OPTIMUM OPERATING CONDITIONS FOR A REAL SCALE AMMONIA STRIPPING TOWER:

AN EXPERIMENTAL CASE

Maria Cristina COLLIVIGNARELLI[1,2], Marco CARNEVALE MIINO[3], Elena Cristina RADA[4,*], Vincenzo TORRETTA[5], Marco BALDI[6]

In recent years, several studies focused on developing processes aimed at recovering nutrients such as nitrogen. In this paper, a real plant for ammonia stripping has been tested on a real aqueous waste in order to optimize the process conditions (air flow rate and pH). The results of a finite element mathematical model were compared with the ones of experimental tests. The results showed that 500 Nm³/h was the minimum flow rate necessary to allow reaching ammonia nitrogen removals close to 80% in 9 hours of stripping (reactor operating in semi-batch mode). Moreover, the tests showed the possibility of increasing the pH value by exploiting the alkalinity that characterizes the digestates without the dosage of reagents for basification (e.g. NaOH).

Keywords: ammonia recovery; ammonia stripping; circular economy; reactor operating in semi-batch mode.

1. Introduction

Nitrogen compounds represents a diffuse pollutant in surface water and groundwater [1]. Nitrogen compounds can give rise to different deleterious effects, depending on the environmental conditions in which they are found.

These effects concern the environment, such as eutrophication, and acute toxicity towards various species of fish [2–4]. However, the negative effects can also affect human health. In fact, when wastewater (WW) and aqueous waste

[1] Prof., Department of Civil Engineering and Architecture, University of Pavia, via Ferrata 1, 27100 Pavia, Italy, e-mail: mcristina.collivignarelli@unipv.it
[2] Prof., Interdepartmental Centre for Water Research, University of Pavia, Via Ferrata 3, 27100 Pavia, Italy, e-mail: mcristina.collivignarelli@unipv.it
[3] Ph.D. Student, Department of Civil Engineering and Architecture, University of Pavia, via Ferrata 1, 27100 Pavia, Italy, e-mail: marco.carnevalemiino01@universitadipavia.it
[4] Prof., Department of Theoretical and Applied Sciences, University of Insubria, Via G.B. Vico 46, 21100 Varese, Italy, e-mail: elena.rada@uninsubria.it
[5] Prof., Department of Theoretical and Applied Sciences, University of Insubria, Via G.B. Vico 46, 21100 Varese, Italy; e-mail: vincenzo.torretta@uninsubria.it
[6] Prof., Department of Chemistry, University of Pavia, viale Taramelli 10, 27100 Pavia, Italy, e-mail: marco.baldi@unipv.it

(AW) with high concentration of nitrogen compounds are not properly managed and discharged into the environment, they can contaminate the sources of drinking water and becoming the cause of problems for human health [5–8], together with the other contaminants already present in the water [9,10].

At the same time, nitrogen depletion in soils is becoming a significant problem [11,12]. In recent years, many studies have focused on developing and optimizing processes aimed at recovering nutrients in agriculture, for example through the reuse of biosolids as soil improvers [13–16]. Given the high presence of pollutants in some WW, this practice is not always possible, even if the new Circular Economy (CE) concept asks to be considered as a sustainable use [17-19]. In fact, biosolids can be spread on agricultural land only if they meet specific quality requirements [14,20]. A high concentration of pollutants in the biosolids (such as pathogens and heavy metals) makes it impossible to recover them in land [21-23].

Considering the importance to implement a CE based on the recycle and reuse of waste materials and nutrients, in recent years, several researches have been carried out to study other possible recoveries for nitrogen compounds and other residues [24–27].

Due to this high volatility, ammonia in AW can be removed from the liquid to the gas phase using air stripping, in order to obtain, after adsorption, ammonium sulphate to be used as fertilizer [28–32]. In Figure 1 the scheme of the combined stripping-adsorption process used in the research is reported. Temperature, air flow rate and pH are parameters that influence the ammonia stripping process. High temperature, high air flow rates and basic pH values are able to stimulate the stripping process [33,34].

In this paper, a real plant for ammonia stripping was tested on a real AW in order to optimize the process conditions (air flow rate and pH). The results of a finite element mathematical model were compared with the ones of experimental tests varying the air flow rate. Moreover, in a following step, the possibility of increasing the pH to optimal value by exploiting the alkalinity that characterizes the digestates without the dosage of reagents for basification (e.g. NaOH) was investigated and discussed.
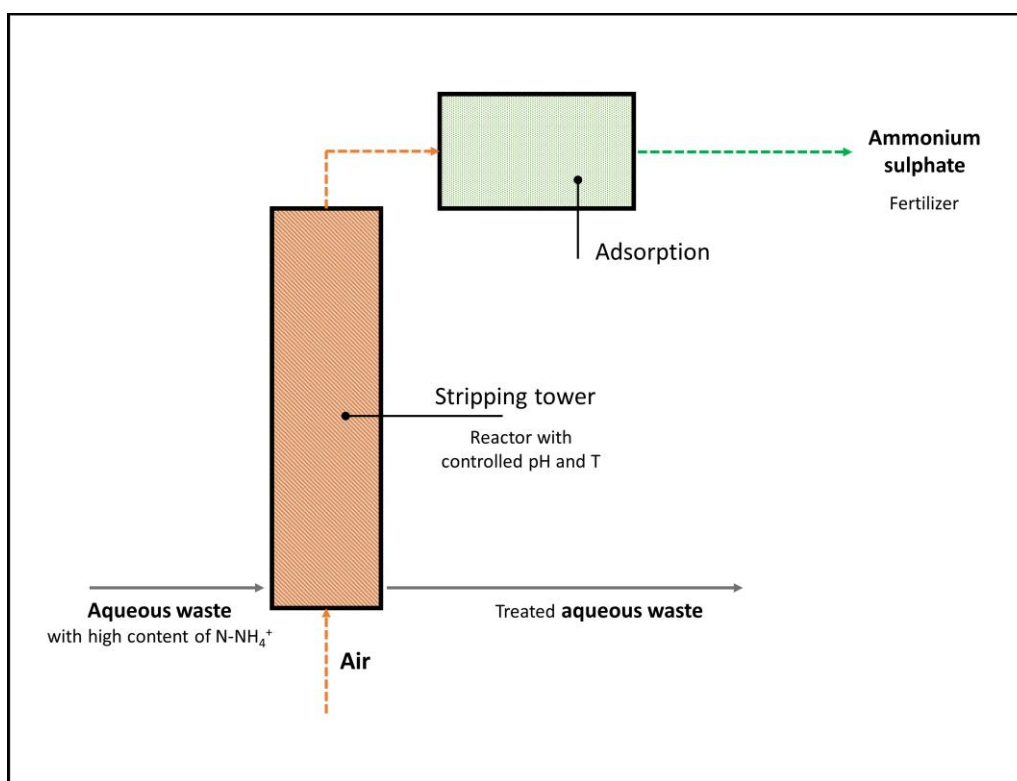
Fig. 1. Scheme of the combined stripping-adsorption process typically used for the recovery of nitrogen compounds as ammonium sulphate from aqueous waste

2. Materials and Methods

2.1. Air flow rate model

In order to compare the theoretical predictions of stripped NH_3 with experimental results obtained by managing the stripping tower (operating in semi-batch mode), a series of simulations of the concentration of NH_3 in aqueous phase as a function of time was carried out under the following conditions:

- initial NH_3 concentration: 2300 mg/L
- liquid volume in the semi-batch reactor: 12 m^3
- imposed air flow rates: 120 - 240 - 480 - 720 Nm^3/h.

2.2. Experimental procedure and chemical analysis

The experimental stripping of ammonia from real AW (initial $N-NH_4^+$ concentration = 1900 mg/L) was tested insufflating air with a flow rate of 500 Nm^3/h in the real stripping tower (volume = 12 m^3) operating in semi-batch condition. pH and temperature were maintained at 9.2 and 60 °C, respectively. NaOH and HCl reagents used for preparing solutions for titration tests were

purchased from Merck. The tests of the variation of pH have been made maintaining the temperature equal to 60 °C and the air flow rate equal to 500 Nm^3/h.

Samples were immediately analysed after collection according to the Standard Method for the Examination of Water and Wastewater [35]. pH and temperature were measured using a portable multiparameter instrument (WTW 3410 SET4) with the probe WTW-IDS, Model SenTix® 940.

3. Results and Discussion

3.1. Air flow rate optimization

In order to compare the theoretical predictions of ammonia stripping with experimental results obtained by managing a real plant operating in semi-batch conditions, a series of simulations of the concentration of NH_3 as a function of time was carried out. Figure 2 shows the results of the processing developed with a finite element model. These results were compared with experimental test conducted at 60 °C and 500 Nm^3/h of air flow rate and are reported in Figure 3.

The comparison showed that, according to the model, the removal of ammonia after 6 hours was 55%, substantially aligned with the experimental data (52%). Therefore, the transfer of ammonia from the liquid phase to the gas phase was almost in conditions of equilibrium and followed Henry's equation. The results also showed that the air flow rate of 500 Nm^3/h was the minimum one necessary to allow reaching ammonia nitrogen removals close to 50% in 6 hours. After 9 hours of stripping, 78% of ammonia was removed, a value slightly higher than that estimated by the model (65%).

Better results have been obtained by increasing the flow of air blown into the real scale system; for example, using an air flow rate of 700 Nm^3/h, the mathematical model estimated an ammonia removal close to 70%. Experimental tests also confirmed this result . The stripping tower improved the ammonia removal yield by 30% varying air flow rate from 500 to 680 Nm^3/h. In fact, an increase in removal, which proceeds almost linearly with the flow of air introduced, has been observed.
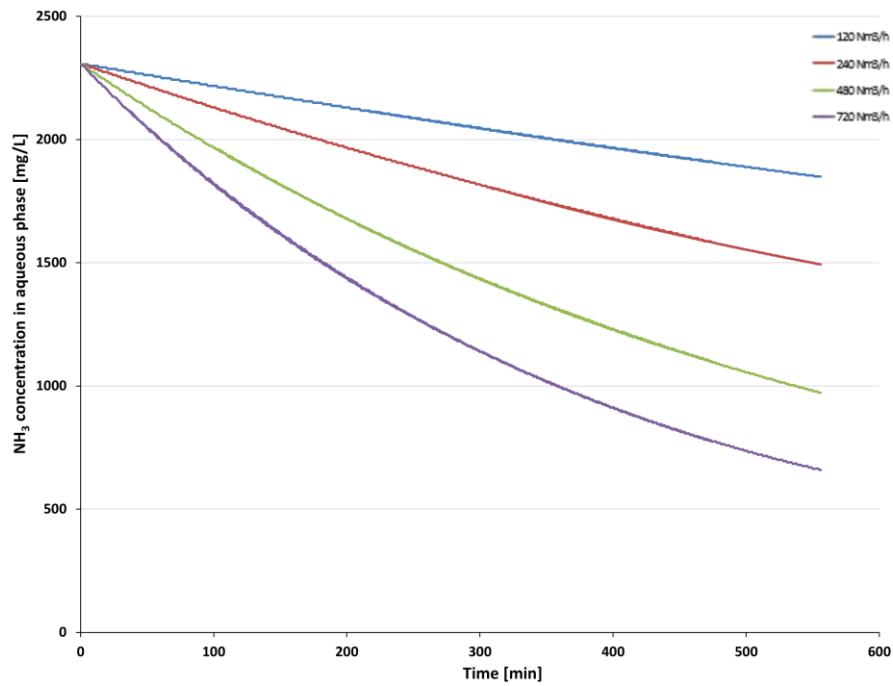
Fig. 2. Simulation by finite volume model of the variation of the ammonia concentration in a semi-batch stripping plant with different air flow rates (T= 60°C; pH=9.2)
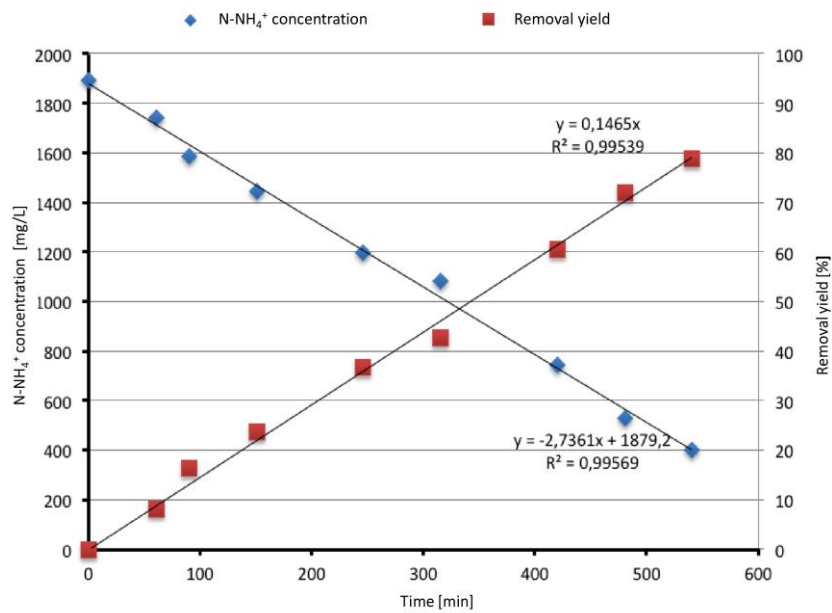

Fig. 3. Experimental data of the ammonia concentration in a real stripping tower (T= 60 °C; Air flow rate= 500 Nm^3/h; pH= 9.2; reactor operating in semi-batch mode)

3.2. pH optimization

Experimental titration tests with 1 M NaOH solution have shown the need to dose a quantity of base higher than that theoretically foreseeable as can been seen in Figure 4a. Specifically, to reach the pH value of 11.2 (above the pKa of the NH_4^+ ion), 56 kg of 32 wt.% NaOH for 1 m^3 of reactor were required (more than three times the estimated value). This result could be due to: (i) the concomitant presence of weak organic acids both in solutions and in the solid phase with pKa similar to that of the ammonium ion, or (ii) presence of bicarbonate ion in solution. In order to verify the possibility of reducing the necessary dosage of NaOH, titration tests on centrifuged AW were conducted. The removal of the solid phase did not influence the quantity of base necessary for the titration (Fig. 4a), therefore not even that necessary to shift ~~move the~~ pH to the desired value. The acid compounds, which induced the high consumption of NaOH, were in solution.

Titrations of the AW were carried out with 1 M HCl solution in order to identify which acid compounds were present in the solution. The presence of a buffer around pH 6.5 attributable to the bicarbonate ion has been identified. The hypothesis that the high consumption of NaOH could be attributed substantially to the presence of bicarbonate ion is confirmed by the fact that by managing the stripping tower plant continuously, with a significant removal of ammonia (63%), the pH has risen from 7.7 to near values to 9.2 after 9 hours of stripping time (Fig. 5). By converting the continuously stirred tank reactor (CSTR) to operate in semi-batch conditions, it was possible to observe that the pH reached values even close to 9.8 without the dosage of basifying reagent allowing a higher removal of ammonia content up to 80% after 9 hours of stripping time (Fig. 6).

These results can be explained by the fact that in the two cases, despite the removal of a base (NH_3), the bicarbonate ion is then converted into CO_2 and released determining an increase of pH. By operating in a semi-batch mode, the buffering effect given by the presence of carbonates in the AW was better exploited and the use of reagents for basification (such as NaOH) was avoided minimizing the costs.
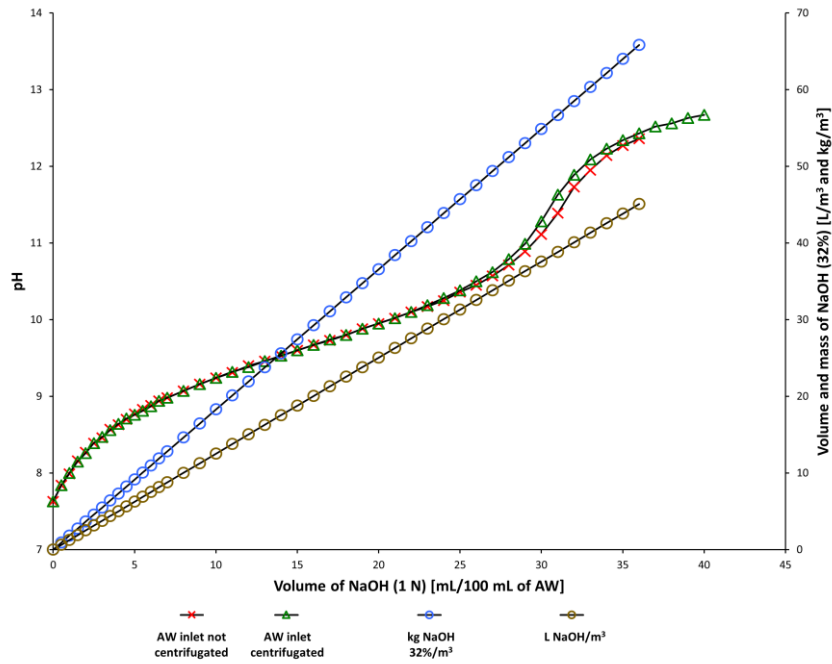
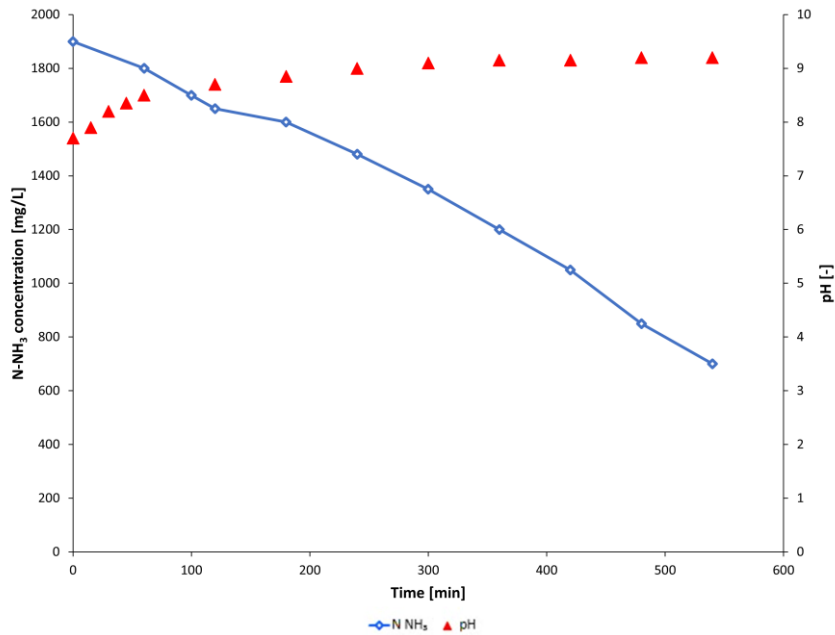Fig. 4. Titration curves of 100 mL of AW with 1 M NaOH solution

Fig. 5. Variation of the pH and N-NH$_3$ concentration of the AW in a real CSTR stripping plant (T= 60 °C; Air flow rate= 500 Nm^3/h)
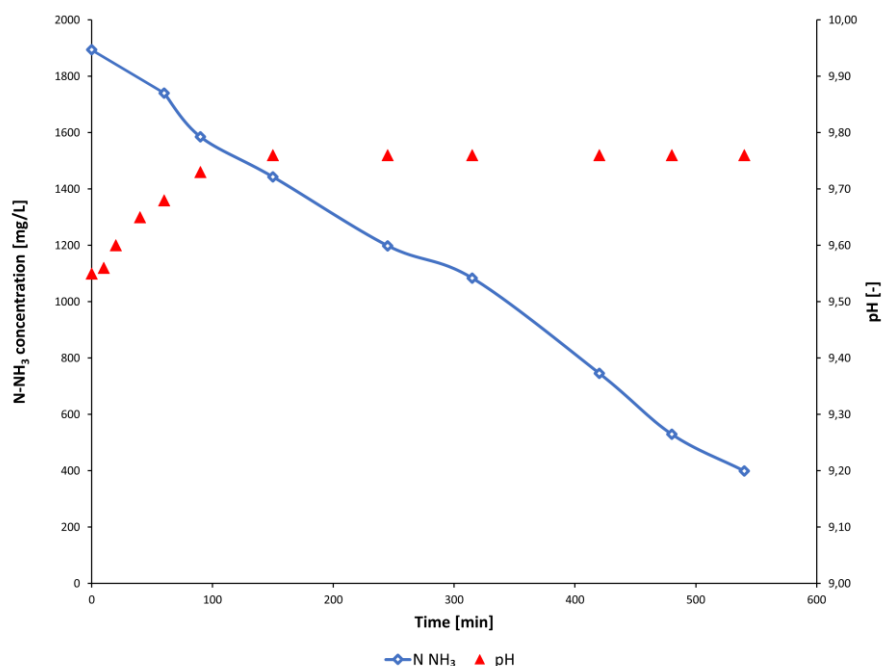
Fig. 6. Variation of the pH and N-NH$_3$ concentration of the AW in a real semi-batch ~~CSTR~~ stripping plant (T= 60 °C; Air flow rate= 500 Nm^3/h)

4. Conclusions

A real ammonia stripping tower has been tested on a real AW in order to optimize the process conditions (air flow rate and pH).

In the first phase, the results of a finite element mathematical model, developed in order to estimate the stripping efficiency of ammonia at a temperature of 60 °C, were compared with the ones of experimental tests. The results showed that the air flow rate of 500 Nm^3/h was the minimum one necessary to allow obtaining ammonia nitrogen removals close to 50% in 6 hours and closer to 80% in 9 hours of stripping (reactor operating in semi-batch mode).

In order to obtain a good N-NH$_3$ removal yield, the tests showed the possibility of increasing the pH by exploiting the alkalinity that characterizes the digestates without the dosage of reagents for basification (e.g. NaOH). Thanks to the removal of CO$_2$ in equilibrium in the liquid phase, it is possible to reach pH values equal to 9.2 with the CSTR reactor and equal to 9.8 operating in semi-batch mode. In the latter, after 9 hours of stripping time, there was a greater removal of ammonia (80%) compared to the CSTR reactor (63%).

Therefore, pH of 9.8 and air flow rate equal to 500 Nm^3/h in semi-batch operating reactor represented the optimal conditions for N-NH$_3$ stripping with avoidance of the dosage of reagents for basification.

R E F E R E N C E S

[1]. *X.M. Wang, W.H. Ji, L.Z. Chen, J.M. Lin, X. Wang, R.S. Zhao*, Nitrogen-rich covalent organic frameworks as solid-phase extraction adsorbents for separation and enrichment of four disinfection by-products in drinking water, Journal of Chromatography A., 2020, 460916.

[2]. *W. Dodds, V. Smith*, Nitrogen, phosphorus, and eutrophication in streams, Inland Waters, **vol. 6**, no. 2, 2016, pp. 155–164.

[3]. *J. Huang, C. Xu, B.G. Ridoutt, X. Wang, P. Ren*, Nitrogen and phosphorus losses and eutrophication potential associated with fertilizer application to cropland in China, Journal of Cleaner Production, **vol. 159,** 2017, pp. 171–179.

[4]. *C.E. Boyd*, Nitrogen, in: Water Quality – An Introduction, Springer International Publishing, 2020, pp. 223-241.

[5]. *M.A. Hoaghia, O. Cadar, G.G. Hognogi, E. Levei, C. Moisa, C. Roman*, Quality and human health risk assessment of metals and nitrogen compounds in drinking water from an urban area near a former non-ferrous ore smelter, Analytical Letters, **vol. 52,** no. 8, 2019, pp. 1268–1281.

[6] *Y. Sato, M. Ishihara, K. Fukuda, S. Nakamura, K. Murakami, M. Fujita, H. Yokoe*, Behavior of nitrate-nitrogen and nitrite-nitrogen in drinking water, Biocontrol Science, **vol. 23,** no.3, 2018, pp. 139–143.

[7]. *Y. Zhang, J. Wu, B. Xu*, Human health risk assessment of groundwater nitrogen pollution in Jinghui canal irrigation area of the loess region, northwest China, Environmental Earth Science, **vol. 77,** no. 7, 2018, 273.

[8]. *H. Su, W. Kang, Y. Xu, J. Wang*, Assessing groundwater quality and health risks of nitrogen pollution in the Shenfu mining area of Shaanxi province, Northwest China, Exposure and Health, **vol. 10,** no. 2, 2018, pp. 77–97.

[9]. *S. Sorlini, M.C. Collivignarelli, F. Castagnola, B.M. Crotti, M. Raboni*, Methodological approach for the optimization of drinking water treatment plants' operation: a case study, Water Science and Technology, **vol. 71,** no. 4, 2015, pp. 597–604.

[10]. *S. Sorlini, M.C. Collivignarelli, M. Carnevale Miino*, Technologies for the control of emerging contaminants in drinking water treatment plants, Environmental Engeneering and Management Journal, **vol. 18,** no. 10, 2019, pp. 2203-2216.

[11]. *J. Balkovič, R. Skalský, C. Folberth, N. Khabarov, E. Schmid, M. Madaras, M. Obersteiner, M. van der Velde*, Impacts and uncertainties of +2°C of climate change and soil degradation on European crop calorie supply, Earth's Future, **vol. 6,** no. 3, 2018, pp. 373–395.

[12]. *P. Zdruli, R. Lal, M. Cherlet, S. Kapur*, New World Atlas of Desertification and Issues of Carbon Sequestration, Organic Carbon Stocks, Nutrient Depletion and Implications for Food Security, in: Carbon Management, Technologies, and Trends in Mediterranean Ecosystems, *S. Erşahin, S. Kapur, E. Akça, A. Namlı, H.E. Erdoğan* (Eds.), Springer, 2017, pp. 13–25.

[13]. *M.C. Collivignarelli, A. Abbà, M. Carnevale Miino, V. Torretta*, What advanced treatments can be used to minimize the production of sewage sludge in WWTPs?, Applied Science, **vol. 9**, no. 13, 2019, 2650.

[14]. *M.C. Collivignarelli, A. Abbà, A. Frattarola, M. Carnevale Miino, S. Padovani, J. Katsoyiannis, V. Torretta*, Legislation for the reuse of biosolids on agricultural land in Europe: Overview, Sustainability, **vol. 11**, no. 21, 2019, 6015.

[15]. *M.C. Collivignarelli, M. Canato, A. Abbà, M. Carnevale Miino*, Biosolids: what are the different types of reuse?, Journal of Cleaner Production, **vol. 238**, 2019, 117844.

[16]. *N. Kathijotes, E. Zlatareva, S. Marinova, V. Petrova, V.,* Soil fertilization with wastewater biosolids -monitoring changes in the 'soil-fertilizer-plant' system and phosphorus recovery options,* Water Science and Technology, **vol. 74,** no. 6, 2016, pp. 1499-1508.

[17]. *M.C. Collivignarelli, M. Carnevale Miino, M. Baldi, S. Manzi, A. Abbà, G. Bertanza*, Removal of non-ionic and anionic surfactants from real laundry wastewater by means of a full-scale treatment system, Process Safety and Environmental Protection, **vol. 132,** 2019, pp. 105–115.

[18]. *M.C. Collivignarelli, A. Abbà, M. Carnevale Miino, H. Arab, M. Bestetti, S. Franz*, Decolorization and biodegradability of a real pharmaceutical wastewater treated by H_2O_2-assisted photoelectrocatalysis on TiO_2 meshes, Journal of Hazardous Material, **vol. 387,** 2019, 121668.

[19]. *A.V. Kiselev, E.R. Magaril, E.C. Rada,* Energy and sustainability assessment of municipal wastewater treatment under circular economy paradigm, WIT Transactions on Ecology and the Environment, **vol. 237**, 2019, pp. 109-120

[20]. *M.C. Collivignarelli, A. Abbà, S. Padovani, M. Frascarolo, D. Sciunnach, M. Turconi, M. Orlando*, Recovery of sewage sludge on agricultural land in Lombardy: current issues and regulatory scenarios, Environmental Engeneering and Management Journal, **vol. 14,** no. 7, 2015, pp. 1477–1486.

[21]. *B. Sharma, A. Sarkar, P. Singh, R.P. Singh*, Agricultural utilization of biosolids: A review on potential effects on soil and plant grown, Waste Management, **vol. 64,** 2017, pp. 117–132.

[22]. *M.C. Collivignarelli, A. Abbà, M. Bestetti, B.M. Crotti, M. Carnevale Miino*, Electrolytic recovery of nickel and copper from acid pickling solutions used to treat metal surfaces, Water, Air and Soil Pollution, **vol. 230,** no. 5, 2019, 101.

[23]. *A. Chiavola, P. Tedesco, M.R. Boni,* Fate of some endocrine disruptors in batch experiments using activated and inactivated sludge, Water Air and Soil Pollution, **vol. 227,** no. 11, 2016, 424.

[24]. *J. Korhonen, A. Honkasalo, J. Seppälä*, Circular Economy: The concept and its limitations, Ecol. Econ., **vol. 143**, 2018, 37–46..

[25]. *M. Ragazzi, S. Fedrizzi, E.C. Rada, G. Ionescu, R. Ciudin, L.I. Cioca,* Experiencing urban mining in an Italian municipality towards a Circular Economy vision, Energy Procedia, **vol. 119,** 2017, pp. 192-200.

[26]. *K. Chojnacka, K. Gorazda, A. Witek-Krowiak, K. Moustakas*, Recovery of fertilizer nutrients from materials - Contradictions, mistakes and future trends, Renewable and Sustainable Energy Reviews, **vol. 110,** 2019, pp. 485–498.

[27]. *P. Ricciardi, G. Cillari, M. Carnevale Miino, M.C. Collivignarelli*, Valorization of agro-industry residues in building and environmental sector: a review, Waste Manag. Res., **vol. 38**, 2020, in press. https://doi.org/10.1177/0734242X20904426

[28]. *G. Provolo, F. Perazzolo, G. Mattachini, A. Finzi, E. Naldi, E. Riva*, Nitrogen removal from digested slurries using a simplified ammonia stripping technique, Waste Management, **vol. 69,** 2017, pp. 154–161.

[29]. *W. Huang, T. Yuan, Z. Zhao, X. Yang, W. Huang, Z. Zhang, Z. Lei*, Coupling hydrothermal treatment with stripping technology for fast ammonia release and effective nitrogen recovery from chicken manure, ACS Sustainable Chemistry and Engineering, **vol. 4,** 2016, pp. 3704–3711.

[30]. *M. Baldi, M. Collivignarelli, A. Abbà, I. Benigna*, The valorization of ammonia in manure digestate by means of alternative stripping reactors, Sustainability, **vol. 10,** 2018, 3073.

[31]. *L. Cao, J. Wang, S. Xiang, Z. Huang, R. Ruan, Y. Liu*, Nutrient removal from digested swine wastewater by combining ammonia stripping with struvite precipitation, Environmental Science Pollution and Research, **vol. 26**, 2019, pp. 6725–6734.

[32]. *W. Jiao, S. Luo, Z. He, Y. Liu*, Applications of high gravity technologies for wastewater treatment: A review, Chemical Engineering Journal, **vol. 313**, 2017, pp. 912–927.

[33]. *M.-H. Yuan, Y.-H. Chen, J.-Y. Tsai, C.-Y. Chang*, Ammonia removal from ammonia-rich wastewater by air stripping using a rotating packed bed, Process Safety and Environmental Protection, **vol 102,** 2016, pp. 777–785.

[34]. *A. Limoli, M. Langone, G. Andreottola*, Ammonia removal from raw manure digestate by means of a turbulent mixing stripping process, Journal of Environmental Management, **vol. 176**, 2016, pp. 1–10.

[35]. *APHA*, Standard Methods for the Examination of Water and Wastewater, 22nd edition, 2012.