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Technical Note

A membrane-integrated advanced scheme for treatment of industrial wastewater: Dynamic modeling towards scale up

Ramesh Kumar, Parimal Pal *

Environment and Membrane Technology laboratory, Department of Chemical Engineering, National Institute of Technology, Durgapur 713 209, India

HIGHLIGHTS

- Mathematical model developed for an advanced integrated water treatment plant.
- Highly integrated scheme is novel in ensuring by-product recovery and water reuse.
- Model successfully predicted plant performance.
- Study will facilitate industrial scale up of this new and advanced scheme.

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ABSTRACT

Modeling and simulation was carried out for an advanced membrane-integrated hybrid treatment process that ensures reuse of water with conversion and recovery of ammoniacal nitrogen as value-added struvite fertilizer from coke wastewater. While toxic cyanide was largely removed in a pre-chemical treatment unit using Fenton's reagents under optimized conditions, more than 95% of NH_4^+–N could be recovered as a valuable by-product called struvite through addition of appropriate doses of magnesium and phosphate salts. Water could be turned reusable through a polishing treatment by nanofiltration membranes in a largely fouling free membrane module following a biodegradation step. Mathematical modeling of such an integrated process was done with Haldane–Andrew approach for the associated microbial degradation of phenol by *Pseudomonas putida*. Residual NH_4^+ was degraded by nitrification and denitrification following the modified Monod kinetics. The model could successfully predict the plant performance as reflected in reasonably low relative error (0.03–0.18) and high Willmott *d*-index (>0.98).

1. Introduction

Since the early 1970s efforts have been directed towards modeling of wastewater treatment processes. Activated sludge process (ASP) is one such wastewater treatment scheme for which some models were developed by the task group of International Water Works Association. However, these models have been used in carbon oxidation, nitrification, denitrification and biological phosphorus removal processes (Gujer and Henze, 1991) primarily for domestic wastewater treatment only and there is significant limitation to their application to industrial wastewater treatment. With development of highly selective membranes in the area of separation and purification, membrane-integrated novel processes are now emerging with the promise of much better quality of treated water. However, modeling studies on such membrane-integrated treatment processes are extremely scanty. In some typical highly water-intensive industries like coke making and metallurgical industries, problems of effective treatment of enormous quantities of complex wastewater persist in the absence of scale up confidence. This is where modeling and simulation studies of modern membrane-integrated treatment schemes are absolutely essential.

Coke wastewater generated in the coal carbonization plants contains substantial amounts of toxic compounds such as thiocyanate, cyanide along with NH_4^+ and organic compounds like phenols, aromatic nitrogenated compounds and polycyclic aromatic compounds. Often wastewater discharges from coke making industries enter into the river bodies causing severe pollution to surface waters. Thus for environmental preservation the enormous quantities of coke plant wastewater should be treated at relatively low cost. This could be done in biological treatment units for major pollutants like phenol, NH_4^+ and hydrocarbons but presence of cyanide compounds very often turns survival of the microbes difficult in the environment of the treatment system and this often leads to failure of such plants (Ghose, 2002). Individual studies on cyanide, phenol and nitrogen removal kinetics have been documented.

* Corresponding author. Tel.: +91 343 2755055; mobile: +91 9434788105; fax: +91 343 2754078.
E-mail address: parimalpaul1999@yahoo.co.in (P. Pal).

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Chemical treatment of cyanide by oxidation using hydrogen peroxide in presence of copper catalyst has been reported (Sarla et al., 2004) to follow pseudo-first order model. Biodegradation of phenol has been described by Haldane–Andrew growth kinetics model for the entire concentration range (Kumar et al., 2005). Dincer and Kargi (2000) found that nitrogen removal in sequential nitrification and denitrification processes follow the Monod kinetics. Development of new techniques to recover nitrogen is essential in the current scenario. NH_4^+–N in high concentration may be separated and recovered by adding magnesium and phosphate salt which on reaction with ammonium nitrogen precipitate out as magnesium ammonium phosphate hexahydrate (MAP), a useful by-product (Lee et al., 2003; Wang et al., 2006). However, very little has been reported till date on the modeling of an integrated processing scheme leading to reuse of water while simultaneously adding economy to the process. Through recovery of valuable struvite by-products from wastewater as proposed in the present study, economic viability is likely to improve substantially towards sustainable management. The new scheme also saves on consumption of fresh water from external sources as it turns treated water reusable within the same industry. Though, literature abounds in experimental studies of activated sludge process, Fenton's treatment and similar chemical treatments, studies on schemes integrating biological, chemical and membrane based treatments using microporous and nanofiltration membranes have hardly been reported. Modeling and simulation studies of such plants are absolutely essential for industrial scale-up. The present study intends to develop a realistic mathematical model for such an integrated process. Such a model if succeeds in predicting the performance of the membrane-integrated bio-chemical treatment plant will pave the way for industrial scale up. To our knowledge, no such studies have been reported in the literature.

2. Theory and model development

2.1. Chemical and biological treatment unit

Toxic cyanide compounds as present in coke oven wastewater can be degraded into less harmful compounds using Fenton's reagent. Cyanide removal in such chemical treatment follows the first-order kinetics. Similarly, NH_4^+ present in high concentration may also be precipitated out in the form of magnesium ammonium phosphate or MAP (also known as Struvite, $MgNH_4PO_4{\cdot}6H_2O$) by adding magnesium and phosphate salts to such wastewater where first order kinetics (Nelson et al., 2003) are followed.

Modeling of phenol, NH_4^+ and nitrate degradation process involves mass balance of these pollutants, which in the present case, requires the knowledge of the flow pattern of the liquid phase and the process kinetics. The following assumptions were made while formulating the model: (a) micro-organisms are pre-acclimated to the substrate and can metabolize substrate in the aqueous phase only; (b) during biodegradation, the pH of the system remains constant; (c) no degradation of substrate takes place in the settling tanks; (d) dissolved oxygen (DO) content is sufficient enough to sustain the aerobic reactions in the nitrification process; (e) food to microorganism ratio (F/M) was maintained in the ranges of 0.06–0.1 kg COD kg^{-1} VSS d^{-1} in the nitrification unit; (f) dissolved oxygen concentration (DO) was maintained at less than 0.5 mg L^{-1} in the denitrification unit and (g) substrate-specific treatment occurs in each reactor and other substrates remain inert if present simultaneously.

To simulate the continuous operation of the phenol, NH_4^+ and nitrate degradation in the reactor, the treatment scheme as presented in Fig. SM-1 of Supplementary material (SM) is modeled. The mass balance for the reactors has been done with variable parameters like substrate, biomass and specific growth rate of micro-organism. The reflux ratio, for all the three recycles is taken to be 10%. The intentional wasting coefficient (β) is a parameter used to maintain sludge retention time (SRT). When effluent substrate concentration (S_e) reaches below detection limit; β can be optimized to stabilize the system. Material balance and model development for the combined reactor and clarifier system may be seen online in SM Section 2.1.

2.2. Nanofiltration membrane separation

Based on the present scheme of separation of ionic contaminants specifically chloride and bicarbonate ions from chemically and biologically treated effluent using cross flow nanofiltration membrane module a mathematical model has been developed by using extended Nernst–Planck approach (ENP). Model equations are formulated with the assumptions that (a) the membrane consists of a bundle of identical straight cylindrical pores of radius r_p and length Δx (with $\Delta x \gg r_p$); (b) the effective membrane volume charge (X_d) is constant throughout the membrane and is mainly controlled by the feed concentration and (c) concentration of component i inside the membrane and electric potential are defined in terms of radially averaged quantities.

In the modeling, the linearization approach of Bowen and Welfoot (2002) was adopted. In the present investigation, transport model has been developed for chloride and bicarbonate ions through NF membrane. The details of nano-transport model development, determination of physico-chemical parameters and computational procedure may be seen online in SM Section 2.2. The values of the parameters used in the model development have been summarized in Table SM-1.

3. Experimental

3.1. Materials

All the chemical reagents used during investigation were of reagent grade and were used as such without further purification. NH_4^+ and cyanide standard solutions were procured from Merck (Germany). The chemicals like methanol for calibrating phenyl column (Sigma–Aldrich, WI, USA), phenol and other chemicals were purchased from Merck (India). Thin film composite polyamide nanofiltration (NF1, NF2, NF3 and NF20) as well as poly vinylidene fluoride (PVDF) microfiltration membranes were procured from Sepromembranes (USA) and Membrane solution (USA) respectively.

3.2. Wastewater sampling and characterization

The industrial wastewater used in the reactor was actual coke-oven wastewater (ammoniacal liquor) from an operating plant (Durgapur Project, West Bengal, India) which is a coal based power plant manufacturing coke as by product. Its physico-chemical characterization is presented in Table 1.

3.3. Experimental set-up

The integrated wastewater treatment plant consists of a series of continuous stirred tank reactors (CSTR). All the CSTRs (made of stainless steel, SS 316) are positioned in vertically lowering order allowing free flow of the liquid to the next stage reactors by gravity eliminating the need for use of pumps in between the reactors as shown in Fig. 1. Two membrane modules were connected in series for micro and nanofiltration. While membrane modules like hollow fibre and spiral bound are prone to rapid fouling the