.14	96.59	100	86.65	100	87.39	98.69	0	91.42
DAF	39.58	37.34	16.53	9.78	11.03	2.24	0.43	0.48	1.33
Treated	1.66	1.08	0	1.08	0	0.58	0	0.55	0.03
Reduction %	95.80	97.10	100	88.95	100	74.10	100	0	97.74
Bio	55.77	29.8	11.64	9.32	8.84	25.97	11.11	4.45	10.41
Treated	2.86	1.2	0	1.2	0	1.66	0.25	1.01	0.4
Reduction %	94.87	95.97	100	87.12	100	93.60	97.74	77.30	96.15
Chemical DAF	4.7	1.89	0	1.21	0.68	2.81	1.63	0.08	1.1
Treated	0.59	0.38	0	0.38	0	0.21	0.017	0.19	0
Reduction %	87.44	79.89	NA	68.59	100	92.52	98.95	0	100
Pond	12.18	8.54	4.57	2.25	1.72	3.64	2.64	0	1
Treated	1.19	0.69	0.41	0.28	0	0.5	0.41	0.09	0
Reduction %	90.22	91.92	91.02	87.55	100	86.26	84.46	0	100

Note: BD, below detection limit; NA, not available.

wastewater with the removal efficacies of 87.4%, 99.4%, and 96.6%, respectively. The removal efficacies for TDS, nitrate nitrogen, and TKN were moderate with removal efficiencies of 22.5%, 31.4%, and 55.3%, respectively. For the effluent of DAF, the removal efficiencies of COD and FOG were 43.9% and 77.8%, respectively. We observed the slightly increased level of TSS from 17 to 36 ppm in MNP-treated effluent of DAF. This increase in TSS is likely resulting from experimental limitations as the amount of TSS present was approaching the detection limit of the method. It was also observed that COD was removed at lower efficiencies when the wastewater samples contained less TSS, indicating that removed COD was likely associated with particulates. Indeed, the COD in particulates forms are major COD species in wastewater [45].

Activated carbon is used commonly to reduce COD in wastewater [46,47]. Powdered activated carbon and powdered zeolite can only remove 38% and 17% of COD, respectively, in landfill leachate after 30 h of treatment [48], while in another study, a 30% to 50% of COD reduction in dairy wastewater was observed using organo-zeolite [49]. The enhanced adsorption efficacy was attributed the organic molecule (stearin-dimethyl-benzyl ammonium chloride) used for zeolite modification. The same material could remove 70% of nitrate nitrogen and 20% of phosphate. About 42% of COD and 69% of TSS reduction were obtained using porous concrete containing iron slag, and sand filtration removed 11% of COD and 53% of TSS in storm runoffs [50]. Granular ferric hydroxide adsorbent yielded a 16% COD removal in the secondary effluents of a municipal wastewater treatment [51]. Comparing with the reported adsorbents, our Al-MNP removed the major wastewater contaminants favorably.

3.5. P speciation in treated wastewater

P speciation was conducted in the treated wastewaters to examine the removal preference of Al-MNP on P species. The results can be found in Table 3. It was observed that almost all reactive phosphorus (orthophosphate) and organic phosphorus either in soluble or particulate forms were removed preferably over acid hydrolysable phosphorus (polyphosphate), as shown in Figs. 5 and 6. The total soluble P residuals (TsP) in the treated Raw, DAF, Bio, chemical DAF, and pond were roughly 43%, 65%, 42%, 65%, and 58% of TP, respectively, while the percentages of TsP before the treatment were 73.3%, 94.3%, 53.4%, 40.2%, and 70.1%, respectively. Reduced TsP removal was observed in the effluent of chemical DAF. This may be caused by the presence of ferric chloride, which may interfere with the adsorption of TsP on the active sites of Al-MNP.

3.6. MNP residue in treated water

The contents of iron and aluminum in the treated wastewaters were compared with those before the Al-MNP treatment to determine the residue of Al-MNP in the treated wastewaters. The results can be found in Table 4. Negligible

Table 4
Iron and aluminum contents in wastewater

	Fe (ppm)		Al (ppm)	
	Before Al-MNP	After Al-MNP	Before Al-MNP	After Al-MNP
Raw	0 ± 0	0.054 ± 0.0035	0.003 ± 0	0 ± 0
DAF	0 ± 0	0.22 ± 0.14	0.029 ± 0.018	0.096 ± 0.0071
Biological	5.014 ± 0.18	0.24 ± 0.012	0.053 ± 0.011	0.0855 ± 0.011
Chemical DAF	1.23 ± 0.015	0.012 ± 0.0035	0 ± 0	0 ± 0
Pond	0.97 ± 0.07	0.07 ± 0.0057	0 ± 0	0.016 ± 0

amounts of Fe and Al were found in the MNP-treated wastewaters, indicating that almost all of the MNP were recovered from liquid media using an external magnet. In fact, the levels of Fe in the MNP-treated Bio, chemical DAF, and pond wastewaters were lower than before the treatment. It is likely the Fe in particulates were removed by MNP.

The phosphorus laden Al-MNP can be reused multiple times by stripping off the attached phosphorus through the competitive binding method [14] and the stripped phosphorus species could be converted to fertilizer to achieve P recovery and recycling. Alternatively, P-laden MNP can be directly applied in the soil to provide the needed nutrients including iron and P to the plants. It has been discovered that iron oxide nanoparticles including magnetite (Fe_3O_4) supply iron, which increased growth parameters, photosynthetic pigments, and total protein contents in the treated plants significantly without any manifestation of oxidative stress in plants [52,53].

4. Conclusion

Wastewater samples were collected at a local poultry wastewater treatment plant. They were characterized with high contamination levels of COD, FOG, TSS, and TP. The first DAF system can remove over 98% of TSS, 90% of FOG, 67% of COD, 52% of TKN, and 36% of TP; while over 90% of TP reduction was achieved in the chemical DAF. P speciation analysis was performed on the wastewater collected at the different treatment stages to monitor the changes and removal of P species. The percentages of TsP varied from 73%, 94%, 53%, 40%, and 70% of TP along the treatment chain. Particularly, the bioavailable sRP varied from 35%, 42%, 21%, 0%, and 38% at the different treatment stages. Treatment of Al-MNP on wastewater samples not only reduced TP significantly (over 90%) in all the wastewater samples but also decreased the levels of other contaminants including COD (20% to 87%), TSS (50% to 97%), and FOG (78% to 99%). Based on these removal efficiencies, the suggested application point of Al-MNP in the poultry wastewater treatment process will be to treat the effluent of DAF, where the COD, FOG, and TSS have been removed significantly. The combination of high removal efficiencies on P species, low cost and ease of application make the Al-MNP a promising material for wastewater treatment.

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References

[1] North American Meat Institute, The United States Meat Industry at a Glance, North American Meat Institute, 2012.
[2] B.H. Kiepper, Characterization of Poultry Processing Operations, Wastewater Generation, and Wastewater Treatment Using Mail Survey and Nutrient Discharge Monitoring Methods, The University of Georgia, 2003.
[3] U.S. Poultry, Process Overview, U.S. Poultry & Egg Association, 2011.
[4] U.S. EPA, Technical Development Document for the Final Effluent Limitations Guidelines and Standards for the Meat and Poultry Products Point Source Category (40 CFR 432), U.S. EPA, 2004.
[5] J.T. Sims, R.R. Simard, B.C. Joern, Phosphorus loss in agricultural drainage: historical perspective and current research, J. Environ. Qual., 27 (1998) 277–293.
[6] D.J. Conley, H.W. Paerl, R.W. Howarth, D.F. Boesch, S.P. Seitzinger, K.E. Havens, C. Lancelot, G.E. Likens, Controlling eutrophication: nitrogen and phosphorus, Science, 323 (2009) 1014–1015.
[7] T.C. Daniel, A.N. Sharpley, J.L. Lemunyon, Agricultural phosphorus and eutrophication: a symposium overview, J. Environ. Qual., 27 (1998) 251–257.
[8] EPA, Quality Criteria for Water, Office of Water Regulations and Standards, Washington, D.C., 1986.
[9] The Code of Ordinances City of Gainesville, Georgia, Pretreatment Design Parameters, 1991.
[10] S.T. Muserere, Z. Hoko, I. Nhapi, Characterisation of raw sewage and performance assessment of primary settling tanks at Firle Sewage Treatment Works, Harare, Zimbabwe, Phys. Chem. Earth, Parts A/B/C, 67–69 (2014) 226–235.
[11] M. Henze, Biological Wastewater Treatment: Principles, Modelling and Design, IWA Publishing, 2008.
[12] N. Rastetter, A. Gerhardt, Toxic potential of different types of sewage sludge as fertiliser in agriculture: ecotoxicological effects on aquatic and soil indicator species, J. Soils Sediments, 15 (2015) 565–577.
[13] F.P. Camargo, P. Sérgio Tonello, A.C.A. dos Santos, I.C.S. Duarte, Removal of toxic metals from sewage sludge through chemical, physical, and biological treatments—a review, Water Air Soil Pollut., 227 (2016) 433.
[14] J. Xu, L. Luu, Y. Tang, Phosphate removal using aluminum-doped magnetic nanoparticles, Desal. Wat. Treat., 58 (2017) 239–248.
[15] B. Simpson, D. France, B. Lewis, Wastewater Sampling, U.S. EPA, 2013.
[16] U.S. EPA, Methods for Chemical Analysis of Water and Wastes, Cincinnati, Ohio, USA, 1983.
[17] U.S. EPA, Phosphorous, All Forms (Colorimetric, Ascorbic Acid, Single Reagent), 1971.
[18] B.Y. Spivakov, T.A. Maryutina, H. Muntau, Phosphorus speciation in water and sediments, Pure Appl. Chem., 71 (1999) 2161–2176.

[19] Y. Okano, T. Nakamura, Hydrothermal synthesis of aluminum bearing magnetite particles, Colloids Surf., A, 139 (1998) 279–285.
[20] C.E.T. Caixeta, M.C. Cammarota, A.M.F. Xavier, Slaughterhouse wastewater treatment: evaluation of a new three-phase separation system in a UASB reactor, Bioresour. Technol., 81 (2002) 61–69.
[21] I.S. Arvanitoyannis, D. Ladas, Meat waste treatment methods and potential uses, Int. J. Food Sci. Technol., 43 (2008) 543–559.
[22] M. Baskar, B. Sukumaran, Effective method of treating wastewater from meat processing industry using sequencing batch reactor, Int. Res. J. Eng. Technol., 2 (2015) 27–31.
[23] M.R. Johns, Developments in wastewater treatment in the meat processing industry: a review, Bioresour. Technol., 54 (1995) 203–216.
[24] A. Tawfik, B. Klapwijk, F. el-Gohary, G. Lettinga, Treatment of anaerobically pre-treated domestic sewage by a rotating biological contactor, Water Res., 36 (2002) 147–155.
[25] M. Karhu, T. Leiviskä, J. Tanskanen, Enhanced DAF in breaking up oil-in-water emulsions, Sep. Purif. Technol., 122 (2014) 231–241.
[26] Q. Zhang, S. Liu, C. Yang, F. Chen, S. Lu, Bioreactor consisting of pressurized aeration and dissolved air flotation for domestic wastewater treatment, Sep. Purif. Technol., 138 (2014) 186–190.
[27] I.R. de Nardi, T.P. Fuzi, V. Del Nery, Performance evaluation and operating strategies of dissolved-air flotation system treating poultry slaughterhouse wastewater, Resour. Conserv. Recycl., 52 (2008) 533–544.
[28] W.-H. Zhang, J. Zhang, B. Zhao, P. Zhu, Microbubble size distribution measurement in a DAF system, Ind. Eng. Chem. Res., 54 (2015) 5179–5183.
[29] A.J. Dassey, C.S. Theegala, Evaluating coagulation pretreatment on poultry processing wastewater for dissolved air flotation, J. Environ. Sci. Health, Part A, 47 (2012) 2069–2076.
[30] P. Jokela, E. Ihalainen, J. Heinänen, M. Viitasaari, Dissolved air flotation treatment of concentrated fish farming wastewaters, Water Sci. Technol., 43 (2001) 115–121.
[31] C.C. Ross, J.P. Pierce, G.E. Valentine, Phosphorus Removal from Industrial Wastewater Using Dissolved Air Flotation to Meet Discharge Requirements for the Chesapeake Bay Watershed, 87th Annual Water Environment Federation Technical Exhibition and Conference, New Orleans, Louisiana, 2014.
[32] P. Chowdhury, T. Viraraghavan, A. Srinivasan, Biological treatment processes for fish processing wastewater – a review, Bioresour. Technol., 101 (2010) 439–449.
[33] A.P. Annachhatre, S.M.R. Bhamidimarri, Activated Sludge Treatment of Meat Processing Wastewater, T. Yano, R. Matsuno, K. Nakamura, Eds., Developments in Food Engineering: Proc. 6th International Congress on Engineering and Food, Springer US, Boston, MA, 1994, pp. 1008–1010.
[34] J. Bohdziewicz, E. Sroka, Integrated system of activated sludge–reverse osmosis in the treatment of the wastewater from the meat industry, Process Biochem., 40 (2005) 1517–1523.
[35] N. Thayalakumaran, Treatment of Meat Processing Wastewater for Carbon, Nitrogen and Phosphorus Removal in a Sequencing Batch Reactor, Process & Environmental Technology Massey University, 2002.
[36] I.R. de Nardi, V. Del Nery, A.K.B. Amorim, N.G. dos Santos, F. Chimenes, Performances of SBR, chemical–DAF and UV disinfection for poultry slaughterhouse wastewater reclamation, Desalination, 269 (2011) 184–189.
[37] D.H. Kwak, K.C. Lee, Enhanced phosphorus removal in the DAF process by flotation scum recycling for advanced treatment of municipal wastewater, Water Sci. Technol., 72 (2015) 600–607.
[38] A.Z. Gu, L. Liu, J.B. Neethling, H.D. Stensel, S. Murthy, Treatability and fate of various phosphorus fractions in different wastewater treatment processes, Water Sci. Technol., 63 (2011) 804–810.
[39] L.S. Clesceri, A.E. Greenberg, A.D. Eaton, Standard Methods for the Examination of Water and Wastewater, 20th ed., American Public Health Association, Washington, D.C., 1998.
[40] J.G. Vieira, A.G.d.S. Manetti, E. Jacob-Lopes, M.I. Queiroz, Uptake of phosphorus from dairy wastewater by heterotrophic cultures of cyanobacteria, Desal. Wat. Treat., 40 (2012) 224–230.
[41] M. Maurer, M. Boller, Modelling of phosphorus precipitation in wastewater treatment plants with enhanced biological phosphorus removal, Water Sci. Technol., 39 (1999) 147–163.
[42] B. Kim, M. Gautier, C. Rivard, C. Sanglar, P. Michel, R. Gourdon, Effect of aging on phosphorus speciation in surface deposit of a vertical flow constructed wetland, Environ. Sci. Technol., 49 (2015) 4903–4910.
[43] H.K.G.R. Millier, P.S. Hooda, Phosphorus species and fractionation – why sewage derived phosphorus is a problem, J. Environ. Manage., 92 (2011) 1210–1214.
[44] H.P. Jarvie, C. Neal, P.J.A. Withers, Sewage-effluent phosphorus: a greater risk to river eutrophication than agricultural phosphorus?, Sci. Total Environ., 360 (2006) 246–253.
[45] I. Pasztor, P. Thury, J. Pulai, Chemical oxygen demand fractions of municipal wastewater for modeling of wastewater treatment, Int. J. Environ. Sci. Technol., 6 (2009) 51–56.
[46] S.H. Nekoo, S. Fatemi, Experimental study and adsorption modeling of COD reduction by activated carbon for wastewater treatment of oil refinery, Iran. J. Chem. Chem. Eng., 32 (2013) 81–89.
[47] S. Verma, B. Prasad, I.M. Mishra, Adsorption kinetics and thermodynamics of COD removal of acid pre-treated petrochemical wastewater by using granular activated carbon, Sep. Sci. Technol., 49 (2014) 1067–1075.
[48] F. Kargı, M.Y. Pamukoglu, Adsorbent supplemented biological treatment of pre-treated landfill leachate by fed-batch operation, Bioresour. Technol., 94 (2004) 285–291.
[49] K. Srđan, S. Dragoslav, M. Dragan, T. Slaviša, M. Slobodan, K. Slobodan, A. Ljiljana, Effects of reactive filters based on modified zeolite in dairy industry wastewater treatment process, Chem. Ind. Chem. Eng. Q., 19 (2013) 583–592.
[50] N. Soheila Saghaian, K. Jahangir Abedi, B. Kiachehr, M.-F. Saman, J. Koupai, Reduction of urban storm-runoff pollution using porous concrete containing iron slag adsorbent, J. Environ. Eng., 142 (2016) 1–7.
[51] B. Zhao, Y. Zhang, X. Dou, H. Yuan, M. Yang, Granular ferric hydroxide adsorbent for phosphate removal: demonstration preparation and field study, Water Sci. Technol., 72 (2015) 2179–2186.
[52] N. Pariona, A.I. Martínez, H. Hernandez-Flores, R. Clark-Tapia, Effect of magnetite nanoparticles on the germination and early growth of *Quercus macdougallii*, Sci. Total Environ., 575 (2017) 869–875.
[53] M. Askary, M.R. Amirjani, T. Saberi, Comparison of the effects of nano-iron fertilizer with iron-chelate on growth parameters and some biochemical properties of *Catharanthus roseus*, J. Plant Nutr., 40 (2017) 974–982.