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Development of an anaerobic co-metabolic model for degradation of phenol, *m*-cresol and easily degradable substrate



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1. Introduction

ABSTRACT

Phenol and *m*-cresol are common and refractory organic wastes in industrial wastewater. Anaerobic digestion is one of the most widespread technologies in dealing with this kind of wastewater. For the purpose of providing more useful information for the design and operation of the biodegradation trials of phenolic wastewater, two new modified Monod-type kinetics, the mutual inhibition between phenol and *m*-cresol, the co-metabolism between refractory substrates and easily degradable substrates were developed to simulate existing experimental data. Parameter *K* and parameters of mutual inhibition *I* are introduced to successfully present the promoting impact and mutual inhibition, respectively. The results of the simulations reproduce well the experimental data and therefore the developed model was validated. Based on the experimental data and model predictions from this study, it can be concluded that *m*-cresol affects the degradation. The developed model can be used as a useful tool by the treatment plant operators in order to design optimal operation conditions for phenol degradation.

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Phenols occur in wastewater of a number of industries. Industrial wastes from refineries, wood preservation plants, pulp and olive mills as well as, slaughterhouse, animal and household wastes contain large amount of phenolic compounds [1–3]. Phenols are toxic and difficult to degrade biologically [4], and therefore, these compounds can be found in high concentrations in the surrounding environment of the aforementioned industries. These pollutants are harmful for the environment, toxic to organisms and recognized as carcinogenic compounds [5]. For the above reasons, phenolic compounds have been listed as priority pollutants for degradation by many governmental environmental agencies and by individual researchers [6–9]. Therefore, there is a real increasing interest to find and optimize methods for phenolic compounds degradation.

There are many methods to treat phenolic compounds including physical, chemical and biological methods. Biological methods offer potential advantages like low cost and high efficiency in

http://dx.doi.org/10.1016/j.bej.2015.11.003 1369-703X/© 2015 Elsevier B.V. All rights reserved. degradation of phenolic pollutants. Biological treatment processes include aerobic and anaerobic degradation. Aerobic treatment is the most common method used for phenolic compound degradation. On the other hand, anaerobic treatment technologies have gained wide acceptance in the past decades for the treatment of high-strength industrial wastewater. Compared with the more conventional aerobic processes, anaerobic processes save the energy for aeration, produce substantially lower quantities of sludge and convert organic pollutants into a readily usable fuel, methane. However, anaerobic degradation of these pollutants has only been studied more recently. Phenolic compounds are the self-inhibited compounds, which are toxic to microorganisms in biological wastewater treatment at high concentration, and anaerobic digestion cannot handle effectively high concentration of phenolic compounds alone. Current research shows that the cometabolism between refractory substrates and easily degradable substrates can promote the degradation of the refractory substrates [10–12]. There are some attempts to accelerate the degradation efficiency of phenolic compounds in wastewater via addition of the easily degradable substrates, such as glucose, sucrose, volatile fatty acid and methanol. Degradation of the easily degradable substrates not only keeps microbes active but also provides ATP and hydrogen to enhance the degradation of phenolic compounds via hydrogena-



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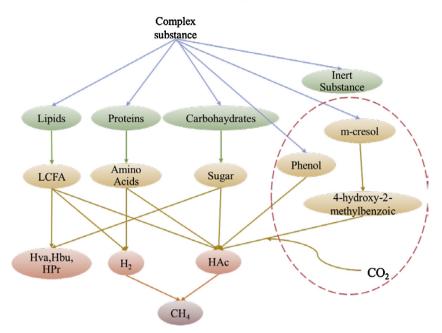


Fig. 1. Schematic diagram of ADM1 inserted with degradation of phenol and *m*-cresol.

tion, phenyl ring cleavage and bond broken [13,14]. Therefore, there is a need to investigate the effect of easily degradable substrates on the anaerobic degradation of phenolic compounds.

Industrial wastewater often contains more than one phenolic compound, the coexistence of phenol and *m*-cresol are quite common, while it has been reported that the presence of *m*-cresol affects phenol degradation and vice-versa [15]. The development of a model based on the commonly used Anaerobic Digestion Model No. 1 (ADM1) [16], which will include both phenol and *m*-cresol, in an integrated approach, to predict and simulate the phenolic compounds degradation will determine optimal operation conditions and will assist to control the phenolic degradation processes in anaerobic treatment plants. Up to now, anaerobic process modeling of phenol degradation was reported only in a few studies [16–18]. However, in these research works co-metabolism of phenol and *m*-cresol has not be included in the models development [17–19], although as aforementioned the coexistence of phenol and m-cresol are guite common and *m*-cresol affects phenol degradation. Taking into consideration the above key issues, the main objective of this research work is to develop a co-metabolic model based on ADM1 which considers (1) self-inhibition of phenol; (2) mutual inhibition between phenol and *m*-cresol; (3) the sucrose effect on the degradation of phenol and *m*-cresol via co-metabolism. The outcomes of this study are anticipated to extend the application of ADM1 and gain better understanding of the design and operation for the degradation process of phenolic wastewater.

2. Model development

2.1. The inhibition model of phenol and m-cresol

Phenol is a key intermediate in the anaerobic degradation of many complex aromatic chemicals. Benzoate is detected as an intermediate in the degradation of phenol and chlorophenol by anaerobic consortia. Currently, the universal pathway for anaerobic phenol digestion is that phenol is oxidized to benzoate, then via ring cleavage, β -oxidation (RBO) reactions, is finally oxidized to acetate [20]. Furthermore, in most of the research results benzoate has not been detected in the effluent while acetate accumulation was observed, so it was concluded that the process from phenol to benzoate is the rate-limiting step [21–23]. Due to the above reason and in order to simplify the degradation of phenol in ADM1, it is defined that phenol is directly degraded to hydrogen and acetate, while intermediate products are not taken into account.

Under the condition of available external carbon sources, the pathway for *m*-cresol in anaerobic digestion reaction is that *m*-cresol is oxidized to 4-hydroxy-2-methylbenzoic acid, then via ring cleavage, β -oxidation (RBO) reactions, is finally oxidized to acetate. Just like phenol degradation, it is defined that *m*-cresol is degraded to 4-hydroxy-2-methylbenzoic acid, then is oxidized to acetate and hydrogen, any other intermediates have been ignored in order to simplify the ADM1 model [24]. According to the above assumptions the conversion processes of phenol and *m*-cresol which were used on ADM1 are shown in Fig. 1.

In ADM1 system, the key rate equation is substrate uptake, which is based on substrate level Monod-type kinetics. When inhibitory substrates are present in an anaerobic system, a negative effect on the metabolism of anaerobic organisms occurs; in this case the basic Monod-type kinetics are not enough to simulate the anaerobic process. In order to get more accurate results the Monod-type kinetics are modified as follows:

The Monod-type kinetics is described in Eq. (1)

$$-\frac{\mathrm{d}S}{\mathrm{d}t} = \frac{k_{\mathrm{m}}XS}{(K_{\mathrm{S}}+S)} \tag{1}$$

The self-inhibited Monod-type kinetics is given in Eq. (2)

$$-\frac{\mathrm{d}S}{\mathrm{d}t} = \frac{k_{\mathrm{m}}XS}{\left(K_{\mathrm{s}} + S + \frac{S^{2}}{K_{\mathrm{i}}}\right)}$$
(2)

Where, K_i is the metabolic coefficient describing the inhibition of the metabolism of anaerobic organisms.

Phenol and *m*-cresol are inhibitory refractory substrates. It is established that the presence of *m*-cresol has not prevented complete phenol assimilation but has significant delaying effect on the phenol degradation dynamics [15,25,26], so a new parameter *I* is introduced to simulate the inhibition model between phenol and

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