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# Contribution of sludge adsorption and biodegradation to the removal of five pharmaceuticals in a submerged membrane bioreactor

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ABSTRACT

A submerged membrane bioreactor was set up to investigate the removal efficiencies of five pharmaceuticals from synthetic domestic wastewater. Batch experiments were conducted with sterilized sludge and activated sludge to explore the contributions of sludge adsorption and biodegradation for those pharmaceuticals. Notable difference of those pharmaceuticals removal efficiencies was observed, at about 92.2, 90.0, 55.4, 38.5 and 3.2% for acetaminophen, 17β-estradiol, naproxen, diclofenac sodium, and carbamazepine, respectively. Results of batch adsorption experiments via sterilized sludge showed that the removal efficiencies of five pharmaceuticals by sludge adsorption were 7.9, 68.2, 60.1, 40.1 and 71.5%, respectively, which were positively correlated with their octanol–water partition coefficients. Results of batch experiments via activated sludge showed that 83.4% of acetaminophen, 98.0% of 17β-estradiol, and 46.8% of naproxen were removed through the combination of sludge adsorption and biodegradation, while adsorption accumulation in sludge phase was only 1.8, 1.3 and 7.0%. This implies that the removals of these three drugs were mainly achieved by biodegradation. The total removal efficiency of diclofenac sodium was 19.7%, and the contributions of sludge adsorption and biodegradation were 14.9 and 4.8%, which indicated that the removal of diclofenac sodium was mainly achieved by sludge adsorption. The total removal efficiency of carbamazepine was only 8.9% and this implies that neither sludge adsorption nor biodegradation is effective for its removal.



## 1. Introduction

The occurrence and removal of pharmaceuticals in surface waters and sewage treatment plants have received increasing attention in recent decade [1–3]. Although pharmaceuticals are present at only trace-level concentrations of $\sim ng\,L^{-1}$ to $\sim \mu g\,L^{-1}$ in the aquatic environment, several questions have been raised regarding their chemical persistence, microbial resistance, and synergistic effects [4,5]. The discharge of sewage treatment plants (STPs) is identified as one of the major routes of pharmaceuticals exposed to the surface waters.

Studies on the removal of pharmaceuticals in sewage treatment have suggested that conventional activated sludge treatment processes usually show lower elimination efficiency than submerged membrane bioreactor (SMBR) in which higher biomass concentrations might increase the biodegradation potential and the longer sludge retention times (SRT) could promote biota diversity and enhance pharmaceuticals biodegradation [6–9]. In a SMBR, organic matters removal was mainly achieved through the combination of sludge adsorption, biodegradation and membrane interception. However, the membrane interception has little or no effect on the low molecular weight organic removal. Therefore, low molecular weight pharmaceuticals removal in the SMBR was mainly achieved by sludge adsorption and biodegradation. Some investigations on the removal of pharmaceuticals in SMBR differed greatly, ranging from nearly complete removal for some pharmaceuticals to almost no removal for other ones [7,8]. Some pharmaceuticals showed very different removal efficiencies even though they belong to the same therapeutic groups and the reasons are not fully understood [10].

It has been reported that the removal efficiencies of pharmaceuticals were influenced by their physicochemical properties [11]. For instance, higher removal efficiency of diclofenac was achieved under acidic condition (pH lower than its $pK_a$ value) than that under neutral pH condition, which can be explained by the compound changing from hydrophilic ionic forms to much more hydrophobic forms that are in favor of sludge adsorption [12]. No clear conclusion has been made on the relationship between octanol–water partition coefficients ($K_{ow}$) and their adsorption

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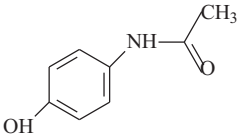
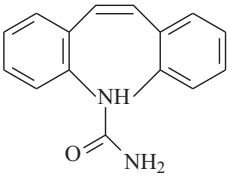
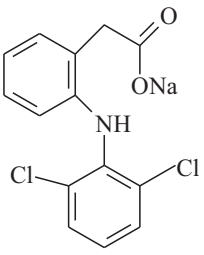
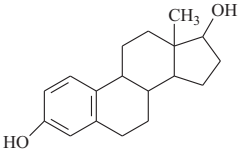
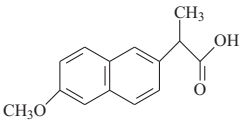
**Table 1**
Basic information and physicochemical properties of five selected pharmaceuticals.

| Compound names | Molecular formula | Molecular weight | Structural formula | $pK_a$ | $K_{ow}$[a] | Henry's law constants atm $m^3/mol$[a] |
|---|---|---|---|---|---|---|
| ACE | $C_8H_9NO_2$ | 151 |  | 9.7 | 0.46 | $6.42 \times 10^{-13}$ |
| CBZ | $C_{15}H_{12}N_2O$ | 236 |  | 13.9 | 2.45 | $1.08 \times 10^{-10}$ |
| Na-DCF | $C_{14}H_{10}Cl_2NNaO_2$ | 318 |  | 4.15 | 0.70 | $4.75 \times 10^{-12}$ |
| E2 | $C_{18}H_{24}O_2$ | 272 |  | 10.71 | 4.01 | $1.41 \times 10^{-12}$ |
| NAP | $C_{14}H_{14}O_3$ | 230 |  | 4.15 | 3.18 | $3.39 \times 10^{-10}$ |

[a] Available from "EPI Suite" software developed by USEPA.

removal efficiencies. Biodegradation of trace pharmaceuticals was mainly affected by their chemical structures. It has been suggested that pharmaceuticals containing chlorine or complicated circular structure were usually not easily biodegraded [13]. Functional groups of pharmaceuticals have been divided into two types: the electronic donating group which is considered as an oxidation promoting group and the electronic withdrawing group which imposes restrictions on biodegradation [11]. Therefore, pharmaceuticals physicochemical properties and their removal efficiencies need further investigations.

There are three widely achieved approaches of adsorption and biodegradation on pharmaceuticals in wastewater treatment. In the first approach, distributions of pharmaceuticals in wastewater and sewage sludge of the conventional activated sludge (CAS) and MBR treatment have been obtained [8,14]. In the second approach, mathematical model development for sludge adsorption was used to fit by the experiments result [15]. In another approach, mathematical model development for the biological process (including adsorption and biodegradation) was used to estimate the pharmaceuticals removal [15]. But the contributions of adsorption and biodegradation have been rarely reported especially obtained by experiments results.

The objectives of this study were as follows: (1) to explore the contributions of sludge adsorption and biodegradation on different pharmaceuticals removal and (2) to demonstrate the influence of physicochemical properties of pharmaceuticals on their elimination. For these purpose, five typical pharmaceuticals with different physicochemical properties such as $pK_a$, $K_{ow}$ and different functional groups were selected, including acetaminophen (ACE) and 17β-estradiol (E2) with electronic donating groups, carbamazepine (CBZ) and diclofenac sodium (Na-DCF) with electronic withdrawing groups, and naproxen (NAP) with both of these two kinds of functional groups. In addition, all the selected pharmaceuticals are used widely and detected frequently in water environment [16,17].

## 2. Materials and methods

### 2.1. Chemicals

All the standard pharmaceuticals were purchased from Sigma–Aldrich (USA) and were of high purity grade (≥98%). A stock solution of each pharmaceutical was prepared in methanol at a concentration of 1.0 g $L^{-1}$. In order to avoid degradation during the test period, the methanolic solutions were kept at −20 °C. Chromatographic grade methanol and acetonitrile were provided by Fisher (USA), and ultra-pure water (≥18.0 MΩ cm) was produced by an ELGA unit (UK). Relevant information of those pharmaceuticals is given in Table 1.

### 2.2. Chemical analysis

#### 2.2.1. Analysis of pharmaceuticals in aqueous phase

Solid phase extraction (SPE) was used as a pre-concentration technique followed by a High Performance Liquid Chromatography (HPLC 2695, Waters, USA) equipped with diode array detector