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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 semibatch mode). Moreover, the tests showed the possibility of increasing the pH value by exploiting the alkalinity that characterizes the digestates without the dosage of basifying reagents (e.g. NaOH).

Keywords: ammonia recovery; ammonia stripping; circular economy; resources recovery.

1. Introduction

Nitrogen 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

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(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 ask 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 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 flowrate 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 [32,34].

In this paper, a real plant for ammonia stripping was tested on a real AW in order to optimize the process conditions (air flowrate and pH). The results of a finite element mathematical model were compared with the ones of experimental tests varying the air flowrate. 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 basifying reagents (e.g. NaOH) was investigated and discussed.



Fig. 1. Scheme of the combined stripping-adsorption process typically used for the recovery of nitrogen as ammonium sulphate from aqueous waste.

2. Materials and Methods

2.1. Air flowrate model

In order to compare the theoretical predictions of stripped NH_3 with experimental results obtained by managing the stripping tower (operating in semibatch 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 NH₃ concentration: 2300 mg/L
- liquid volume in the semi-batch reactor: 12 m³
- imposed air flow rates: 120 240 480 720 Nm³

2.2. Experimental procedure and chemical analysis

The experimental stripping of ammonia from real AW (initial N-NH₄⁺ concentration= 1900 mg/L) was tested insufflating air with a flow rate of 500 Nm³/h in the real stripping tower (volume = 12 m³) operating in semi-batch condition. pH and temperature were maintained at 9.2 and 60 °C, respectively. NaOH and HCl for titration tests were purchased from Merck. The tests of the evolution of pH have been made maintaining the temperature equal to 60 °C and the air flow rate equal to 500 Nm³/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 Nm³/h of air flow rate and are reported in Figure 3.

The comparison showed that, according to the model, the removal of ammonia was 55 %, substantially aligned with the experimental data (52 %). Therefore, the transfer of ammonia from the liquid phase to the gas phase was in conditions of almost equilibrium and followed Henry's equation. The results also showed that the air flow rate of 500 Nm³/h was the minimum one necessary to allow reaching ammonia nitrogen removals close to 50% in 6 hours and closer to 80% in 9 hours of stripping.

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 Nm³/h, the mathematical model estimated an ammonia removal close to 70%. Experimental tests also confirmed this result (data not shown). The stripping tower improved the ammonia removal yield by 30% varying air flow rate from 500 to 680 Nm³/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 evolution of the ammonia concentration in a semi-batch stripping plant with different air flow rate ($T=60^{\circ}C$; pH=9.2).



Fig. 3. Experimental data of the ammonia concentration in a real stripping tower (T= 60 °C; Air flow rate= 500 Nm³/h; pH= 10.2; reactor operating in semi-batch mode).

3.2. pH optimization

Experimental titration tests with NaOH 1N 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/m³ of 32 % weight/weight (w/w). NaOH were required (more than three times the estimated value).

This result could be due to: (i) the contemporary 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 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 HCl 1 N in order to identify which acid compounds were present in the solution. The results are reported in Figure 4b. 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, the pH has risen from 7.7 to near values to 9.2 (data not shown). 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 removal of ammonia content close to 80% after 9 hours of stripping time. All these data can be seen in Figure 5.

These results can be explained by the fact that in the two cases, despite the removal of a base (NH₃), 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 basified agents (such as NaOH) was avoided minimizing the costs.



Fig. 4. (a) Titration curves of 100 mL of AW with NaOH 1N and (b) titration curve of 100 mL of AW with HCl 1N.



Fig. 5. Evolution of the pH and N-NH₃ concentration of the AW in a real semi-batch CSTR stripping plant (T= 60 °C; Air flow rate= 500 Nm³/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 Nm³/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-NH₃ removal yield, the tests showed the possibility of increasing the pH by exploiting the alkalinity that characterizes the digestates without the dosage of basifying reagents (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 semibatch mode.

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-NH₃ stripping and to avoid the dosage of basifying reagents.

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