Catalytic hydrothermal treatment of pharmaceutical wastewater using sub- and supercritical water reactions

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Abstract

Application of subcritical and supercritical water technology for destruction of pharmaceutical compounds (carbamazepine, metoprolol and sulfamethoxazole) was investigated. The experiments were conducted inside batch reactor at a temperature ranging from 473 to 773 K and with different residence times of 5 to 50 min. The results show that carbamazepine, metoprolol and sulfamethoxazole are destructed by 90.27%, 99.99% and 98.84% after a 20 min exposure to 623 K, 673 K and 573 K, respectively. In comparison with the conventional methods of pharmaceutical waste treatment, the current technology provides a higher destruction efficiency (approximately 90–100%) which is achievable in shorter durations. NaOH and CuSO4·5H2O were also applied as catalysts in the temperature range of 473 K to 723 K. Comparing these catalysts, CuSO4·5H2O demonstrates a higher destruction efficiency, especially at lower temperatures. Based on the proposed pathway, the products of destruction can be classified as environmentally-friendly compounds. The results show that this technology can be used as a green alternative for efficient removal of pharmaceutical compounds from wastewater streams.

Keywords: Batch reactor
Destruction efficiency
Pharmaceutical compound
Carbamazepine
Metoprolol
Sulfamethoxazole
Sub- and supercritical water
Wastewater treatment

1. Introduction

The presence of pharmaceuticals in wastewater streams, surface waters, ground waters and related soil environments can have undesirable effects and has therefore attracted a great deal of attention in recent years. As a result, researchers have focused on devising new approaches for wastewater treatment [1–5]. The presence of these organic contaminants in the environment stems from inadequate pharmaceutical compound treatment in wastewater treatment plants (WWTPs) and may lead to chronic changes and ecotoxicity [3].

Many studies have focused on the ineffectiveness of conventional contaminated water treatment facilities. In one study, some β-blockers like metoprolol, propranolol, sotalol and psychiatric drugs such as carbamazepine and hormones were shown to be present in the effluent of a water treatment plant in Spain [3]. Behara et al. studied 5 wastewater treatment plants in South Korea using conventional biological treatment methods and found inefficient removal of 20 pharmaceuticals [2]. Another research on 57 pharmaceutical compounds of 4 wastewater treatment plants in Taiwan showed low removal efficiencies for most drugs, including atenolol, sulfamethoxazole, carbamazepine and metoprolol [4].

There are many other studies elucidating the low removal efficiencies of pharmaceutical compounds such as chloramphenicol, metoprolol, carbamazepine, sulfamethazine, sulfamethoxazole and diazepam [6–8]. The continuous discharge of antibiotics from WWTP and their adverse effects on human health by promoting microbial drug resistance have raised concern about their adverse effects in the environment [9].

An alternative wastewater treatment technology that has gained much attention in recent years is sub-critical and supercritical water technology which is based on the unique behavior of water in its near-critical, critical ($T_c = 647.1$ K, $P_c = 22.1$ MPa, $\rho_c = 0.322$ g/cm$^3$) and supercritical regions [10]. Raising the self-association of water ($k_w$) as a result of increasing temperature has severe effects on hydrolysis and acid-base equilibrium; therefore, water can act as an acid or base catalyst precursor because of its high content of H$_3$O$^+$ and OH$^-$ ions [10,11]. Increasing temperature also brings about increasing viscosity ($\eta$) at gas-like densities and decreasing $\eta$ at liquid-like densities which result in high fluidity, high molecular mobility and, subsequently, high thermal conductivity of water [10]. Dielectric constant ($\varepsilon$) of water, which shows solvent behavior and ionic dissociation of salts in water, decreases by increasing temperature and decreasing density (a non-polar
state of water), causing an increase in the solubility of hydrophobic organic compounds (HOC) at such conditions [10,12–15]. Briefly, supercritical water is an excellent solvent for homogeneous media without phase boundaries and also provides fast and complete reactions [16,17]. Treatment of some materials such as methane [18–20], methanol [21–25], ethanol [26,27], propane [28], nitrogen [29] and phenol [30–33] has been conducted in subcritical and supercritical water. Furthermore, efficient removal of some compounds including benzene [34], biphenyls [35–39], amines [40,41] and pyridine [42,43] have also been studied in subcritical and supercritical water. Finally, this process can be considered as a green and environmental-friendly technology since it emits no harmful materials to the environment [17,35,39,44,45].

In this study, sub- and supercritical water technology was applied to water contaminated with three pharmaceutical compounds; carbamazepine, metoprolol and sulfamethoxazole, and the effect of changing temperature and time on destruction of these compounds was examined in a batch reactor. Moreover, the effects of potential catalysts, NaOH and CuSO₄·5H₂O in destruction efficiency were studied.

Fig. 2. Effect of temperature and pressure on the final concentration of pharmaceutical compounds at 30 min and with no catalyst.

2. Materials and methods

2.1. Chemicals

The 99.8% purified carbamazepine and metoprolol used in this experimental study was obtained from Loghman Co., Pursina Co. and Pars Daroo Co. (Tehran, Iran). Sulfamethoxazole was purchased from RoozDaroo Co. (Tehran, Iran). Fig. 1 shows the chemical structure of the above-mentioned compounds. H₂O used throughout the study was distilled and deionized by a laboratory apparatus. Sodium hydroxide (97% pure), copper(II) sulfate pentahydrate (CuSO₄·5H₂O) (99% pure) were obtained from Merck (New Jersey, USA).

2.2. Experimental apparatus

A tubular batch reactor made of stainless steel 316 SUS (volume 42 mL; length 29.48 cm; i.d. 2.13 cm) was built for this study. Swedgelok caps were used to reach the desired pressure and temperature based on thermodynamic calculations. The aqueous solution containing selected pharmaceutical compounds (initial concentration of 50 mg/L) with an amount of 5.0 to 30.0 mL (based on the pressure and temperature) were charged into the reactor. The reactor was then heated using an electrical furnace. The reactions were conducted in the temperature range of 498 to 773 K and pressure range of 1.5 to 30.0 MPa. After a certain reaction time, the reaction was terminated by immersing the reactor inside ice and water mixture until reaching room temperature.

2.3. Sample preparation

After hydrothermal destruction of pharmaceutical compounds with and without catalyst (NaOH 1.0 M, CuSO₄·5H₂O 0.01 M), the liquid content was removed, centrifuged and analyzed. By analyzing different temperatures, the optimum temperature for each compound was determined and consequently, the furnace temperature was set on the optimum temperature for each compound and the experiments were done at various residence times of 5, 10, 20, 35 and 50 min.
at temperatures near critical point of water could be explained by enhancing the organic compounds solubility in water due to the decreasing dielectric constant of water which was already boosted by hydrolysis reaction power based on maximum ion product of water ($k_w$). The figure also provides the pressure changes under reaction condition were taken in experiments.

3.2. Effect of residence time on destruction of pharmaceutical compounds in the absence catalyst

Fig. 3 illustrates the effect of different residence times of 5 to 50 min at fixed optimum temperature of 623 K. The conversion of pharmaceutical compounds increased by enhancing the residence time of reactions from 5 min to 20 min. The optimum residence time for all compounds was found to be 20 min and conversion of carbamazepine, metoprolol and sulfamethoxazole reached 91%, 96% and 96.4%, respectively. As shown, decreasing intensity in the range of 5 to 20 min for sulfamethoxazole was higher than that of the other two compounds due to its resistance to destruction at lower temperatures which gets back to its structure. However, comparing these results and the studies done by Jelic et al. (biological treatment of carbamazepine and metoprolol with 11% and 0% efficiency over a period of 16 days) [1], Lin et al. (activated sludge treatment of carbamazepine (40%), metoprolol (66%) and sulfamethoxazole (26%) in 12 h) [5] and Yu et al. (biodegradation of sulfamethoxazole (59%) over a period of 14 days) [46], showed that sub- and supercritical water treatment has high removal efficiency at low residence times.

3.3. Effect of catalyst on destruction of pharmaceutical compounds

3.3.1. Catalytic effect of NaOH and CuSO₄·5H₂O on carbamazepine destruction

The catalytic effects of NaOH (1.0 M) and CuSO₄·5H₂O (0.01 M) on destruction of carbamazepine as a function of reaction temperature for a reaction time of 30 min is shown in Fig. 4 and the results of these experiments was compared to that of catalysts-free conditions. It is obvious that the presence of catalyst enhances the destruction of carbamazepine. Comparing the two catalysts, CuSO₄·5H₂O illustrated higher destruction efficiency at lower temperature (88.5% at 473 K for 30 min compared to 15.7% with NaOH) while at higher temperatures above 500 K, both catalysts reached similar efficiency (maximum of 98% at 623 K). The obtained results show that using catalysts makes the destruction phenomenon occur at milder hydrothermal condition with less energy consumption. However, since NaOH caused severe corrosion in the

3. Results and discussion

3.1. Effect of temperature on destruction of pharmaceutical compounds in the absence of catalyst

The effect of temperature (in the range of 523 to 773 K) on final concentration of selected pharmaceutical compounds at residence time of 30 min is shown in Fig. 2. As shown in the figure, the final concentration of the compounds decreased by enhancing the temperature with destruction efficiency of 90.5% (623 K), 100% (723 K) and 100% (573 K) for carbamazepine, metoprolol and sulfamethoxazole, respectively. The maximum efficiency for carbamazepine and sulfamethoxazole was obtained under sub-critical condition, whereas the maximum destruction of metoprolol occurred at supercritical temperature. The reason for reaching such efficiency
Fig. 8. Proposed pathway for carbamazepine degradation in sub-and supercritical water.

Table 1
Comparison of the removal efficiency of carbamazepine, metoprolol and sulfamethoxazole between conventional wastewater treatment plants and sub- & supercritical water technology.

<table>
<thead>
<tr>
<th>Pharmaceutical compound</th>
<th>Removal efficiency (%)</th>
<th>Ref.</th>
<th>Sub- and supercritical technology (This research)</th>
<th>T (°C)</th>
<th>Time (min)</th>
<th>Presence of CuSO₄·5H₂O</th>
<th>Removal efficiency (%)</th>
</tr>
</thead>
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<tr>
<td>Carbamazepine</td>
<td>31</td>
<td>[3] 2011</td>
<td>350</td>
<td>30</td>
<td>No</td>
<td>90.27</td>
<td></td>
</tr>
<tr>
<td>Sulfamethoxazole</td>
<td>51.9</td>
<td>[2] 2011</td>
<td>300</td>
<td>30</td>
<td>No</td>
<td>98.84</td>
<td></td>
</tr>
<tr>
<td></td>
<td>44</td>
<td>[7] 2009</td>
<td>300</td>
<td>20</td>
<td>No</td>
<td>96.39</td>
<td></td>
</tr>
<tr>
<td></td>
<td>59</td>
<td>[46] 2011</td>
<td>300</td>
<td>20</td>
<td>No</td>
<td>96.39</td>
<td></td>
</tr>
<tr>
<td></td>
<td>86</td>
<td>[51] 2011</td>
<td>350</td>
<td>30</td>
<td>Yes</td>
<td>97.81</td>
<td></td>
</tr>
</tbody>
</table>
3.3. Catalytic effect of CuSO$_4\cdot$5H$_2$O on metoprolol destruction

Fig. 5 depicts the effect of temperature on metoprolol destruction efficiency in the presence and absence of CuSO$_4\cdot$5H$_2$O in a reaction time of 30 min. In the catalyst-free conditions, metoprolol acts as a refractory material under hydrothermal condition (and even at supercritical state of water), while in the presence of CuSO$_4\cdot$5H$_2$O, destruction efficiency reached 100% at 673 K (supercritical state). However, to avoid the limitations of supercritical state and to optimize the energy consumption and destruction efficiency, temperature of 623 K (92% efficiency) could be used.

3.3.3. Catalytic effect of CuSO$_4\cdot$5H$_2$O on sulfamethoxazole destruction

Fig. 6 presents the final concentration of sulfamethoxazole with and without CuSO$_4\cdot$5H$_2$O at different reaction temperatures. Results indicate that at low temperatures below 550 K, CuSO$_4\cdot$5H$_2$O enhanced the destruction efficiency; however, at high temperatures, the presence of catalyst does not have any advantages over catalyst-free conditions. The optimum destruction conditions were in 573 K, for 30 min and without catalyst (99% efficiency), which may be due to the break down of sulfur bond on sub-critical water condition.

The effect of CuSO$_4\cdot$5H$_2$O catalyst in 0.01 M on final concentration of the 3 tested pharmaceutical compounds is plotted for
As shown, carbamazepine was affected more than sulfamethoxazole and metoprolol was affected the least under the optimum (for all compounds) temperature of 623 K (sub-critical water) (with destruction efficiencies of 98%, 98% and 92%, respectively).

3.4. Main reaction pathways

Proposed reaction pathways for carbamazepine, metoprolol and sulfamethoxazole destruction are shown in Figs. 8–10, respectively. The degradation occurs in three steps:
Step 1: 200 °C T + 250 °C: hydrolytic degradation
Step 2: 250 °C < T < 350 °C: water addition to aromatic (and/or) aliphatic bonds
Step 3: T > 350 °C: free radical degradation of saturated aliphatic alcohols [47].

In the temperature range of conducted experiments, the reaction products are saturated aliphatic alcohols, CO₂, H₂O and N₂ which do not possess any reported harmful and toxic effects on the environment.

3.5. Environmental benefits of applying sub- and supercritical water technology

Most WWTPs are based on activated sludge processes where microorganisms are utilized to convert the pollutants to water and carbon dioxide, or degrade them to acceptable forms. Removal of pollutants from water can also be achieved by stripping into air or by sorption onto sludge with regular discharge [6]. The adverse environmental effects of carbamazepine in low concentrations (1–50 μg/L) are very negligible: however, ecotoxicological studies have shown reproduction toxicity, decreased enzymatic activity and bioaccumulation in different test organisms. In concentrations above 30.6 mg/L of carbamazepine and 12.6 mg/L of metoprolol, growth retardation and tail deformation of fish embryo was observed [48]. In addition, metoprolol presentation in aquatic environments can accelerate the heart beat rate in Daphnia magna and it has toxic effects on algae and daphnia [49,50].

Sulfamethoxazole has been found in μg/L concentrations in waste and surface waters. Although usually low levels of antibiotics are seen, their continuous discharge from WWTPs raises concern about their potential adverse ecological effects and their contribution to the development of microbial drug resistance that might impact human health [9].

It can be concluded that even low concentrations of pharmaceutical compounds discharged from WWTPs are important issues to be considered for environmental safety. The comparison between conventional WWTPs and sub- and supercritical water technology removal efficiencies, as presented briefly in Table 1, shows that sub- and supercritical water technology has the highest removal efficiency for carbamazepine, metoprolol and sulfamethoxazole. Additionally, as discussed in Section 3.4, the products of water treatment using this technology are environmentally-friendly compounds.

4. Conclusion

In this study, the application of subcritical and supercritical water as an alternative for pharmaceutical wastewater treatment was investigated. Experiments were conducted on three pharmaceutical compounds of carbamazepine, metoprolol and sulfamethoxazole in the temperature range of 473–723 K and reaction time of 5–50 min with and without addition of catalyst (NaOH and CuSO₄·5H₂O) in the batch reactor. Results show that destruction of selected compounds will increase by increasing temperature and time. Destruction efficiency of 90.7% (623 K) for carbamazepine, 96% (673 K) for metoprolol and 96.39% (573 K) for sulfamethoxazole was gained in catalyst-free conditions. Using CuSO₄·5H₂O for carbamazepine is preferred over NaOH, since CuSO₄·5H₂O is capable of increasing the destruction of carbamazepine at lower temperatures and plus, NaOH causes severe corrosion in the batch reactor. In addition, the presence of CuSO₄·5H₂O enhanced the conversion of carbamazepine and metoprolol; however, it decreased sulfamethoxazole’s conversion. Conversions of 98% at 350 °C for 30 min for carbamazepine, 99.9% at 400 °C for 30 min for metoprolol and 97.81% at 350 °C for 30 min for sulfamethoxazole were gained by the addition of CuSO₄·5H₂O as a catalyst. Table 1 compares removal efficiencies gained for these pharmaceutical compounds by conventional treatment methods with sub- and supercritical water technology. The proposed pathway for degradation of above mentioned pharmaceutical compounds illustrates that the products of applying sub- and supercritical water technology are environmentally friendly compounds and do not pose any risks to the environment from an eco-toxicological viewpoint.

In summary, based on the obtained results in this study, subcritical and supercritical water technology can be used as a green alternative in wastewater treatment plants for complete removal of pharmaceutical compounds.

References


