

# Decomposition of phenol by hybrid gas/liquid electrical discharge reactors with zeolite catalysts

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## Abstract

Application of hybrid gas/liquid electrical discharge reactors and a liquid phase direct electrical discharge reactor for degradation of phenol in the presence and absence of zeolites have been investigated. Hybrid gas/liquid electrical discharges involve simultaneous high voltage electrical discharges in water and in the gas phase above the water surface leading to the additional OH radicals in the liquid phase and ozone formation in the gas phase with subsequent dissolution into the liquid. The role of applied zeolites, namely NH<sub>4</sub>ZSM5, FeZSM5 and HY, were also studied. Phenol degradation and production of primary phenol by-products, catechol and hydroquinone, during the treatment were monitored by HPLC measurements. The highest phenol removal results, 89.4–93.6%, were achieved by electrical discharge in combination with FeZSM5 in all three configurations of corona reactors. These results indicate that the Fenton reaction has significant influence on overall phenol removal efficiency in the electrical discharge/FeZSM5 system due to the additional OH radical formation from hydrogen peroxide generated by the water phase discharge.

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**Keywords:** Gas/liquid corona; Phenol degradation; Zeolites; FeZSM5

## 1. Introduction

Advanced oxidation processes (AOPs) are based on the generation of highly reactive species, such as hydroxyl radicals that rapidly and non-selectively oxidize a broad range of organic pollutants [1–4]. Common AOPs involve Fenton and Fenton “like” processes, ozonation, photochemical and electrochemical oxidation, photolysis with H<sub>2</sub>O<sub>2</sub> and O<sub>3</sub>, high voltage electrical discharge (pulsed streamer corona and corona-like) processes, TiO<sub>2</sub> photocatalysis, radiolysis, wet oxidation, electron beams or  $\gamma$ -beams, and various combinations of these methods [5–7].

Pulsed corona, or corona-like, discharge processes utilize chemical radicals ( $\bullet$ OH, H $\bullet$ , O $\bullet$ , HO<sub>2</sub> $\bullet$  and O<sub>2</sub> $\bullet^-$ ) and highly reactive molecules (H<sub>2</sub>O<sub>2</sub>) produced from a high voltage

pulsed electrical discharge that is sustained in an aqueous medium [8–13]. Hybrid gas/liquid electrical discharge reactors involve simultaneous high voltage electrical discharges in the liquid phase and in the gas phase above the liquid surface [14–16]. Two types of hybrid gas/liquid corona reactors, hybrid-series and hybrid-parallel corona reactors, have different electrode configurations and these differences affect the efficiency for organic compound degradation [17]. In both types of hybrid reactors the high voltage needle-point electrode is placed in the liquid phase as in the standard-reference corona reactor. The ground electrode, made from reticulated vitreous carbon (RVC), is submerged in the liquid in the standard-reference and hybrid-parallel case reactor, while in the hybrid-series reactor the RVC ground electrode was placed above the liquid surface. The parallel configuration of hybrid corona reactor employs an additional high voltage electrode made from RVC in the gas phase. These two reactor configurations, hybrid-series and hybrid-parallel, showed

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higher efficiency for degradation of organic compounds than the standard-reference corona reactor [15,17,18]. The hybrid reactors are more effective due to the formation of ozone in the gas phase which can either directly react with species in the liquid phase or, at high pH, can react with  $H_2O_2$  formed in the liquid phase to produce OH radicals via peroxone chemistry, and the hybrid reactors may increase hydroxyl radical formation by the discharge at the gas–liquid interface [16]. Measurements of ozone produced in the gas phase in both hybrid reactors showed that approximately seven times more ozone is produced in the hybrid-parallel than in the hybrid-series corona reactor [14].

Phenol, one of the most abundant pollutants in industrial wastewater, was chosen as a model compound in this study due to extensive literature on phenol degradation by different types of advanced oxidation technologies [19–23], especially by applications including high voltage electrical discharge in water [15,16,24–28].

Zeolites were chosen as catalysts in this study due to demonstrated enhancement of organic dye compound degradation, particularly in the hybrid-parallel reactor, which was reported in previous work [17], and because it has been reported that highly oxidative media promotes oxidation reaction of organic molecules adsorbed on the surface of solid particles [28–31]. Additionally, the influence of different types of solid particles combined with corona discharge reactors for phenol degradation has been studied [25,28,31]. Furthermore, synthetic zeolites of ZSM5 and Y type showed rather good adsorption of phenol [32]. Zeolites may also act as ion exchangers because the loosely bound nature of the extra-framework metal ions allows for exchange of other types of metals when in aqueous solution [33–35]. The FeZSM5 zeolite is also of interest since the iron from the zeolites may react with  $H_2O_2$  formed by the liquid phase electrical discharge to

enhance organic compounds degradation as reported in the literature [36,37].

The aim of this study was to investigate the efficiency of the three different types of corona reactors including the standard-reference, hybrid-series and hybrid-parallel, in combination with the synthetic zeolites,  $NH_4ZSM5$ , FeZSM5 and HY, for phenol degradation.

## 2. Experimental

Three different types of pulsed corona reactors, namely standard-reference, hybrid-series and hybrid-parallel, were used for phenol degradation in this work (Fig. 1). The glass reactor vessel with a capacity of 1 l was used with the three different electrode configurations for each type of discharge. The reactor setup and electrode configurations were described in detail by Lukes et al. [14]. The pulse power supply was the same as in previous work, including pulse repetition frequency of 60 Hz and charging capacitance of 2 nF [3,8,14–18,27,28,31]. The applied peak voltage was 45 kV for each experiment which corresponds to the power input of approximately 60 W. Peak voltage, rise time and pulse width were measured by placing a Tektronix P6015A high voltage probe coupled to a Tektronix TDS 460 fast digital storage oscilloscope to the input of the pulsed power to the reactor. It should be noted that the measured peak voltage of 45 kV, rise time of the order of 20 ns and pulse width of approximately 3  $\mu$ s FWHM are comparable with those given by Lukes et al. [14]. Moreover, the same waveform profiles were observed in experiments with and without zeolite addition into the reactors. Reactor current was measured with a P6021 Tektronix current probe. The corresponding energy per pulse of 1.06 ( $\pm 0.05$ ) J applied in all three reactor types was determined

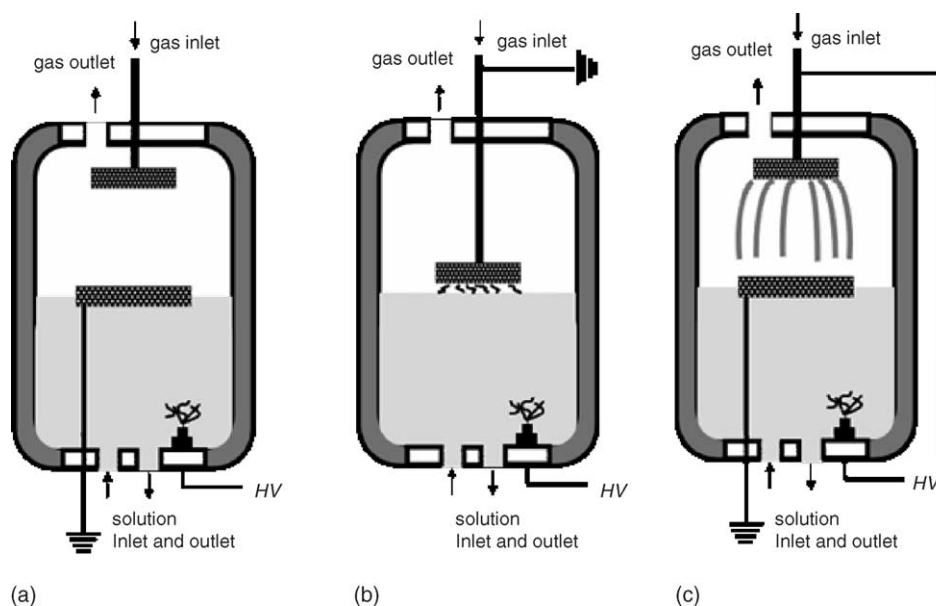


Fig. 1. Schematic of the three reactor configurations: (a) reference reactor, (b) series reactor and (c) parallel reactor.

by integration of voltage and current waveforms. Current and voltage were measured three times for each experiment and averages are reported.

The total volume of the treated solutions was 550 ml in all cases, while the solution was recirculated through the reactors by a peristaltic pump at a flow rate of  $0.41 \text{ min}^{-1}$ . The initial conductivity of the treated model solutions was adjusted with 0.1 M KCl to give approximately  $150 \mu\text{S cm}^{-1}$  for each experiment. In one set of experiments for determination of the major mechanisms responsible for phenol degradation in each reactor, methanol, 0.5 M, was used as an OH radical scavenger. Experiments were performed with the two different methanol concentrations in the bulk, 0.09 and 0.18 M, with negligible differences in the phenol removal results obtained for these two concentrations. Methanol was added just prior to turning on the electrical discharge. The inlet gas consisted of a mixture of argon and oxygen with an argon flow rate of  $0.21 \text{ min}^{-1}$  and an oxygen flow rate of  $0.151 \text{ min}^{-1}$ . In previous work, this mixture was found to be optimal for ozone generation and discharge stability [14]. The duration of each experiment was 60 min. All experiments were repeated three times and averages are reported, while reproducibility of the experiments was within 5%.

All chemicals used in this study, namely phenol, catechol, hydroquinone, potassium chloride, methanol, acetonitrile and acetic acid were obtained from Fisher Scientific. All solutions were prepared with deionized water with conductivity less than  $1 \mu\text{S cm}^{-1}$ . Experiments were performed with initial concentration of the phenol model solution of  $0.1 \text{ g l}^{-1}$ . The zeolites were supplied by Zeolyst International, USA.  $\text{NH}_4\text{ZSM5}$  and HY were used as received, while FeZSM5 zeolite was prepared according to the procedure described by Rauscher et al. [38]. For each experiment performed with zeolites, the concentration of zeolites was  $1 \text{ g l}^{-1}$ . Samples in portions of ca.  $100 \mu\text{l}$  were taken periodically each 15 min (0, 15, 30, 45 and 60) from the reactor, and thereafter immediately filtered through  $0.45 \mu\text{m}$  nitrocellulose filters, supplied by Micron Separations Inc., Westboro, MA, USA, in order to remove the zeolites and thereafter immediately analyzed by HPLC. The initial and final values of pH and conductivity were measured by a Cole-Parmer Model 1484-10 conductivity/pH meter. Phenol removal and its by-products, catechol and hydroquinone, production during the experiments were monitored by Perkin-Elmer HPLC. Samples were analyzed using a Supelco Supercosil C18 column ( $25.0 \text{ cm} \times 4.6 \text{ mm}$ ) with a mobile phase consisting of 2% acetic acid, 20% acetonitrile and 78% deionized water. The mobile phase flow rate was  $1.0 \text{ ml min}^{-1}$ . A Perkin-Elmer Spectrophotometer LC80 was connected to the HPLC and all analysis of samples was performed at a fixed wavelength of 280 nm. The recorded peaks were first identified and then concentrations of residual phenol and its produced primary oxidation by-products, catechol and hydroquinone were determined from their calibration standards. Phenol removal is reported as percentage,  $100 \times [\text{phenol}]/[\text{phenol}]_{\text{initial}}$ , and catechol and hydroquinone production are reported rel-

ative to initial phenol,  $100 \times [\text{catechol}]/[\text{phenol}]_{\text{initial}}$  and  $100 \times [\text{hydroquinone}]/[\text{phenol}]_{\text{initial}}$ .

### 3. Results and discussion

The set of control experiments with the addition of zeolites,  $\text{NH}_4\text{ZSM5}$ , FeZSM5 and HY, into the phenol solution in the absence of electrical discharge were run for 1 h. This set of experiments was conducted in order to investigate phenol adsorption characteristics on the zeolites and the results are shown in Table 1 and Fig. 2. Changes of pH and conductivity of the phenol solution caused by the zeolite addition are also presented in Table 1. It can be seen that the addition of  $\text{NH}_4\text{ZSM5}$  zeolite into the phenol solution does not affect the pH and conductivity (Table 1). On the other hand, the addition of Fe-exchanged ZSM5 zeolite changed both of these parameters, particularly the conductivity after 1 h in solution (Table 1). The conductivity change may be due to the possible leaching of a small amount of  $\text{Fe}^{2+}$  ions from

Table 1  
Experimental conditions and overall phenol removal with zeolites,  $\text{NH}_4\text{ZSM5}$ , FeZSM5 and HY, in the absence of electrical discharge

	Type of zeolite		
	$\text{NH}_4\text{ZSM5}$	FeZSM5	HY
pH			
Phenol	5.1	5.0	5.1
After zeolite addition	5.1	4.1	3.8
Final	5.0	3.5	3.8
Conductivity ( $\mu\text{S cm}^{-1}$ )			
Phenol	2.1	1.9	2.0
After zeolite addition	2.4	36.4	2.2
Final	3.9	365.7	2.8
Phenol removal (%)	30.4	33.2	7.0

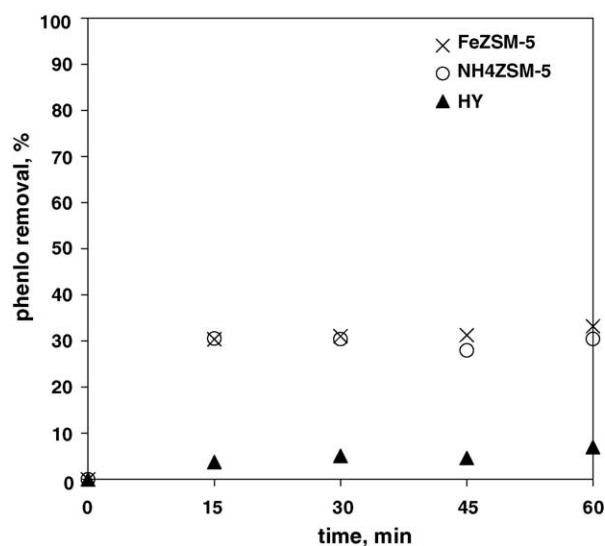


Fig. 2. Phenol removal by zeolites,  $\text{NH}_4\text{ZSM5}$ , FeZSM5 and HY, in the absence of electrical discharge.

Table 2

Experimental conditions and results for overall phenol removal and overall by-products formation in the reference reactor ( $U = 45$  kV,  $f = 60$  Hz and  $C = 2$  nF)

	Type of zeolites and additives				
	None	NH <sub>4</sub> ZSM5	FeZSM5	HY	Methanol
pH					
Initial	5.2	5.2	4.2	3.9	5.1
Final	4.5	4.9	3.4	4.8	4.2
Conductivity ( $\mu\text{S cm}^{-1}$ )					
Initial	147.8	145.6	146.2	151.4	150.2
Final	171.9	161.9	491.7	162.2	221.3
Phenol removal (%)	34.7	45.0	89.4	18.4	7.3
Catechol production (%)	12.7	7.4	13.5	3.3	0.2
Hydroquinone production (%)	7.4	3.2	4.2	0.7	0.2

the zeolite framework into the solution. With the addition of HY zeolite only the pH value changed as expected due to the H<sup>+</sup> cation of this zeolite. Furthermore, the amounts of phenol removed from the initial solution are shown in Table 1 and Fig. 2. It can be seen that the ZSM5 type of zeolite, either in the form with NH<sub>4</sub><sup>+</sup> or Fe<sup>2+</sup> cations, can adsorb phenol, where up to 33.2% of the phenol was removed. On the other hand, phenol diffusion into the Y zeolite pores was restricted as indicated by the only 7.0% of phenol removal found with this zeolite. The ZSM5 type zeolite has a pentasyl structure which is characterized by parallel channels with pore sizes of 0.53–0.56 nm with crossed channels with pore sizes of 0.51–0.55 nm, while Y zeolite has a basic cubic structure with pore sizes of 0.74 nm [34,35]. The previously mentioned geometrical entrance diameter of the micropores of the ZSM5 zeolite, 0.51–0.56 nm, conflicts with the observation that phenol molecules with an aromatic ring size of 0.68 nm in diameter adsorb into the zeolite micropores. A plausible explanation of this contradiction may be related to the flexibility of the phenol molecule as well as the thermal motion of pore opening of zeolites [32]. The low phenol adsorption into the HY zeolite differs from the results of Kawai and Tsutsumi [32] and Okolo et al. [39] who reported much larger amounts of phenol adsorption into the same type of zeolite, Y, but with other cation, in NaY form. Fig. 2 shows that for all three types of zeolites the adsorption of phenol into the

pores of the zeolites occurred in the first 15 min of the process which is in accordance with data given in the literature [32,39].

Before conducting experiments in all three types of corona reactors, an additional set of preliminary control experiments was conducted. The phenol solution with an initial concentration of 0.1 g l<sup>-1</sup> was circulated through all corona reactors for 1 h in order to exclude contributions to phenol removal by sorbate volatilization or adsorption onto the reactors parts and tubes that provide solution circulating through the peristaltic pump. It was found that the initial concentration of the phenol solution was decreased for 5.7% and 7.7% in parallel/reference, both containing the same liquid phase part of the reactor and series setups, respectively. All results for phenol removal expressed in percentage obtained during the treatment in the corona reactors were corrected with respect to these numbers subtracted from the initial phenol concentration. Tables 2–4 summarize pH and conductivity changes, final phenol removal and final amounts of primary oxidation by-products, catechol and hydroquinone, obtained in all three types of corona reactors. The small changes of pH indicate the formation of small amounts of organic acids which is in accordance with proposed mechanism of phenol decomposition given by Roig et al. [40] and is consistent with by-products reported previously [41–43], while changes of conductivity indicate that ionic products are generated during

Table 3

Experimental conditions and results for overall phenol removal and overall by-products formation in the hybrid-parallel reactor ( $U = 45$  kV,  $f = 60$  Hz and  $C = 2$  nF)

	Type of zeolites and additives				
	None	NH <sub>4</sub> ZSM5	FeZSM5	HY	Methanol
pH					
Initial	5.1	5.4	4.2	3.8	5.1
Final	4.0	4.0	3.3	4.3	4.1
Conductivity ( $\mu\text{S cm}^{-1}$ )					
Initial	145.4	141.9	146.9	151.1	151.4
Final	224.7	222.7	518.0	224.3	255.3
Phenol removal (%)	41.1	66.0	93.6	51.1	16.6
Catechol production (%)	8.5	8.3	9.0	6.9	0.6
Hydroquinone production (%)	6.4	4.9	3.4	2.1	0.6

Table 4

Experimental conditions and results for overall phenol removal overall by-products formation in the hybrid-series reactor ( $U = 45$  kV,  $f = 60$  Hz and  $C = 2$  nF)

	Type of zeolites and additives				
	None	NH <sub>4</sub> ZSM5	FeZSM5	HY	Methanol
pH					
Initial	5.0	5.5	4.3	3.8	5.1
Final	4.2	4.3	3.6	4.4	4.1
Conductivity ( $\mu\text{S cm}^{-1}$ )					
Initial	150.2	151.7	156.2	151.0	149.7
Final	226.3	217.7	518.7	191.1	277.7
Phenol removal (%)	50.7	64.1	91.9	35.3	17.4
Catechol production (%)	14.2	12.4	11.3	6.8	1.0
Hydroquinone production (%)	6.6	4.9	2.7	1.5	0.5

the experiments, especially in experiments with the addition of FeZSM5 zeolite.

The phenol removal results for all three reactors, over 1 h of treatment are shown in Fig. 3. It can be seen that partial decomposition of phenol was obtained in all three reactors and these results are consistent with those reported by Grymonpré et al. [16]. In the reference type corona reactor 34.7% of phenol was removed primarily due to the OH radical attack since the reference reactor does not lead to the formation of ozone. Phenol removal increased to 41.1% in the hybrid-parallel and to 50.7% in the hybrid-series reactors. Part of this enhancement is clearly due to the reactions of ozone, generated in the gas phase of both hybrid reactors and subsequently transferred into the liquid phase.

The larger phenol removal in the series reactor than the parallel is due to significant differences in the natures of the gas phase discharges. The gas phase discharge in the parallel reactor is very similar to conventional gas phase pulsed corona and this reactor produces about seven times more ozone than the series reactor as measured in the outlet gas

streams from the reactor [14]. The discharge in the gas phase of the series reactor leads to the intense plasma channels near and on the water surface [16]. Thus, despite the higher ozone in the bulk gas phase of the parallel reactor more oxidative species clearly reach the liquid phase to react with phenol in the series reactor. It is possible that additional hydroxyl radicals may be formed in the hybrid-series reactor [41,42] and that mass transfer may be more limiting in the hybrid-parallel reactor due to possibly larger electrohydrodynamic flow in the series reactor. Reaction processes occurring at the interface between the gas discharge and liquid surface may also have an effect on the liquid phase reactions [15]. In support of this later argument, He et al. [26] reported that radicals formed in a gas phase very close to a solution surface may diffuse into solution and react with organic in the liquid.

The formation of primary oxidation by-products of phenol, namely catechol and hydroquinone, during treatment in the corona reactors is given in Fig. 4. It should be noted that in addition to these measured phenol by-products other possible by-products, such as benzoquinone and various organic

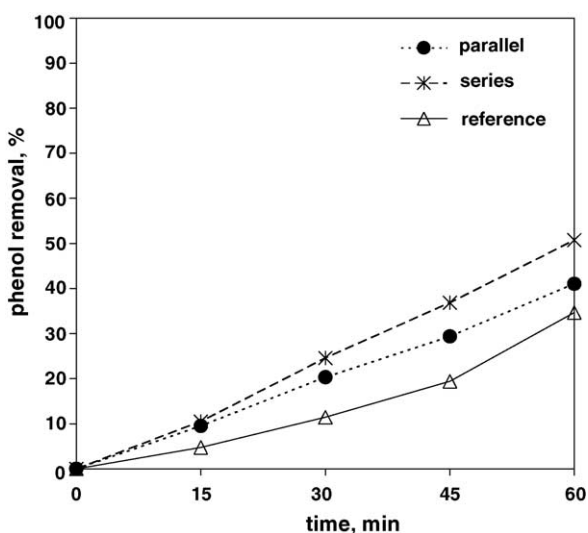


Fig. 3. Phenol removal in all three types of corona reactors in the absence of zeolites ( $U = 45$  kV,  $f = 60$  Hz and  $C = 2$  nF). The lines are only for connecting points and are not model results.

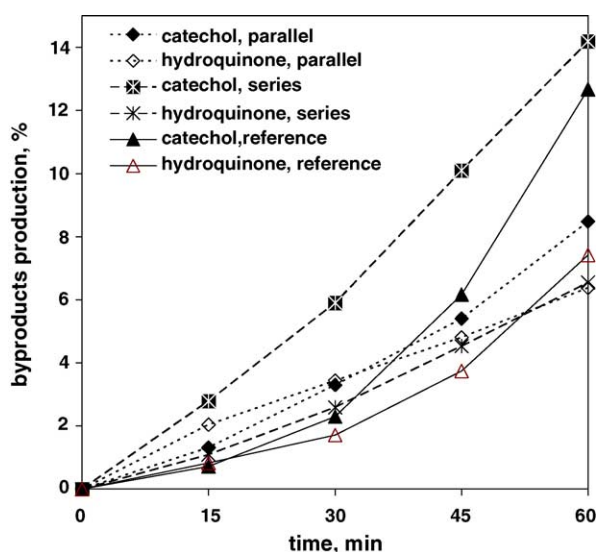


Fig. 4. By-product, catechol and hydroquinone, generation in all three types of corona reactors in the absence of zeolites ( $U = 45$  kV,  $f = 60$  Hz and  $C = 2$  nF). The lines are only for connecting points and are not model results.

acids, can be produced during phenol degradation [40–43]. Lukes and Locke [42] demonstrated the formation of *cis,cis*-muconic acid during phenol degradation in the hybrid-series corona reactor, thus confirming direct ozone attack on the phenol, however direct hydroxyl attack was also demonstrated. It can be seen that the largest amount of phenol by-products in the present experiments was observed in the hybrid-series reactor, 14.2% catechol and 6.6% hydroquinone, which is consistent with the larger percentage of phenol decomposition, 50.7%, in the same reactor in comparison to other two reactors. In contrast, the parallel reactor produces less catechol than the reference reactor despite the higher overall phenol removal in the parallel. This result is consistent with the proposed large role for direct ozone attack in the parallel since direct attack on phenol may lead to less hydroxylated aromatic ring products [41].

A further set of experiments was conducted with the addition of methanol into the all three types of corona reactors since methanol is known as a very active hydroxyl radical scavenging agent [44–47]. These experiments were conducted in order to assess other reaction mechanisms which are involved in phenol degradation in the studied corona reactors. Fig. 5 gives results for phenol degradation with the addition of methanol in all three types of corona reactor. A significant drop in degradation efficiency of phenol in the reference reactor was observed, where only 7.3% removal was found in the case with methanol addition compared to 34.7% in the case without methanol addition. This result confirms previous indications that the major mechanism responsible for phenol degradation in the reference corona reactor is the OH radical attack [7,8]. The results obtained in the other two reactors, hybrid-series and hybrid-parallel, indicate that in addition to oxidation mechanism through OH radical attack other mechanisms are also involved in phenol degradation.

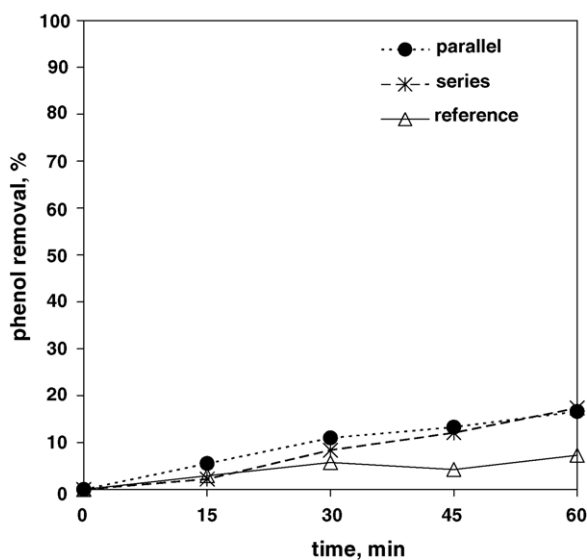
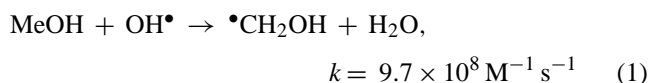
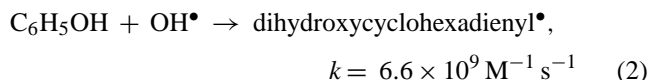


Fig. 5. Phenol removal in all three types of corona reactors in the presence of methanol as a OH radical scavenger ( $U = 45$  kV,  $f = 60$  Hz and  $C = 2$  nF). The lines are only for connecting points and are not model results.

In the hybrid-parallel corona reactor, the other mechanism is mostly direct attack by ozone, but in the case of the hybrid-series reactor another mechanism in addition to ozone attack should be considered due to the similar extents of phenol degradation obtained in both reactors in cases with addition of methanol (Fig. 5) and the approximately seven times lower ozone production in the gas phase in series reactor than in parallel [14]. Lukes et al. [15] reported that possible reaction processes which occur at the interface between the gas discharge and the liquid surface could also enhance the overall efficiency of the electrical discharge process for the removal of pollutants from water. Very low rates of catechol and hydroquinone production in experiments with addition of methanol in all three reactors, below 1% (Tables 2–4), confirm that the hydroxyl radical reactions are quenched since these products arise primarily by hydroxyl radical attack and not, for example, direct ozone attack. The value of rate constant for reaction (1), the reaction between methanol and OH radical [48]:



is almost seven times lower than that for the reaction (2), the reaction between phenol and OH radical [49]:



The concentration of methanol, 0.09 or 0.18 M, was significantly higher than the concentration of phenol in the bulk,  $0.1 \text{ g l}^{-1}$  which corresponds approximately to 0.001 M. Thus, it is likely that the OH radicals generated by corona discharge reacted with methanol rather than with phenol, i.e. they were mostly quenched by methanol, and no or only small amounts of OH radicals were available for reaction with phenol. Also, Kirkpatrick [50] reported that the addition of methanol into corona discharge reactor, besides quenching of OH radicals, leads to the formation of large amounts of hydrogen gas. These fine bubbles may affect the mass transfer characteristics for ozone in the both hybrid reactors and thus also lower phenol degradation by direct ozone attack.

After determining the amounts of phenol adsorption onto the  $\text{NH}_4\text{ZSM5}$ ,  $\text{FeZSM5}$  and  $\text{HY}$  zeolites, further experiments were performed in order to investigate the amounts of phenol degradation in each corona reactor with the addition of zeolites. Fig. 6 shows results for phenol decomposition obtained during the treatment in all three reactors with the addition of  $\text{NH}_4\text{ZSM5}$  zeolite. Total phenol removal was enhanced in all three types of reactors, but not in the order as would be expected from the results of phenol adsorption into the  $\text{NH}_4\text{ZSM5}$  zeolite (Fig. 2) where 30.4% of phenol was removed and from phenol decomposition results in the corona reactors without zeolite addition (Fig. 3), with 34.7%, 41.1% and 50.7% of phenol removal in reference, in hybrid-parallel and in hybrid-series corona reactors, respectively. It can be

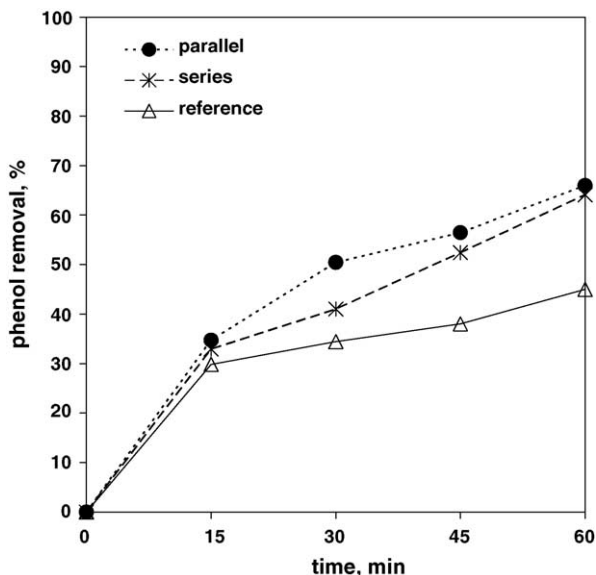


Fig. 6. The effects of  $\text{NH}_4\text{ZSM5}$  zeolite addition on phenol removal in all three types of corona reactors ( $U = 45 \text{ kV}$ ,  $f = 60 \text{ Hz}$  and  $C = 2 \text{ nF}$ ). The lines are only for connecting points and are not model results.

seen that the major process responsible for phenol removal in the first 15 min of treatment was adsorption of phenol to the zeolite, while at later times phenol in the bulk was degraded as in the case without zeolite.

Despite the larger overall phenol removal, lower degradation rates in all three corona reactors were observed with this zeolite. In reactors where the major degradation mechanism is likely OH radical attack, i.e. the reference and hybrid-series, phenol removal is significantly lower in comparison to the expected sum of phenol removal obtained by adsorption and phenol removal obtained in these corona reactors in the absence of zeolite,  $30.4\% + 34.7\% = 65.1\% \gg 45\%$  obtained in reference and  $30.4\% + 50.7\% = 81.1\% \gg 64.1\%$  obtained in hybrid-series corona reactor. These results lead to the conclusion that the zeolite may quench OH radicals [17]. On the other hand, in the case of hybrid-parallel corona reactor, the difference between the expected sum of phenol removal obtained by adsorption and phenol removal obtained in that corona reactor in the absence of zeolite is not as large,  $30.4\% + 41.1\% = 71.5\% > 66.0\%$  obtained in hybrid-parallel. If the zeolite  $\text{NH}_4\text{ZSM5}$  suppresses hydroxyl radicals in the reference and hybrid-series reactors, it is likely to suppress hydroxyl radical in the hybrid-parallel. In addition to suppressing OH radicals, it appears that the addition of zeolite enhanced phenol degradation in the hybrid-parallel in comparison to the cases of other two reactors in combination with  $\text{NH}_4\text{ZSM5}$  zeolite. This enhancement could be caused by possible ozone–zeolite interactions [17]. Consistent with this conclusion is the observation that the best phenol decomposition with zeolite was achieved in the hybrid-parallel corona reactor, 66.0% phenol removal.

Catechol and hydroquinone production during the treatment with the same systems, all three types of corona reactors/

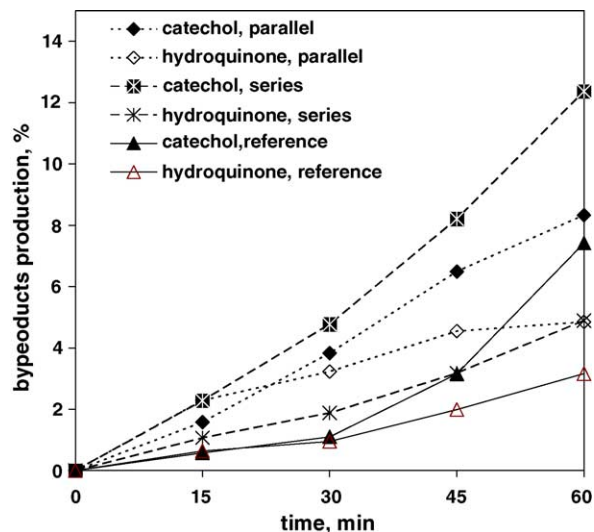


Fig. 7. The effects of  $\text{NH}_4\text{ZSM5}$  zeolite addition on by-product formation, i.e. catechol and hydroquinone, in all three types of corona reactors ( $U = 45 \text{ kV}$ ,  $f = 60 \text{ Hz}$  and  $C = 2 \text{ nF}$ ). The lines are only for connecting points and are not model results.

$\text{NH}_4\text{ZSM5}$  zeolite, are shown in Fig. 7. Although profiles of detected by-product generation are similar (Figs. 4 and 7), their concentrations are lower than in case without zeolite addition presumably due to lower rate of phenol degradation obtained in cases with zeolite addition (Tables 2–4). An exception is observed in the case of the hybrid-parallel reactor where almost the same concentrations of catechol were produced by both processes, without and with addition of  $\text{NH}_4\text{ZSM5}$ . This might suggest that some of phenol adsorbed to the zeolite may be degraded by chemical reactions and further work is necessary to assess this possibility.

A further set of experiments was performed with the addition of Fe-exchanged ZSM5 zeolite to all three corona reactors (Figs. 8 and 9). It can be seen that the phenol removal in all three corona reactors was enhanced to similar values, 89.4%, 93.6% and 91.9% in the reference, hybrid-parallel and hybrid-series reactors, respectively (Fig. 8). Such large and similar phenol removal rates in all three reactor configurations can be explained by enhancement of OH radical generation in all three reactors due to Fenton reaction between  $\text{H}_2\text{O}_2$  produced at similar rates in the liquid phase of the discharge of all three reactors [14], and  $\text{Fe}^{2+}$  ions in the zeolite framework as well as those leached into the bulk solution. The results presented here are very consistent with the work of Grymonpré et al. on soluble ferrous sulfate solutions [27] and also suggest minimal effects of adsorption to this zeolite on overall phenol removal. Neamtu et al. [36] proposed a possible degradation mechanism which includes generation of OH radicals in the inner surface of the microporous zeolite due to the Fenton reaction between  $\text{H}_2\text{O}_2$  and  $\text{Fe}^{2+}$  ions from zeolite framework, and thereafter OH radical diffusion into the bulk. Furthermore, Fajerberg et al. [37] found that utilization of FeZSM5 zeolite in the presence of  $\text{H}_2\text{O}_2$  was a very successful method for degradation of phenol.

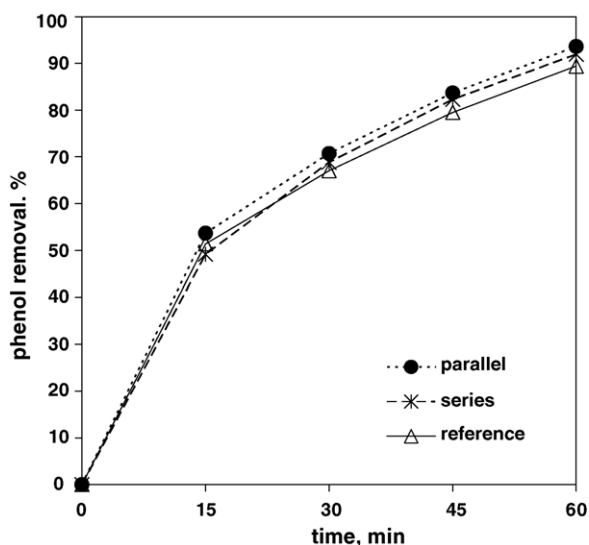


Fig. 8. The effects of FeZSM5 zeolite addition on phenol removal in all three types of corona reactors ( $U = 45$  kV,  $f = 60$  Hz and  $C = 2$  nF). The lines are only for connecting points and are not model results.

According to the study of Rauscher et al. [38] the amount of Fe-content in the FeZSM5 zeolite was  $37.1 \text{ mg g}^{-1}$  of zeolite. That value corresponds to the approximate concentrations of  $0.664 \text{ mM}$  of  $\text{Fe}^{2+}$  ions, which is close to the concentrations of  $\text{Fe}^{2+}$  ions,  $0.485 \text{ mM}$ , used by Grymonpre et al. [16,27] who reported phenol degradation efficiency in the reference and hybrid-series corona reactors in the presence of ferrous sulfate, 89.9% and 97.5% removed phenol, respectively. In Fig. 9, the generation of phenol degradation by-products, catechol and hydroquinone, during the treatment in all three reactors in the presence of FeZSM5 zeolite is shown. The catechol concentration increased over 30 min up to 18% in the

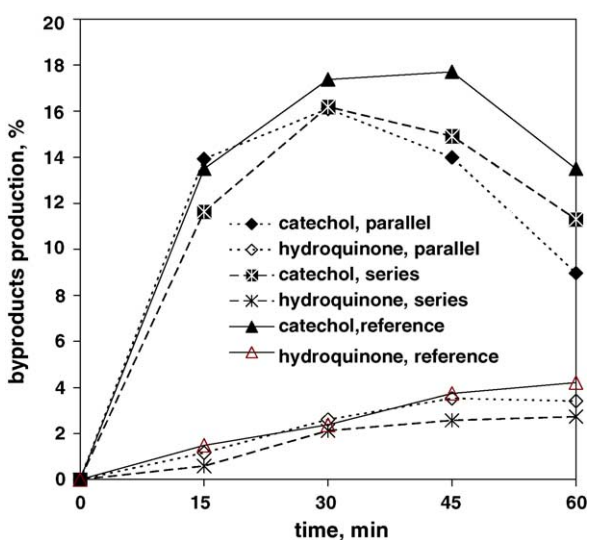


Fig. 9. The effects of FeZSM5 zeolite addition on by-product formation, i.e. catechol and hydroquinone, in all three types of corona reactors ( $U = 45$  kV,  $f = 60$  Hz and  $C = 2$  nF). The lines are only for connecting points and are not model results.

reference and then decreased to 13.5% at the end of the process. A similar trend for catechol production was observed in the case of the hybrid-series and hybrid-parallel corona reactors. Hydroquinone production in all three reactors ranged between 2.7% and 4.2%, which is lower in comparison to the case without any zeolite addition, 6.4–7.4%, where lower extents of phenol removal were achieved. According to studies of Grymonpré et al. [16,27], the results of catechol and hydroquinone production obtained in this study lead to the conclusion that significantly higher mineralization of phenol solution was achieved in processes with addition of FeZSM5 zeolites than in cases without zeolite addition.

One of the major advantages of utilization of FeZSM5 zeolite in the presence of  $\text{H}_2\text{O}_2$  for organic pollutant degradation is that Fenton reaction occurs on the zeolite surface without significant leaching of  $\text{Fe}^{2+}$  ions in the bulk. According to Neamtu et al. [36], less than 10% of the iron leaches into solution. Unpublished work in our laboratory supports this finding in the case without electrical discharge. Further work is necessary to assess leaching in the presence of electrical discharge. Besides avoidance of additional further contamination of the treated wastewater with iron ions, another advantage is that the FeZSM5 zeolite does not release unnecessary counterions as occurs with the addition of iron salts [36].

The next set of experiments was performed in all three corona reactors in the presence of HY zeolite. As shown in Table 1 and Fig. 2, phenol did not diffuse into the HY zeolite pores, as reflected in the small 7% phenol removal without corona discharge. On the other hand, in previous study [17], HY zeolite was shown to be a very effective catalyst when combined with corona discharge for decolorization of organic dye, especially in hybrid-parallel corona reactor. Fig. 10 shows phenol removal results for the combination

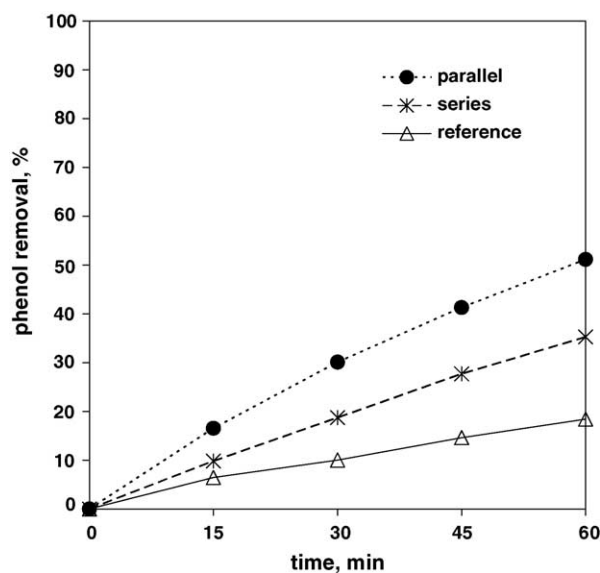


Fig. 10. The effects of HY zeolite addition on phenol removal in all three types of corona reactors ( $U = 45$  kV,  $f = 60$  Hz and  $C = 2$  nF). The lines are only for connecting points and are not model results.



of corona discharge and HY zeolite. The phenol degradation efficiency in the reference and hybrid-series corona reactors, with a putative predominately OH radical mechanism, was significantly reduced to 18.4% and 35.3% of phenol removal, possibly due to quenching of OH radicals by zeolite HY [17]. In the hybrid-parallel corona reactor, phenol removal was enhanced from 41.1% in case without any zeolite up to 51.1% in the case with zeolite. Similar to the case of the corona discharge/ $\text{NH}_4\text{ZSM5}$  system, if the HY zeolite suppresses hydroxyl radicals in the reference and hybrid-series reactor, it is likely to suppress hydroxyl radical in the hybrid-parallel too. Since the hybrid-parallel reactor shows a substantial enhancement with the zeolite, it is likely that the ozone may interact with the zeolite to improve phenol removal [17].

Lukes et al. [15] reported that phenol removal in hybrid-series corona reactor strongly depends on pH value due to ozone produced in gas phase. It is therefore likely that in the case of hybrid-parallel reactor, with a much higher ozone production rate than the hybrid-series, that pH should also affect the liquid phase reactions. It should be noticed that the pH value decreased from 5.1 to 3.8 with the addition of the HY zeolite and that may be an additional reason for the lowering phenol degradation efficiency by those two reactors and consequently formation of detected by-products. Consequently with lower phenol removal due to quenching of OH radicals by HY zeolite, amounts of produced by-products were also lower. Hydroquinone production during the treatment in the same systems, applied corona processes with HY zeolite, is in accordance with the amount of decomposed phenol. The trends for the catechol formation in the two hybrid reactors were slightly different in that the parallel reactor showed a

gradual leveling off in the production and the series reactor showed a more linear increase as seen in the reference reactor (Fig. 11). The same overall amount of catechol was produced in both the hybrid reactors, in spite of the significantly higher phenol removal obtained in the hybrid-parallel reactor. This may be related with above mentioned more pronounced ozone–zeolite interactions in the hybrid-parallel reactor than in the hybrid-series reactor which may result in the formation of other by-products, e.g. *cis,cis*-muconic acid, in the parallel than series reactor. While further experiments are needed to fully explain this result, if it is assumed that hydroxyl radical plays a larger role in the series reactor and reference reactor, the linear increase in by-product is directly related to the hydroxyl radical attack on phenol and the gradual leveling out in the parallel reactor with zeolite may be related to possible saturation effects in the zeolite–ozone interactions.

#### 4. Conclusions

The goal of this study was to investigate the combination of corona discharge reactors with zeolites for effective degradation of organic contaminants in water. Three different types of corona reactors; reference, hybrid-parallel and hybrid-series, in combination with several types of synthetic zeolites,  $\text{NH}_4\text{ZSM5}$ ,  $\text{FeZSM5}$  and HY, for phenol degradation were applied. The percentage phenol degradation achieved strongly depended upon reactor configuration and the type of added zeolite. From the reactor type point of view, the hybrid-series corona reactor showed the highest rate of phenol degradation, 50.7% of removed phenol, primarily due to higher OH radical generation than in the other two types of corona reactors, but also due to ozone production in the gas phase of the reactor. The addition of  $\text{NH}_4\text{ZSM5}$  and HY zeolites enhanced phenol removal in the hybrid-parallel corona reactor, up to 66.0% and 51.1%, respectively, in comparison with the case without zeolites, 41.1% phenol removal. However, the removal of phenol by zeolite with corona was less than expected due to the linear combination of corona reactions without zeolite and adsorption to zeolite. The evidence suggests that hydroxyl radical may be quenched and that ozone reactions may be enhanced by both zeolites. Overall, the best phenol removal results were achieved in all three types of corona discharge reactors with the addition of Fe-exchanged zeolite,  $\text{FeZSM5}$ , where between 89.4% and 93.6% phenol removal was due to additional generation of OH radicals by the Fenton reaction between  $\text{Fe}^{2+}$  ions doped in the zeolites and  $\text{H}_2\text{O}_2$  produced by corona discharge. This new system, corona discharge with  $\text{FeZSM5}$  zeolite, may present a new environmental friendly approach to the dealing with organic pollutants in water due to high efficiency, very low additional contamination of treated wastewater with iron ions and avoidance of unnecessary loading of treated wastewater with anions like in case of well known Fenton reaction.

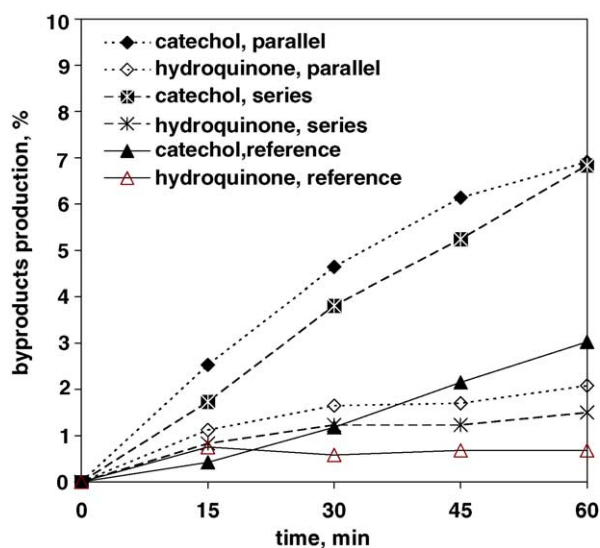


Fig. 11. The effects of HY zeolite addition on by-product formation, i.e. catechol and hydroquinone, in all three types of corona reactors ( $U = 45$  kV,  $f = 60$  Hz and  $C = 2$  nF). The lines are only for connecting points and are not model results.

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