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# Removal of five selected pharmaceuticals by coagulation in the presence of dissolved humic acids and kaolin

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ABSTRACT

Coagulation behaviour of five pharmaceuticals, i.e. acetaminophen (ACE), carbamazepine (CBZ), 17β-estradiol (E2), naproxen (NAP) and diclofenac (DCF), was investigated through jar tests in deionized water, tap water, kaolin containing water and humic acid containing water, respectively, using aluminium sulphate as a coagulant. The effects of dissolved humic acids (DHAs) and kaolin on the removal efficiency of these compounds were studied particularly. The results showed that neither ACE nor CBZ was removed effectively (less than 10%), indicating that compounds with low hydrophobicity ($\log K_{ow} < 3$) are difficult to be removed in coagulation process. In deionized water, DCF achieved the highest removal efficiency due to its relatively strong hydrophobicity. However, in tap water, the removal efficiencies of these pharmaceuticals were much lower than those in deionized water except E2 and CBZ. In the presence of humic acid, the removal efficiencies of acidic pharmaceuticals (NAP and DCF) were much higher than those of neutral pharmaceuticals (ACE, CBZ and E2), especially with high dosage of DHA. The maximum removal efficiencies of NAP and DCF reached 61 and 59%, respectively. In terms of E2, its removal efficiency decreased surprisingly with increasing dosage of DHA. The presence of kaolin enhanced the removal efficiencies of E2, NAP and DCF because they were more readily adsorbed onto the surface of kaolin. DHA and kaolin improved the removal of certain pharmaceuticals during coagulation process.

*Keywords:* Pharmaceuticals; Coagulation; Dissolved humic acid; Kaolin

## 1. Introduction

Recently, pharmaceuticals present in aquatic environment have attracted much attention. In many countries, they were detected in sewage treatment plants, groundwater, surface water and even drinking water at a trace level (ng/L–μg/L) [1–5]. Niina et al. detected ibuprofen, naproxen (NAP) and diclofenac (DCF) in a Finnish sewage treatment plant with the concentration of 3.5–64 ng/L [6]. Buprofen (median = 181 ng/L), benzyl amine methyl oxygen pyrimidine (median < 10 ng/L), erythromycin (median =< 10 ng/L) and propranolol (median =< 1 ng/L) were found in the upstream of a sewage treatment plant, which

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indicated that pharmaceuticals can migrate long distances in aquatic environment and are highly stable [7]. Cleuvers evaluated the ecotoxicity of the non-steroidal anti-inflammatory drugs including DCF, ibuprofen, NAP and acetylsalicylic acid, and found out that these pharmaceuticals would cause serious damage to the ecosystem [8]. Even though concentrations of the pharmaceuticals and their metabolites are rather low, considering some pharmaceutical compounds were proved to be persistent in aquatic environment and polluted source water was used to produce drinking water, their adverse impact to ecosystem and human health is still a potential risk [9–15].

Coagulation is an important technique in conventional drinking water treatment processes. Its primary purpose is to remove suspended solids and colloidal substances present in source water. Some previous studies indicated that conventional drinking water treatment processes, including coagulation, cannot effectively remove most of the pharmaceuticals. The average removal efficiencies of four kinds of anti-inflammatory (DCF, NAP, ibuprofen and ketoprofen), three kinds of blockers (atenolol, metoprolol and scotalol) and one kind of lipid regulator (bezafibrate) by the combination process of coagulation, sedimentation and filtration were all less than 13% [16–20]. However, with the presence of dissolved humic acids (DHA), the removal efficiencies of DCF, ibuprofen and bezafibrate could be enhanced substantially [21]. According to Westerhoff and Yeomin [22], the removal mechanism of pharmaceuticals in coagulation process is that these compounds adhere to the particulate matters present in the source water, or adsorb onto metal hydroxide or carbonate precipitates formed during coagulation. Therefore, it seems that the removal efficiencies of pharmaceuticals by coagulation not only involve their own physicochemical properties, but also relate to the water qualities. Suspended solids and DHA in source water influence pharmaceuticals removal during coagulation process. However, the behaviours of different pharmaceuticals in the presence of DHA and suspended solids in coagulation process remain unclear.

For the purpose of identifying the relationship between the removal efficiencies of these target pharmaceuticals and their properties, the behaviours of different pharmaceuticals during coagulation are investigated. In the meantime, the removal efficiencies of these pharmaceuticals in the presence of DHA and suspended solids are studied during coagulation.

## 2. Materials and methods

### 2.1. Chemical and stock solution

Acetaminophen (ACE), carbamazepine (CBZ), 17β-estradiol (E2), NAP and DCF had been selected as target compounds; all of them were purchased from Sigma-Aldrich (Saint Louis, MO, USA; purity > 98%). All the target compounds had been detected in surface waters and drinking water treatment plants [23,24]. Their chemical structures and properties are summarized in Table 1. Mixed stock solution of these target compounds was prepared in methanol with a concentration of 100 mg/L. DHA stock solution was prepared following the method presented in Rebhun et al. [25].

### 2.2. Experiments

Coagulation experiments were conducted via jar tests using a six-place gang stirrer. Each glass beaker was filled with 1 L source water. Mixed stock solution of the target compounds was spiked into each beaker with 1 mL; hence, the initial concentrations of these target compounds were 100 μg/L. Aluminium sulphate was chosen as the coagulant due to its wide application in drinking water treatment process. Mixing was carried out in three steps, a rapid mixing at 200 rpm for 3 min, a slow mixing at 40 rpm for 20 min and a settling session of 60 min. After all, supernatant sample was withdrawn and filtered through 0.45 μm membrane filter to be analysed. These experiments were repeated to get the final data.

### 2.3. Coagulation in deionized water/tap water

Deionized water and tap water were used as source water, respectively. Some properties of the tap water are presented in Table 2. In the initial stage of the rapid mixing, aluminium sulphate was spiked into each beaker at dosages of 20, 40, 60, 80 and 100 mg/L, respectively.

### 2.4. Coagulation in DHA-containing water

Deionized water was used as the source water. Different dosages of DHA stock solution were spiked into each beaker and their total organic carbon (TOC) concentrations were measured. After that, aluminium sulphate was spiked into each beaker at a dosage of 100 mg/L in the initial stage of the rapid mixing.

Table 1
Properties of five selected pharmaceuticals in this study

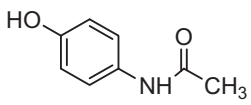
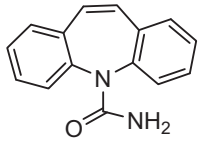
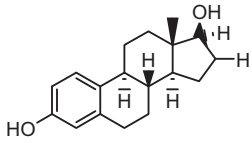
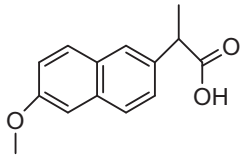
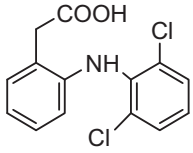
| Compound name | Molecular structure | Molecular weight | $pK_a$ | $\log K_{ow}$ | CAS numbers |
|---|---|---|---|---|---|
| Acetaminophen |  | 151.2 | 9.7 | 0.64 | 103-90-2 |
| Carbamazepine |  | 236.2 | 13.9 | 2.61 | 298-46-4 |
| 17β-Estradiol |  | 272.2 | 10.4 | 4.01 | 50-28-2 |
| Naproxen |  | 230.1 | 4.2 | 3.18 | 22,204-53-1 |
| Diclofenac |  | 318.1 | 4.2 | 4.51 | 78,213-16-8 |

Table 2
Main properties of the tap water in this study

| pH | Turbidity (NTU) | TOC (mg/L) | Conductivity (ms/cm) | TN (mg/L) |
|---|---|---|---|---|
| 6.8 | 2 | 1.95 | 0.491 | 1.5 |

### 2.5. Coagulation in the presence of kaolin

Deionized water was used as the source water. Kaolin was spiked into each beaker to simulate the suspended solids so as to achieve final concentrations of 20, 40, 60, 80 and 100 mg/L, respectively. Before coagulation, the solution was stirred for 30 min to allow the possible adsorption of the target compounds onto kaolin. For the purpose of investigating the adsorption removal of the target compounds by kaolin, supernatant sample was analysed before aluminium sulphate was added. After that, 100 mg/L aluminium sulphate was added to each beaker in the initial stage of the rapid mixing.

### 2.6. Analysis

The analyses of these target compounds were performed by high-performance liquid chromatography (HPLC, Waters 2695, USA) equipped with Waters Symmetry C18 (4.6 × 300 mm, 5 μm) and diode array detector (DAD, Waters 2998). The composition of the mobile phase was methanol (A), acetonitrile (B) and acetic acid (C) (pH 4) with a gradient elution of 1.0 mL/min at 30 °C. The gradient was as follows: B was kept constant at 5%, and A at 40% in the first 10 min, and linearly decreased to 30% in 1 min and kept for 9 min, then decreased to 35% in 5 min and kept for 5 min, and finally increased to 40% in 1 min and kept for 9 min. The DHA content was determined by monitoring TOC with Multi N/C 3100 (Analytik-Jena, German).

## 3. Results and discussion

### 3.1. Removal of pharmaceuticals by coagulation in deionized water/tap water

The removal efficiencies of five selected pharmaceuticals by coagulation process in deionized water

and tap water are shown in Figs. 1 and 2, respectively. In the deionized water, the removal efficiencies of ACE and CBZ were both less than 10%, which were most likely due to their low hydrophobicity ($\log K_{ow} < 3$). In contrast, DCF, with the highest $\log K_{ow}$ value among these target compounds achieved the highest removal efficiency of 33%. Hence, it is highly probable that the coagulation process is more effective in removing compounds with higher hydrophobicity. Previous studies [23] also showed that only high-$\log K_{ow}$ chemicals (e.g. >5) can be removed substantially in coagulation process. In addition, the dosage of aluminium sulphate can hardly affect the removal of CBZ, NAP and E2. However, for ACE, increasing the dosage of coagulant enhanced its removal and the highest removal efficiency was achieved using 80 mg/L coagulant, although the removal efficiency is only about 8%. For DCF, its removal efficiency was only 1.25% at 20 mg/L coagulant dosing but with increasing dosage, its removal efficiency raised dramatically to 33% and became constant at the dosage ranging from 40 to 100 mg/L. As shown in previous studies, pharmaceuticals could be removed through the charge neutralization [26]. In the experiment, the reasons for more effective removal of DCF and NAP than other pharmaceuticals were as follows: these pharmaceuticals have higher hydrophobicity and both were in the form of negative ions which favoured the electric neutralization and complexation.

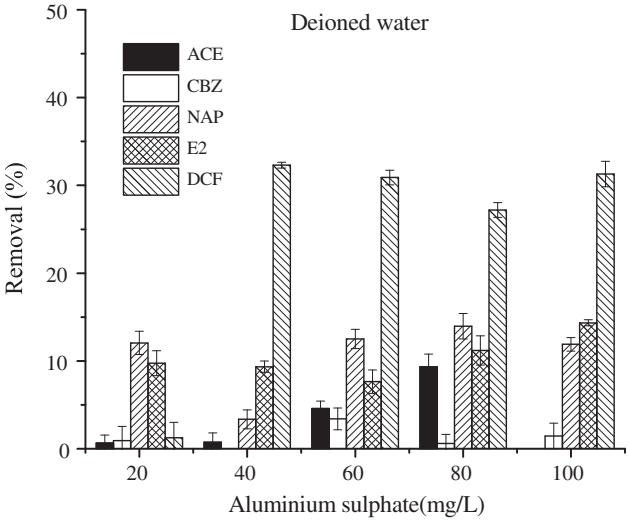



Fig. 1. The coagulation removal of five selected pharmaceuticals in deionized water at different dosages of aluminium sulphate.

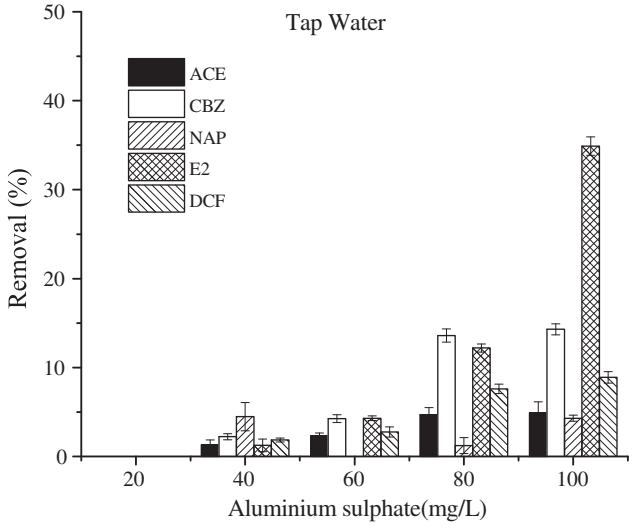



Fig. 2. The coagulation removal of five selected pharmaceuticals in tap water at different dosages of aluminium sulphate.

In the tap water, with the increasing coagulant dosage, the removal efficiencies of all these five selected pharmaceuticals increased accordingly. Compared with those in deionized water, the removals of ACE, NAP and DCF decreased, which indicated that some substrates existing in the tap water may have consumed the coagulant during the coagulation process. The increasing dosage of coagulant greatly enhanced the removals of E2 and CBZ, whose maximum removal efficiencies reached 36.1 and 14.3%, respectively, when 100 mg/L coagulant was used. It is a bit unexpected that although the $\log K_{ow}$ values of E2 and CBZ are lower than that of DCF, their removal efficiencies were much higher than that of DCF. The $pK_a$ values of DCF, CBZ and E2 were 4.2, 13.9 and 10.4, respectively. The pH values of tap water and deionized water are about 6.8 and 5.9. Most of DCF could be ionized at $pH > 6$, therefore, most of them were negatively charged in the source water. For the pH (5.9) in deionized water lower than that in tap water (pH 6.8), a higher proportion of DCF was in the state of the anion in deionized water than that in tap water. According to the previous research [27], for the drugs in source water, it is more likely to be removed in the state of molecules by coagulation. That may be the reason for the removal of DCF decreased in the tap water. Similarly, for E2 and CBZ, a higher proportion of them were in the state of molecules in tap water than in deionized water. The removal of E2 and CBZ increased in tap water, compared with that in deionized water.

### 3.2. Removal of pharmaceuticals by coagulation in DHA-containing water

The coagulation results in DHA-containing water are shown in Fig. 3. Similar results were obtained for ACE and CBZ in the presence of DHA: only less than 10% of them were removed even with different DHA dosages in water. The removal efficiency of E2 decreased from 23.9 to 14.5% as TOC of DHA increased from 2.30 to 4.75 mg/L. As TOC of DHA continued to increase to 7.7 mg/L, the removal efficiency decreased slightly from 14.5 to 12.6%. It indicated that DHA could restrain the coagulation removal of E2 to a certain extent, which proved previous assumption that DHA would consume a certain amount of coagulant and impair the reaction between pharmaceuticals and coagulant. However, the removal efficiencies of DCF and NAP by coagulation in DHA-containing water were surprisingly increased as TOC increased. It seems that the removal efficiencies of these two acidic compounds by coagulation can be enhanced by the existence of DHA. In previous research, a large amount of high-molecular-weight dissolved organic matters had been found to enhance the removal of some acidic pharmaceuticals such as DCF and ibuprofen [28]. According to Rebhun et al. [25], Al(III) and some non-ionic molecules can each react with different sites on DHA and no competition exists between them: hydrophobic sites (e.g. aliphatic and aromatic) can react with the dissolved contaminants to form DHA-contaminant complexes; acidic hydrophilic sites (e.g. carboxylic and phenolic group) are likely to react with the positively charged hydrolysis species of Al(III) to form Al(III)-HA precipitates. Since no competition exists between these two reactions, the bond compound HA-contaminant can be flocculated, precipitated and removed in the same way as DHA. Therefore, for NAP and DCF, they could react more easily with hydrophobic sites on DHA to form

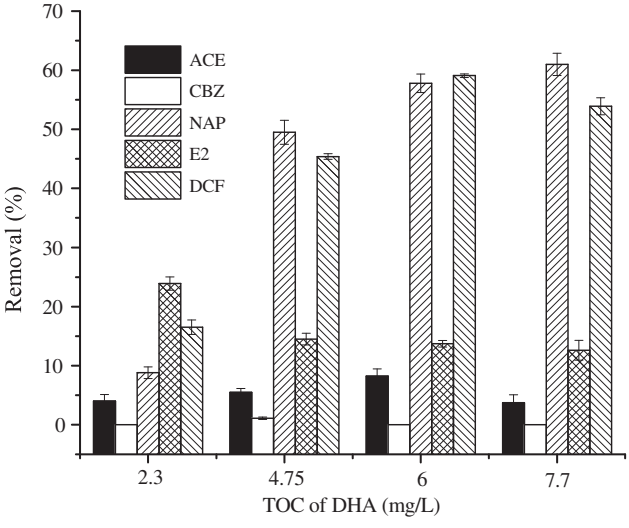



Fig. 3. The coagulation removal of five selected pharmaceuticals at 100 mg/L aluminium sulphate in humic acid solutions.

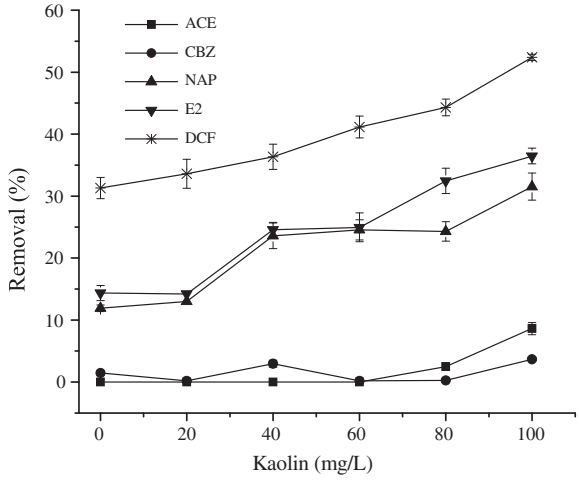



Fig. 4. The coagulation removal of five selected pharmaceuticals with different dosages of kaolin at 100 mg/L aluminium sulphate.

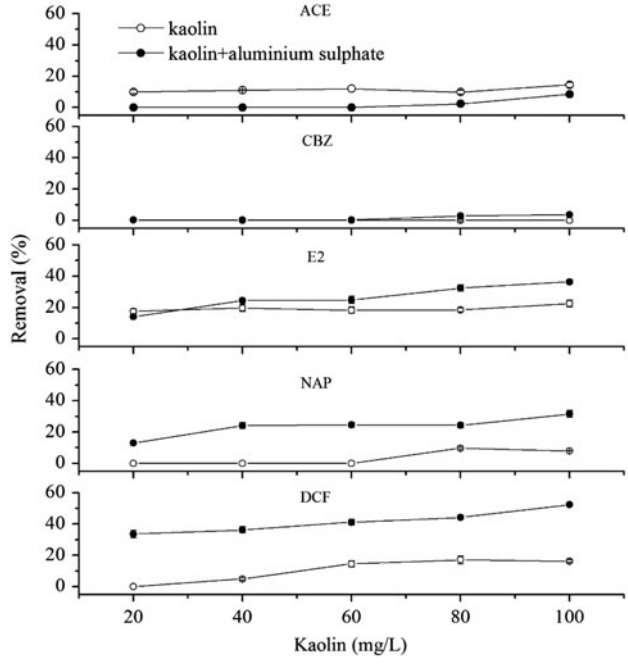



Fig. 5. The removal of five selected pharmaceuticals at different dosages of kaolin with and without 100 mg/L aluminium sulphate.

Table 3
The zeta potential of kaolin before and after coagulation

| kaolin (mg/L) | | 20 | 40 | 60 | 80 | 100 |
|---|---|---|---|---|---|---|
| Zeta (mv) | Before coagulation | −19.9 | −18.4 | −14.5 | −14.6 | −12.9 |
| | After coagulation | 8.26 | 9.72 | 9.28 | 9.21 | 8.22 |

HA-contaminant complexes and be removed more effectively than other pharmaceuticals.

### 3.3. Removal of pharmaceuticals by coagulation in the presence of kaolin

The removal efficiencies of the target compounds by coagulation in the presence of different kaolin dosages can be seen in Fig. 4. Same low removal efficiencies were found for both ACE and CBZ because of their low hydrophobicity. The removal efficiencies of other three target compounds NAP, E2 and DCF raised as the dosage of kaolin increased, and their maximum removal efficiencies were 31.53, 36.46 and 44.3%, respectively. It indicated that the existence of suspended solids could enhance the removal of NAP, E2 and DCF by coagulation. The possible explanation could be that these three compounds are more easily adsorbed onto the particulate matters and removed with them by coagulation. For the purpose of identifying the above assumption, the kaolin adsorption experiments were carried out subsequently. Before coagulant was added, the solution was stirred to allow the possible adsorption of the target compounds on kaolin. Then the supernatant sample was analysed by HPLC and the results are shown in Fig. 5. For ACE and CBZ, their maximal adsorption removal efficiencies by kaolin were only 14.5 and 0.23% even with different dosages of kaolin in source water. However, the adsorption removal of ACE was surprisingly higher than its coagulation removal. Although the adsorption removal efficiencies of NAP and DCF were also not very high (<20%) at each dosage of kaolin, their removals were enhanced dramatically when 100 mg/L aluminium sulphate was used. According to the relationship between pH and $pK_a$ values of these compounds, most of NAP and DCF could be ionized at pH range of 6–14, therefore, most of them were negatively charged in the source water. Before coagulation, the surface charge of kaolin in source water was negative, and these negatively charged compounds can hardly be adsorbed onto the surface of kaolin because of electrostatic repulsion. After aluminium sulphate was added, the surface charge of kaolin became positive (see Table 3); these acidic compounds can be adsorbed more readily onto the surface of kaolin because of electrostatic attraction, therefore they can be removed with suspended solids simultaneously during coagulation process. The adsorption removal efficiency of E2 by kaolin was the highest among these target compounds, nearly 20% at each dosage of kaolin. Since its adsorption removal efficiency was almost constant at different dosage of Kaolin, the reason that its coagulation removal efficiency raised with the increase of kaolin dosage was yet to be investigated.

## 4. Conclusions

For different kinds of pharmaceuticals, it seems that compounds with higher $\log K_{ow}$ values are more easily removed in deionized water. The existence of DHA can enhance the removal efficiencies of acidic pharmaceutics (NAP and DCF): their removal efficiencies reached 61 and 59% in DHA-containing water, respectively. However, the removal efficiencies of neutral pharmaceutics (ACE and CBZ) cannot be affected by DHA and the removal of E2 decreased as the dosage of DHA increased. The presence of kaolin can enhance the removal of E2, NAP and DCF which can be more readily adsorbed onto particulate matters. Therefore, it can be concluded that abundant DHA and high kaolin dosage can substantially enhance the removal of certain pharmaceuticals to a certain extent.

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