JESTECH, 15(2), 85-91, (2012)

JESTECH

# AIR STRIPPING OF AMMONIA FROM COKE WASTEWATER

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## Abstract

In this study, the treatability of ammonia from coke wastewater by the air stripping processes was investigated. The two air stripping reactors were used for finding operation conditions of batch and semi-batch. Effects of various operating parameters such as initial pH, stripping time, air flow and liquid flow (semi-batch condition) on ammonia removal with air stripping process were examined. The maximum removal efficiency in the semi-batch condition was 100%. The values of initial pH, stripping time, air flow and liquid flow in the air stripping carried out using semi-batch reactor were found to be 12, 14 h, 12 L/min and 2.5 ml/min, respectively. In the case of batch conditions, maximum removal efficiency of ammonia was 96.7% at the optimum operating conditions (initial pH 12, stripping time of 24 h and air flow of 12 L/min). During the air striping, the stripping efficiency and mass transfer coefficient in the both semi-batch and batch conditions increased with increasing air flow and initial pH.

**Key words:** Ammonia removal, air stripping, coke wastewater.

## 1. Introduction

Wastewater is generated in coal coking, coal gas purification, and by-product recovery process of coke factories in iron and steel industries. This wastewater is mostly generated from cooling step after coking coals at high temperatures (900-1100 $^{o}$C) and liquid-stripping step of the produced coke oven gas. Coke wastewater commonly contains ammonia, free cyanide, thiocyanate, sulphite, and many toxic organic contaminants such as phenols and polynuclear aromatic hydrocarbons [1-6]. Among the pollutants, ammonia is a major concern and high levels of ammonia are commonly presented in coke wastewater [7-9]. Ammonia contamination of water bodies is a widespread environment problem. The ammonia water causes a promotion of eutrophication which is toxic effect to fish aquatic lives (0.2-2 mg/L). In addition to, ammonia a hindrance to the disinfection of water supplies as well as having an offensive smell and carcinogenesis [10] and wastewater containing ammonia are often toxic, which makes their biological treatment unfeasible [11]. Therefore, ammonia must be properly removed from coke wastewater before it discharges into aquatic systems. The ammonia can be removed or decomposed by several methods such as air stripping [12-14], biological nitrification-denitrification [15,16], breakpoint chlorination [10], struvite precipitation [17,20], membrane separation [21], catalytic liquid- phase oxidation [22], and selective ion exchange [23].

The air stripping process with relatively low cost and simple equipments is widely used in removal of ammonia from wastewater and high rates of ammonia removal can be achieved [14]. In addition ammonia removed by air stripping can be reabsorbed to acid absorption solution. If sulphuric acid is used as an absorber, ammonium sulphate slurry formed can be potentially used for fertilizer production. So, air stripping is an effective method for the removal of ammonia from wastewater. There are various air stripping systems such as packed tower [24, 25], bubble aeration [24], water-sparged aeroclone [26] and micro-fabricated stripping column [27]. Air stripping is usually operated in a packed tower because it can prove a larger mass transfer area [25]. However, air stripping in packed tower usually leads to scaling and fouling on packing because of reaction between $CO_2$ in air and some metal ions in water [26]. Other air striping system is bubble aeration, used for removal of gas contaminators without packing. This kind of air stripping process has a

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number of advantages which does not require any construction, is a simple and is generally inexpensive [24].

In this study, both bubble aeration and packed tower methods were applied to removal of ammonia from coke wastewaters containing for high concentrations of ammonia. The removal efficiency of ammonia was investigated for effects of initial pH, stripping time, air flow and liquid flow (semi-batch condition). Moreover, mass transfer coefficients of both bubble aeration and packed tower process were calculated.

## 2. Methods

### 2.1 Characterizations of coke wastewater

The wastewaters taken from coke plant in Turkey were produced for 600 $m^3$/d. Its physical chemical parameters were shown in Table 1.

**Table 1.** Characterization of the coke wastewater

| Parameter | Average concentration |
|---|---|
| pH | 10.5 |
| Conductivity (mS/cm) | 12.6 |
| COD (mg/L) | 6250 |
| TOC (mg/L) | 2200 |
| Phenols (mg/L) | 1400 |
| $NH_3^-$ (mg/ L) | 2500 |
| $CN^-$ (mg/L) | 210 |
| $SCN^-$ (mg/L) | 420 |
| $S^{2-}$ (mg/L) | 1.4 |
| $SO_3$ (mg/L) | 45 |

### 2.2 Bubble Aeration and Packed Tower experimental setup

A glass reactor with 1L of volume was used for bubble aeration experiments. A plexiglass column was used for packed tower air stripping (50 cm height x 5 cm internal diameter) for semi-batch, batch for the liquid and continuous flow for the gaseous phases (Fig. 1). As the packing material in the air stripping tower, glass beads were used. All runs were performed at constant temperature (25 $^oC$). The efficiency of ammonia removal, $\eta$ is defined according to (Eq.1)

$$\eta = \frac{C_{in} - C_t}{C_{in}} \qquad \text{Eq.1}$$

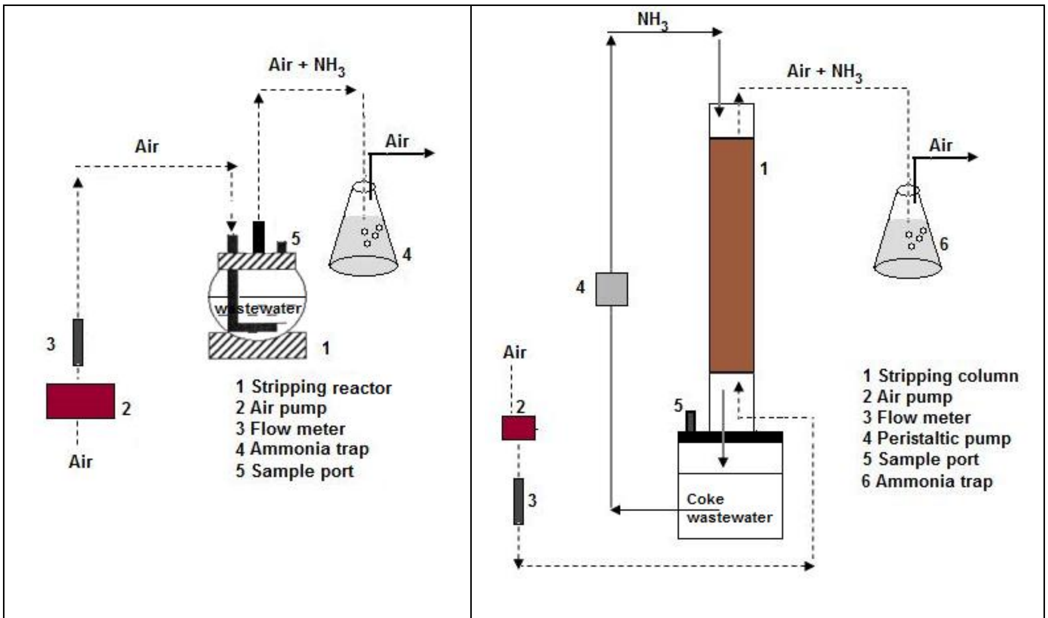
where $C_{in}$ and $C_t$ are the ammonia concentrations (mg/L) in the suspension at the beginning and at any time (h).

For an air stripping system, the mass transfer rate of volatile ammonia from wastewater in a batch stripping unit was derived [28] and shown as follows:

$$-ln\left(\frac{C_{A_t}}{C_{A_0}}\right) = \frac{Q_G H_A}{V_L}\left[1 - \exp\left(-\frac{K_L a V_L}{H_A Q_G}\right)\right] t \qquad \text{Eq.2}$$

where $C_{A_t}$ and $C_{A_0}$ are the liquid phase concentrations (g/$m^3$) of ammonia at any time and at the beginning; $H_A$ is the dimensionless Henry's constant; $K_L$ is the overall liquid mass transfer coefficient (m/min); $a$ is the interface area per unit volume of liquid ($m^2/m^3$); $V_L$ is the total volume of liquid (L), $Q_G$ is the gas flow rate (L/min) and $t$ is the stripping time (min). When $K_L a V_L / H_A Q_G \ll 1$, Eq. (2) predicts as the exit stripping gas was far from saturation. In this study, ammonia is an easily soluble gas and the exit stripping gas is possibly far from saturation, so the calculation of the mass transfer coefficient of ammonia removal was tentatively made according to Eq.(3).

$$-ln\frac{C_{A_t}}{C_{A_0}} = K_L a\, t \qquad \text{Eq. 3}$$




(a) batch stripper/absorber system (b) semi-batch stripper/absorber system

**Figure 1.** A schematic representation of used processes ammonia removal from coke wastewater

### 2.3 Analytical Procedures

Determinations of ammonia, pH, conductivity, COD, TOC, phenols, $CN^-$, $SCN^-$, $S^{2-}$, $SO_3$ were carried out by standard analysis methods [29]. Concentrations of COD, $CN^-$, $SCN^-$, phenols were determined by using a single beam spectrophotometer (UV-VIS, Chebios, Italy). TOC of the samples were analyzed by using TOC analyzer (Apollo 9000, Tekmar-Dohrmann, USA) Turbidity was measured by turbidity meter (Micro TPI, HF scientific, USA). pH and conductivity of samples were measured by a pH meter (C931, Consort, Belgium) and conductivity meter (340i, WTW, USA), respectively. pH adjustments were done by NaOH or $H_2SO_4$ (Merck).

## 3. Results and Discussion

In this study, efficiency of ammonia removal from coke wastewater by air stripping depends on several operating parameters such as initial pH, air flow, stripping time and liquid flow (for packed tower).

### 3.1 Bubble Aeration experiments

Removal of ammonia via direct aeration stripping involving forcing air through a reactor resulted in the release of volatile ammonia to the air. The ammonia in coke wastewater existed in two forms which were ammonium ions and free ammonia. Ammonia equilibrium in aqueous solution depended on pH and temperature was expressed in the following equation:

$$[NH_3] = \frac{[NH_3 + NH_4^+]}{1 + \frac{[H^+]}{K_a}} \qquad \text{Eq. 4}$$

where $[NH_3]$ is free ammonia concentration, $[NH_3 + NH_4^+]$ is total ammonia concentration and $K_a$ is ionization constant. pH was the most important parameter in $[NH_3 + NH_4^+]$ equilibrium and increased by addition of the NaOH or lime. Minocho and Rao [30] stated that using NaOH was more beneficial than lime. Therefore, pH was adjusted using NaOH. Initial pH values were varied in the range of 9.61-13. Experiments were conducted at 10 L/min air flow and 24 h stripping time. In air stripping experiments, effects of initial pH on ammonia removal efficiency was shown in Fig. 2. As seen Fig. 2, as initial pH increased, removal of ammonia from wastewater increased. But there wasn't much difference in removal of ammonia between pH 12 and 13. The highest removal of ammonia was achieved in approximately 24 h when initial pH was 12. Consequently, the optimum initial pH was found to be pH 12. At this pH, concentration and removal efficiency of ammonia were as 116 mg/L and 95.5%, respectively. The above mentioned literature studies were related to investigation of the treatment of ammonia by bubble aeration process. Liao et all [24], investigated ammonia removal from swine manure wastewater by air stripping and obtained high removal of ammonia at initial pH 11.2. In other study, Basakcılardan [31] examined nutrient recovery from source-separated human urine by bubble aeration process at initial pH 12 and 98% of ammonia nitrogen was stripped. The results of present study were similar to the other research results reported in the literature.

Air flow was another important parameter on ammonia removal in air stripping. Especially, high air flow caused for the increased rate of removal ammonia in bubble aeration process. Figure 3 illustrated the effect of air flow on removal ammonia in air stripping (stripping time of 24 h and pH 12). The air flows from 8 to 12 L/min in the bubble aeration were varied. Maximum ammonia removal efficiency at 12 L/min and 24 h was 99%. As seen in Fig. 3, at the 11 h stripping time, ammonia concentration reduced under the 200 mg/L. In these conditions, calculating mass transfer coefficient was 0.157 L/min.

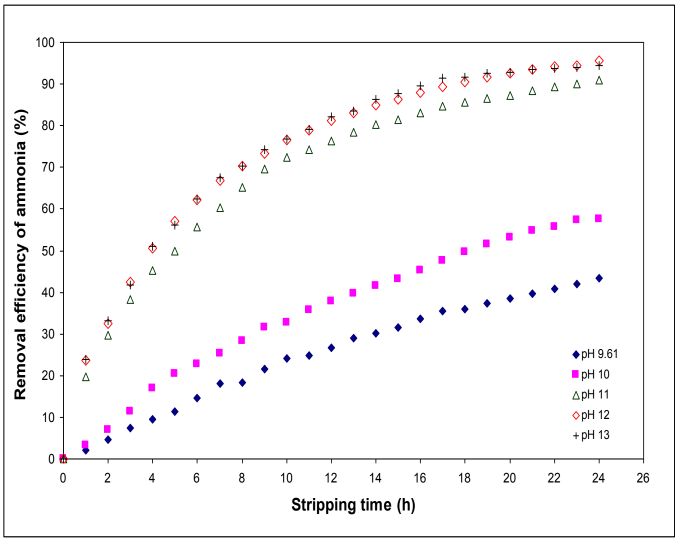



**Figure 2.** Effect of initial pH on removal of ammonia in bubble aeration air stripping (Air flow of 10 L/min, stripping time of 24 h).

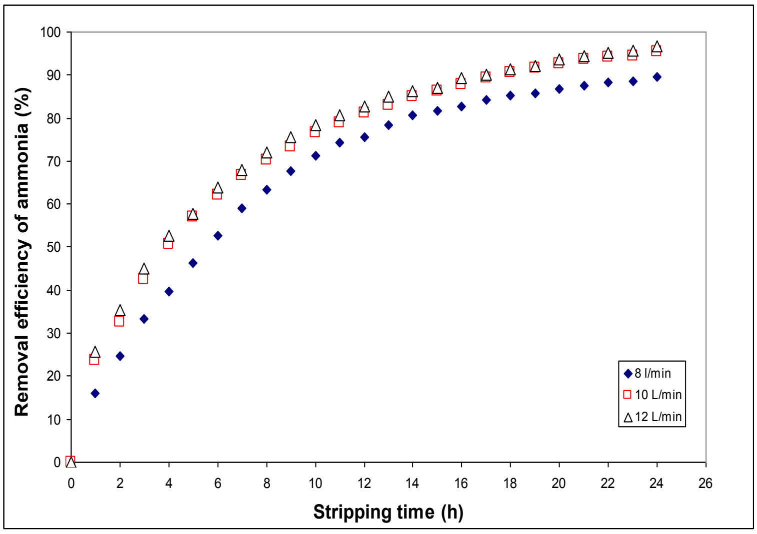



**Figure 3.** Effect of air flow on removal of ammonia in bubble aeration air stripping (Initial pH 12, stripping time of 24 h).

### 3.2 Packed tower experiments

Another air stripping method for removal of ammonia was packed tower. In this study, packed tower in semi-batch condition was operated. The effects of various operating parameters such as initial pH, stripping time, air flow and liquid flow on ammonia reduction with air stripping process were examined. In addition, liquid flow as an operation parameter was examined. To determine the effect of initial pH on the removal of ammonia by packed tower, experiments were conducted at 10 L/min air flow, liquid flow of 10 ml/min and stripping time of 24 h. Effects of initial pH (9.61-13) on removal of ammonia were shown in Fig. 4. As seen as Fig 4, removal efficiency of ammonia increased from 53% to 100% as initial pH increased. Removal of ammonia at pH 12 was almost the same at pH 13. The highest removal of ammonia was obtained at pH 12 and 24 h stripping time. Under these operating conditions, effluent of ammonia concentration was 12 mg/L.

To investigate the effect of air flow on removal efficiency of ammonia in packed tower air stripping was carried out using various air flows (8-12 L/min). Fig. 5 showed effects of air flow on ammonia removal efficiency in packed tower. When the air flow from 8 L/min to 12 L/min was increased, ammonia removal efficiency increased. For 10 L/min and 12 L/min air flows, there wasn't much difference with result. When the air flow was 12 L/min, ammonia concentrations at 14 h and 15 h stripping time were 14.2 mg/L and 0 mg/L, respectively.

Another important operation parameter was liquid flow. Effect of liquid flow on removal efficiency of ammonia was investigated (Figure 6). For these purpose, the liquid flow from 2.5 to 10 mL/min was used. When the liquid flow decreased, ammonia removal rate increased. Moreover, all of liquid flow values at 15 h stripping time ran out of ammonia concentrations. In these conditions, calculating mass transfer coefficient was 0.376 L/min.

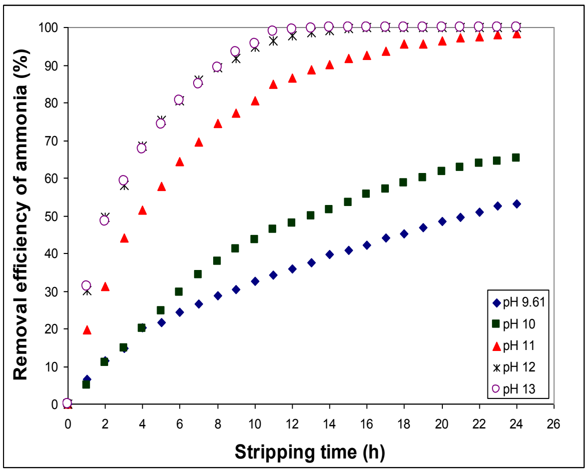



**Figure 4.** Effect of initial pH on removal of ammonia in packed tower air stripping (Air flow of 10 L/min, Liquid flow of 5 ml/min, stripping time of 24 h).

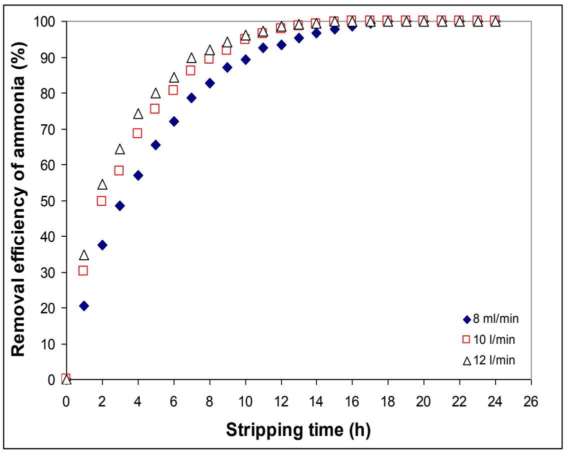



**Figure 5.** Effect of air flow on removal of ammonia in packed tower air stripping (Initial pH 12, Liquid flow of 5 mL/min, Stripping time of 24 h).

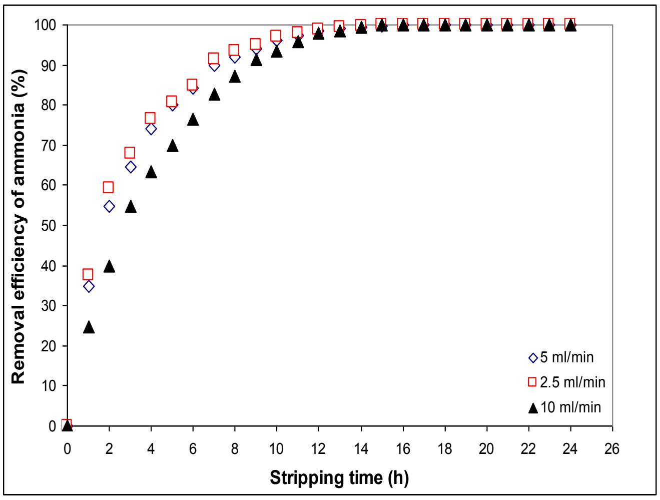



**Figure 6.** Effect of liquid flow on removal of ammonia in packed tower air stripping (initial pH 12, air flow of 12 L/min, Stripping time of 24 h).

## 4. Conclusions

Air stripping of ammonia is a widely used process for the pre-treatment of wastewater. Traditionally, this process is carried out in stripping tanks or packed towers. In this study, removals of ammonia via both bubble aeration process and pocked tower process were investigated. As a result of experiments, packed tower process in removal of ammonia was more effective than bubble aeration process. The optimum operation parameters in removal of ammonia by packed tower process were initial pH of 12, air flow of 12 L/min, liquid flow of 2.5 mL/min and stripping time of 14 h. Under these conditions, residual ammonia concentration and mass transfer coefficient was 0 mg/L and 0.376 $min^{-1}$, respectively. In air stripping by bubble aeration process experiments, optimum operation parameters were initial pH of 12, air flow of 12 L/min and stripping time of 24 h. Removal efficiency of ammonia in these conditions was 96.7%. Consequently, air stripping processes both bubble aeration and pocked tower for removal of ammonia from coke wastewaters were fairly effective processes.

## Acknowledgements

This research was supported by Research Foundation of Cumhuriyet University (Project Code:M-427).

## References

1. Hong-Duck, Y., Young-Ok, C. and Sang-III, Lee., Effect of Ferrous Ion Coagulation on Biological Ammonium Nitrogen Removal in Treating Coke Wastewater, Environmental Enninerring Science, Vol. 26, 12, 1739–1746, 2009.
2. Zhang, M., Tay, J.H., Qian, T., and Gu, X.S., Coke ptant wastewater treatrnent by fixed biofiim systems for COD and $NH_3$-N removal. Water Res. 32, 519-527,1998.
3. Kumar M.S., Vaidya, A.N., Shivaraman, N., and Bal, A.S., Performance evaluation of a full-scale coke oven wastewater treatment plant in an integrated steel plant, Indian J. Environ. Health, 45, 29-38, 2003.
4. Li, Y., Gu, G.W., Zhao, J.F., Yu, H.Q., Qin, Y.L., and Peng, Y.Z., Treatment of coke-plant wastewater by biofilm systems for removal of organic compounds and nitrogen, Chemosphere, 52, 997-1005, 2003.
5. Kim, Y.M., Park, D., Lee, D.S., and Park, J.M., Instability of biological nitrogen removal in a cokes wastewater treatment facility during summer, J Hazard. Mater. 141, 27-32, 2007.
6. Chakraborty, S. and Veeramani, H., Effect of HRT and recycle ratio on removal of cyanide, phenol, thiocyanate and ammonia in an anaerobic—anoxic—aerobic continuous system, Process Biochem. 41, 96-105, 2006.
7. Wong-Chong, G.M. Retrofitting LTV coke plant waste water treatment system to comply with pretreatment discharge limits, Iron Steel Eng. 71, 26-28, 1994.
8. Jeong, Y.S., and Chung, J.S., Simultaneous removal of COD, thiocyanate, cyanide and nitrogen from coal process wastewater using fludized biofilm process, Process Biochem. 41, 1141-1147, 2006.
9. Rong, Q.I., Kun, Y., and Zhao, YU., Treatment of coke plant wastewater by SND fixed biofilrn hybrid system. J. Environ. Sci. 19, 153, 2007.

10. Prasad, B. and Singh, G., Removal of Ammonia from wastewater with special emphasis on coke-oven effluents, Environ. Protec. Eng. Vol. 16, 39, 1990.
11. Vazquez. I., Rodriguez, J., Maranon, E., Castrillon, L., and Fernandez, Y., Simultaneous removal of phenol, ammonium and thiocyanate from coke wastewater by aerobic biodegradation. J. Hazard. Mater. 137, 1773-1780, 2006.
12. Bonmati, A., and Floatats, X., Air stripping of ammonia from pig slurry: characterization and feasibility as a pre- or post-treatment to mesophilic anaerobic digestion, Waste Manage. 23, 261–272, 2003.
13. Basakcilardan-kabakci, S., Ipekoglu, A.N., and Talinli, I., Recovery of ammonia from human urine by stripping and absorption, Environ. Eng. Sci. 24, (5), 615–624, 2007.
14. Ozturk, I., Altinbas, M., Koyuncu, I., Arikan, O. and Gomec-Yangin, C., Advanced physical-chemical treatment experiences on young municipal landfill leachates, Waste Manage. 23, 441–446, 2003.
15. Calli, B., Mertoglu, B., and Inanc, B., Landfill leachates management in Istanbul: applications and alternatives, Chemosphere 59,819–829, 2005.
16. Dempsey, M.J., Lannigan, K.C., and Minall, R.J., Particulate-biofilm, expanded-bed technology for high-rate, low-cost wastewater treatment: nitrification, Water Res. 39, 965–974. 2005.
17. Jeong, Y.K., and Hwang, S.J., Optimum doses of Mg and P salts for precipitating ammonia into struvite crystals in aerobic composting, Bioresour. Technol. 96, 1–6, 2005.
18. Lee, S.I., Weon, S.Y., Lee, C.W. and Koopman, B., Removal of nitrogen and phosphate from wastewater by the addition of bittern, Chemosphere 51, 265–271, 2003.
19. Uludag-Demirer, S., Demirer, G.N., and Chen, S., Ammonia removal from anaerobically digested dairy manure by struvite precipitation, Process Biochem. 40, 3667–3674, 2005.
20. Rensburg, P., Musvoto, E.V., Wentzel, M.C. and Ekama, G.A., Modelling multiple mineral precipitation in anaerobic digester liquor, Water Res. 37, 3087–3097, 2003.
21. Tan, X.Y., Tan, S.P., Teo, W.K. and Li, K. Polyvinylidene fluoride (PVDF) hollow fibre membranes for ammonia removal from water, J.Membr. Sci. 271, 59–68, 2006.
22. Hung, C.M., Lou, J.C. and Lin, C.H., Removal of ammonia solutions used in catalytic wet oxidation processes, Chemosphere 52, 989–995, 2003.
23. Jorgensen, T.C., and Weatherley, L.R., Ammonia removal from wastewater by ion exchange in the presence of organic contaminants, Water Res. 37, 1723–1728, 2003.
24. Liao, P.H., Chen, A. and Lo, K.V., Removal of Nitrogen from Swine Manure Wastewaters by Ammonia Stripping, Bioresource Technology, 54, 17-20, 1995.
25. Djebbar, Y. and Naraitz, R.M., Improved Onda correlations for mass transfer in packed towers, Water Sci. Technol. 38, (6), 295–302, 1998.
26. Quan, X., Wang, F., Zhao, Q., Zhao, T., and Xiang, J., Air Stripping of Ammonia in a water-sparged aerocyclone reactor, Journal of Hazardous Materials, 170, 983-988, 2009.
27. Cypes, S.H. and Engstrom, J.R., Analysis of a toluene stripping process: a comparasion between a microfabricated stripping column and a conventional packed tower, Chemical Engineering Journal, 101, 49-56, 2004.
28. Wu, Y., Li, Q., and Li, F., Desulfurization in the gas-continuous impinging stream gas-liquid reactor, Chem. Eng. Sci. 62, 1814–1824, 2007.
29. APHA, Standart Methods for examination of water and wastewater. American Water Work Association. New York. 1992.
30. Minocho, V.K., and Rao, A.V.S., Ammonia removal and recovery from urea fertilizer plant waste, Environ. Techno. Lett. 9, 655-664, 1998.
31. Basakcılardan-Kabakcı, S., Nutrient Recovery from Source-separated Human Urine, İstanbul Technical University, Instıtute of Science and Technology, 2005.