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The influence of different soil constituents on the reaction kinetics of wet oxidation of the creosote compound quinoline

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Abstract

Creosote contaminated sites have become a widespread problem in industrialized countries. Recently, wet oxidation using high temperature, pressure, water and oxygen followed by activated sludge treatment proved to be an efficient method for removing a wide selection of creosote compounds in contaminated soils. Wet oxidation of the creosote compound quinoline was carried out in the presence of montmorillionite, quartz and humic acid. The products derived from wet oxidation were identified and treated biologically by activated sludge testing their biodegradability. The influence on the oxidation kinetics of quinoline during wet oxidation was pH dependent. Humic acid supported the oxidation of quinoline, whereas the addition of montmorillionite and quartz had either an inhibiting effect or led only to a slight increase in oxidation. In mixtures of soil constituents, especially at low contents of humic acid, the adsorption of quinoline on montmorillionite prevented oxidation at neutral pH. Thus, alkaline extraction of both quinoline and humic acid was needed for an efficient oxidation. A proposed reaction mechanism suggests that quinoline was oxidized by hydroxyl radicals formed during the oxidation of the humic acid. A wide selection of reaction products (mainly carboxylic acids, benzene and pyridine derivatives) derived from the wet oxidation of humic acid and quinoline. The reaction products from humic acid degradation had a rate limiting effect on the wet oxidation of quinoline leaving small residues of quinoline after the treatment. On the contrary, these reaction products also improved the biodegradation of products from the quinoline oxidation due to co-digestion of carboxylic acids. Therefore, the presence of soil components (mainly humic acid) improved the combined wet oxidation and biological activated sludge treatment of quinoline. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Quinoline; Wet oxidation; Humic acid; Oxidation kinetics; Biodegradation

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1. Introduction

Abandoned gasworks, asphalt factories and wood impregnation facilities are contributors to coal tar and creosote contamination in industrialized countries [1]. Contaminated soils typically consist of 85% polyaromatic hydrocarbons, 1–10% phenols, 5–13% heterocyclic aromatics containing nitrogen, sulfur or oxygen, and 1–3% monoaromatic compounds [2,3]. Most creosote compounds including quinoline are thermally and chemically stable, and due to a high toxicity they are a risk for the environment [4,5]. When absorbed on soil organic matter and clays, creosote compounds are difficult to treat by biological methods [6–8], e.g. quinoline was degraded in soil after 10 days under aerobic conditions and after 47 days under anaerobic conditions [9,10]. Considerable amounts of creosote compounds were found in the groundwater near gasworks sites indicating an inefficiency of the biological degradation processes [2,3]. Apparently, other methods than biodegradation have to be found to treat soil contaminated by creosote compounds.

Recently, wet oxidation was identified to be quite effective in cleaning hazardous, toxic, and non-biodegradable waste streams [11–12]. Wet oxidation is defined as the treatment of organic compounds in aqueous medium using elevated temperature up to 320°C and pressure up to 3.0 mPa. With this technique hazardous organic compounds can be transferred to simpler water soluble and biological degradable compounds, CO_2 and water [12]. The use of additional features like nanofiltration membranes [13] or different catalysts [14–16] improved the degradation efficiency of the wet oxidation process for a wide range of organic contaminants. The industrial use includes several applications like municipal sewage sludge treatment, cyanide and nitrile waster water treatment, energy and resource regeneration [11,17]. A combination of partial wet oxidation and subsequent activated sludge treatment was used successfully in reducing creosote in soil [18,19]. Instead of using expensive chemical oxidation, this integrated chemical–biological method is more suitable to clean contaminated soil sites [20]. However, at present only a handful of industrial reactors are in operation world-wide [17].

It was found that soil components have an effect on the degradation of organic contaminants in soil during wet oxidation [21–23]. However, detailed investigations on the influence of individual soil components on the degradation of creosote compounds, on the resulting degradation products, and on the biodegradability of these compounds are still missing. In this paper, the influence of different soil constituents like humic acid, quartz, montmorillionite on the degradation of the creosote compound quinoline during wet oxidation was investigated to identify a possible improvement of the wet oxidation process in cleaning contaminated soil sites. Quinoline was chosen as a model compound for the wet oxidation study due to its similar reactivity to the analogue and most abundant PAH (polyaromatic hydrocarbons) compound naphthalene [24]. Furthermore, different to other PAH compounds (including napthalene) quinoline has a higher water solubility, and, therefore, studies at high concentrations of quinoline in water were possible without the use of a carrier material, which may interfere with effects from the soil constituents added.

2. Material and methods

For wet oxidation, a specially designed loop-autoclave with a total volume of 2 l and a short heating and closing period of 0.5 and 3 min, respectively, was used. The autoclave was made of a base- and acid-resistant steel material (Sandvik Sanicro 28). The wet oxidation experiment was carried out as follows: 1 l of water containing 250 mg quinoline was added to the autoclave together with either quartz, montmorillionite or humic acid. To establish a pH of 10, 2.5 g l^{-1} sodium carbonate was added. After sealing the autoclave lid an oxygen pressure of 2.0 mPa was supplied to obtain 35 times the theoretical amount needed for complete oxidation of 250 mg l^{-1} quinoline. Heating the autoclave to 260°C was done by a salt melt heating bath (50% $NaNO_3$ and 50% KNO_2). After the reaction was completed the autoclave was immersed into an ice bath, cooled down, and a sample was withdrawn. The procedure was continued with a new supply of oxygen (2.0 mPa) until total reaction time elapsed. The heating and cooling phases were not included in the reaction time. As references, two experiments without soil components added were made in the same way at neutral and alkaline pH. The pH was measured twice, before and after the oxidation experiment using a standard pH-meter.

For identification and quantification of the total amount of quinoline (sum of adsorbed and soluble substance) in samples with soil components, the samples were adjusted to pH 8–9. A known amount of D_7-quinoline was added as internal standard before extracting the sample with *iso*-octane. The *iso*-octane extracts were analyzed by gas chromatography with mass spectrometric detection (GC/MS). Quinoline in the water phase was analyzed in filtered samples by high performance liquid chromatography (HPLC). The adsorption of quinoline to soil minerals was calculated as the difference between the total amount of quinoline in suspension and quinoline in the water phase. For product identification, the wet oxidized samples were filtered to remove solid soil components. One aliquot of the sample was adjusted to pH 7 and extracted with diethyl ether. Another part of the sample (2 times 50 ml) was freeze-dried for silylation and esterification. Silylation was done by adding bis-(trimethylsilyl) trifluor acetamid to the freeze-dried sample for 1 h. Esterification was performed by adding methanol and H_2SO_4 (97%) to the freeze-dried sample and refluxing the sample for 6–8 h. NaOH was added for neutralization followed by extraction with diethyl ether. Water was added to improve the phase separation. The isolated products from diethyl ether extraction, silylation and esterification were examined by GC/MS.

GC/MS analyses were performed on a Varian Star 3400 gas chromatograph equipped with an Saturn III ion trap mass spectrometer with direct capillary interface and a Variant 8200cx autosampler. For separation an XTI-5 capillary column was used (Restek, 30 m × 0.25 mm i.d., $d = 0.25\,\mu m$). The temperature program was from 40 to 325°C at a heating rate of 20°C min^{-1}. The mass spectra obtained were compared with those of a standard reference material from the 1992 database of National Institute of Standard and Technology (NIST 92). The water-soluble compounds of the filtered samples were analyzed by HPLC with a Shimatzu binary pump and a diode array detector at 315 nm. Separation was done on a reverse-phase column (Phenomenex Nucleocil5C_{18}, 100 Å, 250 mm × 4.6 mm) with a methanol–water gradient (46–90%). A more detailed description of the analytical procedures is given by Thomsen et al. [25].

To investigate the biological degradation of the reaction products derived from the experiment, a test was used based on the modified OECD guidelines for testing of chemicals (no. 302B). The test was performed in triplicate including a control. Active sludge corresponding to a dry matter content of 0.6 g was added to a 2 l-Erlenmeyer flask equipped with an aerator and a magnetic stirrer. Prior to use the sludge was washed and centrifuged several times to remove soluble total organic carbon (TOC). The wet oxidized testing substance was filtered to remove solid particles and then diluted in tap water corresponding to TOC values in the range of 100–300 mg l^{-1}. The control contained tap water only. The testing period was 28 days and the degradation process was monitored three times a week by determining the TOC values. The values were plotted versus reaction time to give the biodegradation curves. The determination of the TOC content was done by combustion at 680°C followed by IR detection on a Shimadzu TOC-5000 organic carbon analyzer.

All chemicals were of analytical grade quality. Humic acid in the form of sodium humate was obtained from Sigma–Aldrich. The montmorillionite clay was a Yellowstone bentonite from Wyoming, USA. X-ray analysis did not detect minerals other than montmorillionite. Quartz was a purified iron-free powder (Riedel-de Haën). Quinoline purchased from Sigma–Aldrich was distilled prior to use. Deuterium-labeled D_7-quinoline was used as delivered (Sigma–Aldrich).

3. Results

In general, wet oxidation is considered pseudo-first-order reactions when excess of oxygen is added [34]. The $-\ln C_a/C_{ao}$ versus time gives a linear fit, C_a being the concentration of the compound at a given time and C_{ao} the initial concentration. The rate constants calculated are given in Table 1. The results showed that the addition of the soil components quartz, montmorillionite and humic acid had an influence on the oxidation kinetics of quinoline. In general, humic acid supported the decomposition of quinoline while the addition of montmorillionite and quartz had either only a moderate positive effect (at pH 10) or an inhibitory effect (at pH 7) (Fig. 1). Typical for the degradation of quinoline during wet oxidation at pH 7 is an S-shaped reaction course previously described by Thomsen [27]. While quartz led to a delay in decomposition by increasing the induction period, i.e. the low rate reaction phase before the start of the rapid reaction phase, with montmorillionite only 35% of the quinoline was oxidized after 60 min. When using montmorillionite the rate constant of the oxidation was almost two orders of magnitude lower than that for the control experiment (Table 1). A comparison of quinoline analyzed in the water phase with the one of total quinoline in suspension showed that up to 80% of the added quinoline was retained by adsorption on montmorillionite particles (Thomsen et al., unpublished data). Addition of quartz revealed a S-shaped reaction course similar to the reference with a large induction time and a lower reaction rate constant (Table 1). Comparing HPLC with GC/MS analysis only 1–2% of the quinoline added was adsorbed on the quartz particles. Additional to previously reported results [27] the investigation showed a reduced oxidation of quinoline without added soil components (reference experiment) at higher pH (Fig. 1). On the contrary, the addition of quartz and montmorillionite increased the oxidation of quinoline at pH 10 (Fig. 1). At that pH the oxidation of quinoline was almost twice as fast compared to the

Table 1
Rate constants k' and correlation coefficients (r^2) for the wet oxidation of quinoline (250 mg l^{-1}) with or without addition of quartz (Qz), montmorillionite (M) and humic acid (HA) testing pseudo-first order reaction mechanism

Soil compound (addition l^{-1})	Initial pH	Temperature (°C)	k'	r^2
No addition	7	260	0.230[a]	0.83
5 g Qz	7	260	0.150[a]	0.86
5 g M	7	260	0.006	0.94
0.5 g HA	7	260	0.080	0.77
0.5 g HA, 5 g M, 5 g Qz	7	260	0.005	0.98
2.5 g HA, 5 g M, 5 g Qz	7	260	0.026	0.81
No addition	10	260	0.012	0.93
5 g Qz	10	260	0.025	0.98
5 g M	10	260	0.021	0.99
0.5 g HA	10	260	0.043	0.97
0.5 g HA, 5 g M, 5 g Qz	10	260	0.037	0.96
2.5 g HA, 5 g M, 5 g Qz	10[b]	260	0.057	0.95
No addition	7	220	0.220[a]; 0.003[c]	0.96
0.5 g HA	7	220	0.080	0.81

[a] Rapid reaction phase.
[b] End pH = 7.6.
[c] Induction period.

reference experiment when quartz and montmorillionite was added (Table 1). Investigations of the quinoline concentrations in the water phase compared to them in suspension showed at pH 10 an adsorption of 10–20 and 4%, respectively, of the measured quinoline on the montmorillionite and quartz surface, respectively (Thomsen et al., unpublished data).

In soil the organic matter made up only a few percent of the total content of clays and quartz [28,29]. Thus, the amount of humic acid added was lower compared to the amount of quartz and montmorillionite added. With the addition of humic acid the decomposition of quinoline was commenced immediately without any induction (Fig. 1). Although almost 90% of the quinoline was already oxidized after 10 min a residual amount of quinoline (6–8 mg l^{-1}) still was detected after 40 min reaction time (Fig. 1). Even an increase of the amount of humic acid added (1 and 2.5 g l^{-1}, respectively) did not led to a complete oxidation of quinoline as found when nothing or quartz was added to the wet oxidation process. An increase of the pH inhibited the oxidation of quinoline (Fig. 1). However, the addition of humic acid was the most effective way of quinoline oxidation. To identify whether quinoline was actually oxidized and not just absorbed by, e.g. humic acid, the amount of total organic carbon (TOC) was monitored during the experiment. When humic acid was added to the wet oxidation process up to 57% TOC disappeared compared to 62% in the control experiment, indicating that considerable parts of both humic acid and quinoline were oxidized to CO_2 and water (Table 2). At 220°C both quinoline and humic acid was degraded to 47% while no oxidation occurred in the control experiment. The pH was an important parameter when mixtures of soil components were added prior to the wet oxidation of quinoline. This was clearly illustrated by experiments at low contents of humic acid in which a significant oxidation occurred at alkaline pH but not at neutral pH (Fig. 2). With the addition of high amounts of humic acid the influence of increasing pH was less significant for the degradation of quinoline (Fig. 2).

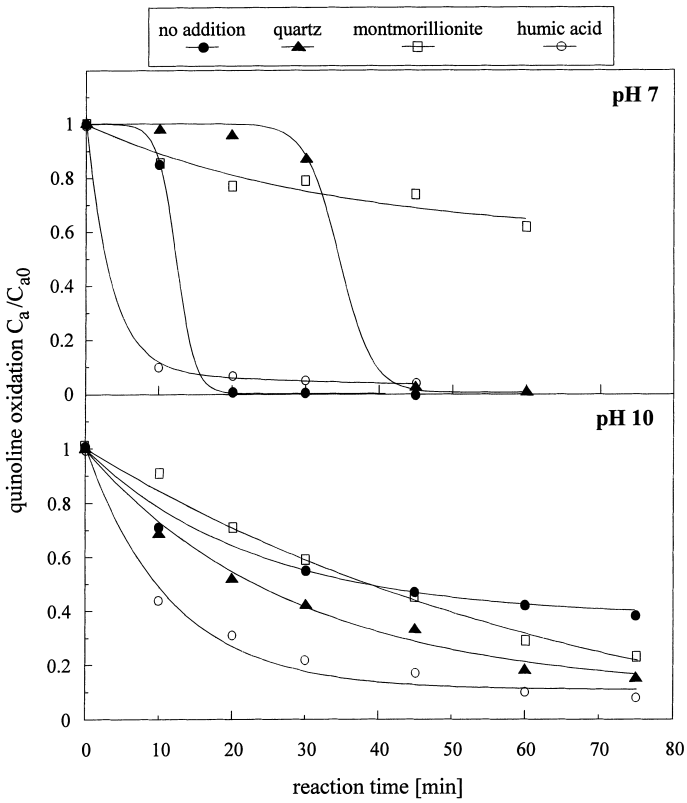

Fig. 1. Influence of the addition of humic acid, quartz and montmorillionite on the reaction kinetics of wet oxidation of quinoline at pH 7 and 10 and a reaction temperature of 260°C.

Table 2
Time dependent conversion of total organic carbon to CO_2 and water during wet oxidation with and without the addition of humic acid at pH 7 and different temperatures

Reaction time (min)	No addition				Addition of humic acid			
	Quinoline degradation (%)		Total organic carbon conversion (%)		Quinoline degradation (%)		Total organic carbon conversion (%)	
	220°C	260°C	220°C	260°C	220°C	260°C	220°C	260°C
0	0	0	0	0	0	0	0	0
10	0	15	0	0	87	90	23	44
20	0	100	0	7.5	95	94	34	53
30	0	100	0	55	96	96	41	55
40	11	100	0	62	97	97	47	57

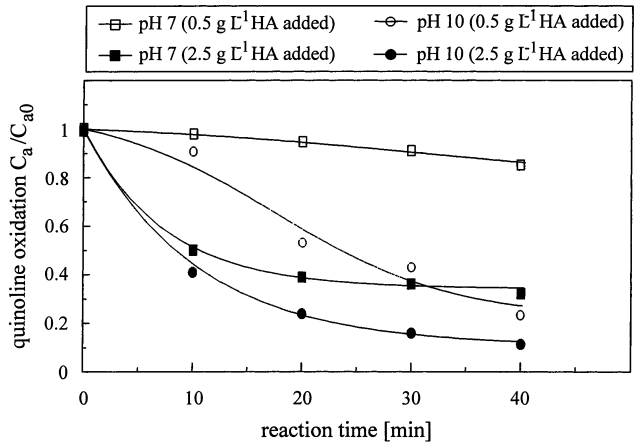

Fig. 2. Reaction kinetics of wet oxidation of quinoline at 260°C with addition of mixed soil components: humic acid (HA), montmorillionite (M; 5 g l^{-1} added), and quartz (Qz; 5 g l^{-1} added) as a function of pH and amount of humic acid added.

The sample derived from the oxidation of quinoline with a soil component mixture was analyzed for reaction products (Table 3). In the diethyl ether extract of a neutralized sample some unreacted quinoline was found together with 2- and 3-pyridine aldehyde, 3-acetyl pyridine and benzeneamine (aniline). After silylation of a neutralized and freeze-dried sample a few aromatic compounds were detected, mainly, 3-pyridinecarboxylic acid (nicotinic acid) and 2-hydroxy-3-pyridinecarboxylic acid, previously found to derive from quinoline oxidation [27]. After esterification, methoxylated and hydroxylated benzoic acids were identified, which mainly were products from the decomposition of humic acid. Aliphatic alcohols, hydroxylated, and methylated carboxylic acids were the main products identified after silylation and esterification. The same sample was tested for biodegradability by activated sludge treatment. The reduction of TOC versus time illustrates the CO_2-production during the observation period (Fig. 3). As no other nutrients were added, the CO_2-production was due to product digestion only. The products from quinoline and humic acid oxidation were completely oxidized to CO_2 and water, whereas in the reference experiment a residual amount was left undigested. No more carbon was detected after 15 days of biodegradation contrary to the reference experiment where 22 mg l^{-1} TOC was still present after 22 days of treatment. With the analytical procedures used in this study no reaction products were found in either of the experiments after biodegradation.

4. Discussion

Liquid-phase oxidation such as wet oxidation of organic compounds with molecular oxygen has been reported to usually proceed by a free radical chain mechanism [26,27,30,31]. The oxidation is of an auto-catalytic nature and known as “auto-oxidant” in which intermediates such as hydroxyl radicals and carboxyl radicals play important roles. Induction

Table 3
List of reaction products from wet oxidation of 250 mg l^{-1} quinoline with additions of quartz (5 g l^{-1}), montmorillionite (5 g l^{-1}) and humic acid (2.5 g l^{-1}) identified by GC/MS after sample work up

Aromatics	Aliphatics
Pyridine derivatives	Carboxylic acids
2-Pyridinealdehyde[a]	3-Hydroxypropanoic acid[b]
3-Pyridinealdehyde[a]	3-Hydroxybutanoic acid[b]
3-Acetylpyridine[a]	2-Hydroxybutanoic acid[b]
2-Pyridinecarboxylic acid[b]	4-Hydroxybutanoic acid[b]
6-Hydroxy, 3-pyridinecarboxylic acid[b]	3-Hydroxyvaleric acid[b]
Benzene derivatives	4-Hydroxyvaleric acid[b]
Benzaldehyde[a]	4-Hydroxypentanoic acid[b]
1,2,4-Benzentriol[a]	2-Hydroxypentanoic acid, 3-methyl[b]
4-Methoxy, 3-hydroxy, benzoic acid[b]	Butanedioic acid (succinic acid)[b,c]
1,2-Benzenedicarboxylic acid (phthalic acid)[b,c]	Hydroxybutanedioic acid[b]
Benzoic acid[c]	Butanedioic acid, 2,2-dimethyl[c]
1,2-Benzenedicarboxylic acid, 4-methyl	Pentandioic acid[c]
1,2,4-Benzenetricarboxylic acid	2-Pentanedioic acid[c]
1,3,5-Benzenetricarboxylic acid	2-Hydroxypentandioic acid[b]
2,5-Thiophenedicarboxylic acid	Pentanedioic acid, 3,3-dimethyl[c]
	Tetradecanoic acid[b]
Aromatic amines	Hexadecanoic acid[b]
Benzeneamine (aniline)[a]	
	Low molecular weight carboxylic acids
	Citric acid, maleic acid, succinic acid
	Oxalic acid, lactic acid, formic acid
	Acetic acid
	Alcohols
	2-Butanol, 2 methyl[c]
	1-Pentanol, 2-ethyl-4methyl[c]
	1-Pentanol, 4 methyl-2propyl[c]

[a] Diethyl ether extraction.
[b] Silylation.
[c] Esterification.

periods are most often explained by the time needed to establish a sufficient concentration of hydroxyl radicals in solution to start the reaction [27,30]. Homogeneous and heterogeneous metal species may be responsible for the production of hydroxyl radicals in this reaction mechanism [32].

The results obtained in this study suggested that initial concentrations of hydroxyl radicals were produced by oxidation of humic acid followed by a co-oxidation of quinoline. Humic acid is composed of a complex network of phenols and methoxy-phenols derivatives [33]. Phenol is far more reactive than its parent compound benzene due to the hydroxyl group, which strongly activates the aromatic ring in its ability to donate electrons [34]. A methoxy group on an aromatic ring plays a similar role with a more moderate effect. Wet oxidation of substituted phenols already showed an initiation of the phenol decomposition at a temperature of 150°C [35–37] compared to the critical temperature of 240°C for decomposing quinoline [27]. Thus, the degradation of humic acid most likely began at a significantly lower temperature, and, therefore, is responsible for the initial production of

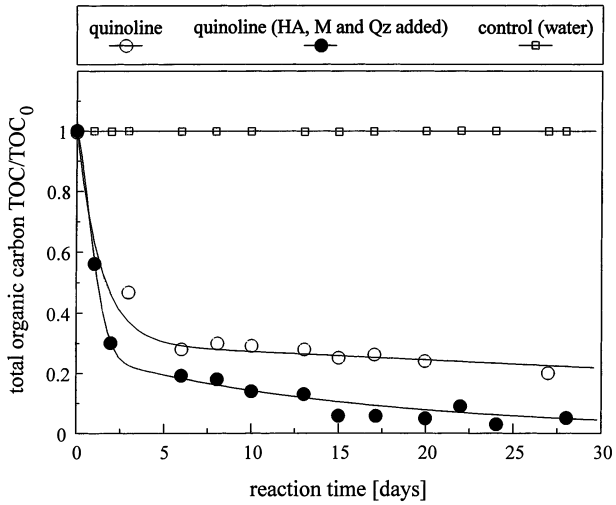

Fig. 3. Biodegradation of reaction products derived from wet oxidation of quinoline shown by analysis of total organic carbon. Effect of addition of soil components: humic acid (HA), montmorillionite (M), and quartz (Qz). Simultaneously, a control was conducted using water only.

hydroxyl radicals leading to a faster degradation of quinoline. This was confirmed by the reduction of TOC at 220°C. The residual amount of quinoline observed in the experiments with humic acid indicated the formation of more stable reaction products, which competed with quinoline for free radicals [27]. These were most likely carboxylic acids that are rate limiting under wet oxidation and stable under alkaline conditions [38]. At pH 7, the presence of quartz and montmorillionite seemed to prevent the initial production of hydroxyl radicals. The formation of these radicals over basic metal oxides has been reported [39]. However, when quartz was present no hydroxyl radicals were formed suggesting that the radicals rapidly reacted with the SiO_2 surface [39]. Thus, the negative effect from quartz on the wet oxidation of quinoline might be due to the neutralization of hydroxyl radicals.

The results illustrated the adsorption of large amounts of quinoline on the montmorillionite surface at pH 7 preventing the quinoline from being oxidized and indicating a cation exchange to play an important role. Montmorillionite is characterized by its large cation exchange [28,29]. Although the pK_a of quinoline is only 4.95 the cationic adsorption of quinoline on montmorillionite containing soil particles at pH values up to 7 was observed, probably due to the formation of a local pH on the soil surface two pH units lower compared to bulk solutions [40]. Compared to the reference experiment at alkaline pH the presence of montmorillionite and quartz seemed to increase the decomposition of quinoline indicating the presence of catalytic effects. Clay minerals have previously been used to enhance the catalytic activity of free radical initiators in polymerization processes due to their small number of metal ions [41]. In alkaline solution, hydroxyl radicals are transformed into less reactive oxygen (O_2^-) radicals [42]. Apparently, compared to the reference experiment increased concentrations of oxygen radicals were formed in experiments at alkaline conditions when quartz and montmorillionite were added to the wet oxidation process. Importantly,

the results illustrated that desorption of quinoline from the montmorillionite surface was necessary to observe this catalytic effect.

It is well known that organic matter can be absorbed to clay minerals and that the solubility of humic acids increase under alkaline conditions [29]. Therefore, the mechanism behind the oxidation of quinoline in the presence of a mixture of different soil components can be suggested. At neutral conditions some of the added humic acid probably was absorbed on the clay minerals and, therefore, together with quinoline prevented from oxidation. With increased amount of humic acid added to the wet oxidation process a saturation level may be reached and the surplus non-absorbed humic acid was oxidized causing an increase in quinoline oxidation. Increasing the pH to more alkaline conditions neutralized the inhibiting effects of the soil minerals due to an extraction of the organic compounds from the mineral surface. As a result more humic acid and, therefore, more quinoline can be oxidized. By these observations the inhibiting effect from soil on, e.g. *m*-xylene at pH 7 [21] may be explained by high amounts of clay responsible for the adsorption of *m*-xylene and the low contents of organic matter resulting in a reduced degree of oxidation.

5. Conclusions

Quartz, montmorillionite and humic acid influenced the decomposition of quinoline during wet oxidation. While quartz and montmorillionite had a more inhibiting effect, addition of humic acid increased the degradation of quinoline. Furthermore, alkaline conditions supported the oxidation of quinoline in the presence of soil components. Thus, to treat soil contaminated by organic pollutants by wet oxidation an alkaline extraction prior to oxidation can increase the degradation efficiency. Under these conditions humic acid together with the organic contaminants will be dissolved from the inorganic material of the soil. The oxidation of the reactive humic acid can support the oxidation of less reactive creosote compounds like, e.g. quinoline. If large amounts of humic acids are present in the soil the alkaline extraction becomes less important as the surplus of humic acid will be directly available for oxidation followed by co-oxidation of the organic pollutants.

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