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Article

Iron catalyst supported on modified kaolin for catalytic wet peroxide oxidation

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Abstract

An iron catalyst supported on the modified Tamazert kaolin has been prepared and tested in catalytic wet peroxide oxidation using phenol and 4-chlorophenol (4-CP) as target compounds (100 mg/L initial concentration). Kaolin is not usually employed as a catalytic support due to its low developed porous structure, but its textural properties may be improved upon calcination and acid and basic treatment. The catalyst was characterized by N_2 adsorption–desorption and chemical analysis by total-reflection X-ray fluorescence spectroscopy. The catalytic tests were carried out in a batch reactor with a stoichiometric amount of H_2O_2. The catalytic efficiency was studied within the temperature range of 25–55°C at an initial pH of 3.3 and 1 g/L catalyst. Complete phenol and 4-CP removal was achieved with no significant differences in phenol and 4-CP conversions within the temperature range tested. Meanwhile, total organic carbon (TOC) reduction was greatly favoured by increasing the temperature, which may be partially attributed to a probable contribution of a homogeneous reaction associated with iron leaching. However, this effect might be of limited significance because the highest concentrations of iron in the liquid phase were below 4.5 and 8.5 mg/L in the experiments with phenol and 4-CP, respectively. At 55°C, TOC was reduced by ~70% after 4 h reaction time, with the remaining by-products corresponding almost completely to low-molecular-weight carboxylic acids of very low ecotoxicity.

Numerous industrial activities such as those of refineries and textile, chemical, plastic and food processing produce considerable amounts of wastewater contaminated by a range of organic species, many of which are recalcitrant and toxic. Removal of those pollutants from aqueous streams has become a crucial problem over recent decades because environmental regulations and water-quality standards have become increasingly stringent, while conventional wastewater treatments do not provide a safe solution. Phenolic compounds are among the most representative toxic species listed by the European Commission and the US Environmental Protection Agency (EPA) as priority pollutants since the mid-1970s (EPA, 1982; European Parliament, 2008). They are ubiquitous in the effluents from various industries, including refineries, coking operations, coal processing, pulp mills and petrochemical industries, among others.

Advanced oxidation processes may provide useful solutions when working in near-ambient conditions. Among them, the Fenton process is the most widely used at full scale, and several Fenton-like technologies have been developed. These include the so-called catalytic wet peroxide oxidation (CWPO), which is the heterogeneous version of the Fenton system. The main advantage of CWPO with respect to the conventional homogeneous process is that it avoids or drastically reduces the continuous loss of iron in the effluent and the subsequent need for dealing with the sludge resulting from iron precipitation upon the neutralization step preceding final discharge. The CWPO of phenol and 4-CP has been much reported in the literature using a diverse range of catalysts mostly based on iron, but also with some other transition metals supported on various materials (Carriazo *et al.*, 2005; Garcia-Molina *et al.*, 2005; Valverde *et al.*, 2005; Zazo *et al.*, 2006; Peraira *et al.*, 2007; Valkaj *et al.*, 2007; Molina *et al.*, 2010, 2011; Catrinescu *et al.*, 2011, 2012; Hailing *et al.*, 2011; Zhou *et al.*, 2011, 2014; Inchaurrondo *et al.*, 2012; Pan *et al.*, 2012; Khanikar & Bhattacharyya, 2013; Munoz *et al.*, 2013; Dominguez *et al.*, 2014; Duan *et al.*, 2014; Kurian *et al.*, 2014; Deka & Bhattacharyya, 2015; Oxana *et al.*, 2016; Tomul, 2016; Wei *et al.*, 2017; Leal *et al.*, 2018), including raw and modified clays. So far, kaolin has attracted limited attention, probably due to its less developed porous texture compared to other clays such as bentonite (Jozefaciuk & Bowanko, 2002). However, its textural properties may be improved upon appropriate treatment (Yavuz & Saka, 2013; Gao *et al.*, 2015, 2016; Boukhemkhem & Rida, 2017).

This work is focused on the application of Tamazert kaolin (KT), a naturally occurring mineral, as a precursor in the preparation of an inexpensive catalyst for CWPO after various treatments followed by impregnation with $FeCl_3$. The catalyst has been tested in the temperature range of 25–55°C using phenol and 4-CP as target pollutants. The evolution of the starting

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Fig. 1. Catalyst preparation steps.

Fig. 2. The –196°C N_2 adsorption–desorption isotherms of KT, KTM and Fe-KTM.

Table 1. Textural properties and chemical compositions of the starting materials and the prepared catalyst.

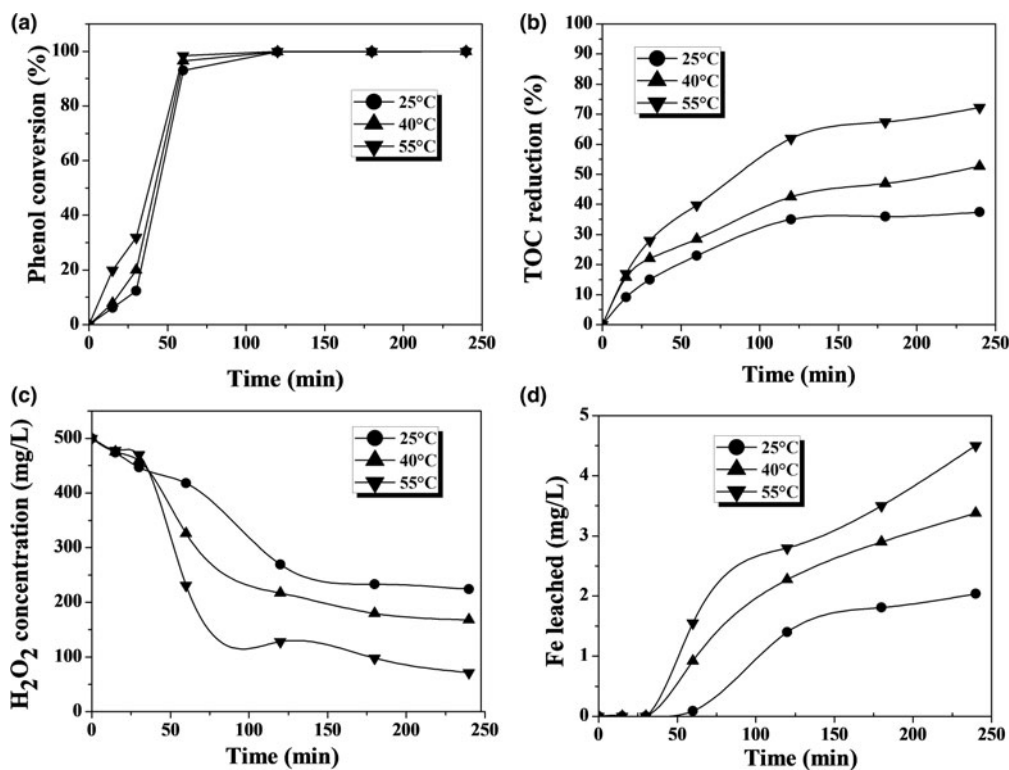| Sample	S_{BET} (m²/g)	Micropore area (m²/g)	V_p (cm³/g)	$V_{\mu p}$ (cm³/g)	Si (mass%)	Al (mass%)	Fe (mass%)
KT	14	2	0.05	0.0011	23.5	17.2	0.8
KTM	45	7	0.07	0.0034	25.1	8.43	0.7
Fe-KTM	106	16	0.17	0.0051	25.7	12.6	9.4

the linear region of the isotherms in the relative pressure range up to 0.35. The micropore volume ($V_{\mu p}$) was calculated by the t-plot method. The Fe content of the samples was determined by total-reflection X-ray fluorescence (TXRF) spectroscopy with a TXRF EXTRA-II spectrometer (Rich and Seifert, Germany).

CWPO tests

The CWPO tests were conducted in a thermostatically controlled batch glass reactor under stirring conditions. To evaluate the contribution of a non-catalytic mechanism to the reaction, preliminary experiments under the same operation conditions as the catalytic tests were performed. In the presence of catalyst (Fe-KTM) and the absence of H_2O_2, the disappearance of phenol or 4-CP after 4 h due to adsorption was marginal; in the presence of H_2O_2 and the absence of catalyst, no conversion of pollutants was observed.

After stabilization of the temperature, the corresponding amount of catalyst (0.2 g) was added to 0.2 L of aqueous phenol or 4-CP solutions (100 mg/L initial concentration). The initial pH value was 3.3 (adjusted with 1 M HCl), the optimum value for Fenton oxidation (Tatibouët *et al.*, 2005). Stirring was maintained for 15 min to ensure wetting of the solid. Then, the stoichiometric amount of H_2O_2 (500 and 344 mg/L for phenol and 4-CP, respectively) was added from a 33 mass% H_2O_2 aqueous solution. The experiments were carried out at 25, 40 and 55°C. The samples containing the reaction medium (25 mL) were collected at various reaction times from 15 min to 4 h, filtered using 0.45 μm pore size polytetrafluoroethylene (PTFE) filters and analysed.

The CWPO of phenol and 4-CP produces aromatic compounds as intermediate by-products and short-chain carboxylic acids as final products, which may undergo further oxidation to CO_2 and H_2O (Molina *et al.*, 2010b). The phenol and 4-CP concentrations in each sample collected from the reaction medium were analysed by high-performance liquid chromatography (HPLC; Varian Pro-Start 240) with a diode array detector at 280 nm wavelength (UV–Vis detector) and a C18 column (Microsorb-MV) as the

compounds, TOC and reaction by-products, as well as iron leaching, was monitored.

Materials

Catalyst preparation

The KT was supplied by the National Society of Sanitary Ceramics located in the region of El-Milia, Jijel Province, east Algeria. The KT was subjected to successive treatments, previously reported elsewhere (Boukhemkhem & Rida, 2017), to obtain the modified kaolin (KTM) used as the catalytic support in this work. Next, 2 g of KTM was added to 100 mL of FeCl₃·6H₂O aqueous solution (37 mM) under vigorous stirring for 24 h. Then, the solid was washed, dried and calcined at 500°C (Fig. 1). The resulting catalyst contained 9.4 mass% of iron.

Experimental

Catalyst characterization

The porous texture of the raw material and the resulting catalyst was characterized by N_2 adsorption–desorption at –196°C using a Micromeritics Tristar 3020 instrument. Before measurements were taken, the samples were outgassed overnight at 160°C and a residual pressure of 5×10^{-3} Torr. The specific surface area (S_{BET}) was calculated by applying the Brunauer–Emmett–Teller (BET) equation in

Fig. 3. CWPO of phenol with the Fe-KTM catalyst at various temperatures: (a) phenol conversion, (b) TOC reduction, (c) H_2O_2 concentration and (d) Fe leaching ([phenol]$_0$: 100 mg/L; [H_2O_2]$_0$: 500 mg/L; [Fe-KTM]: 1 g/L; pH$_0$: 3.3).
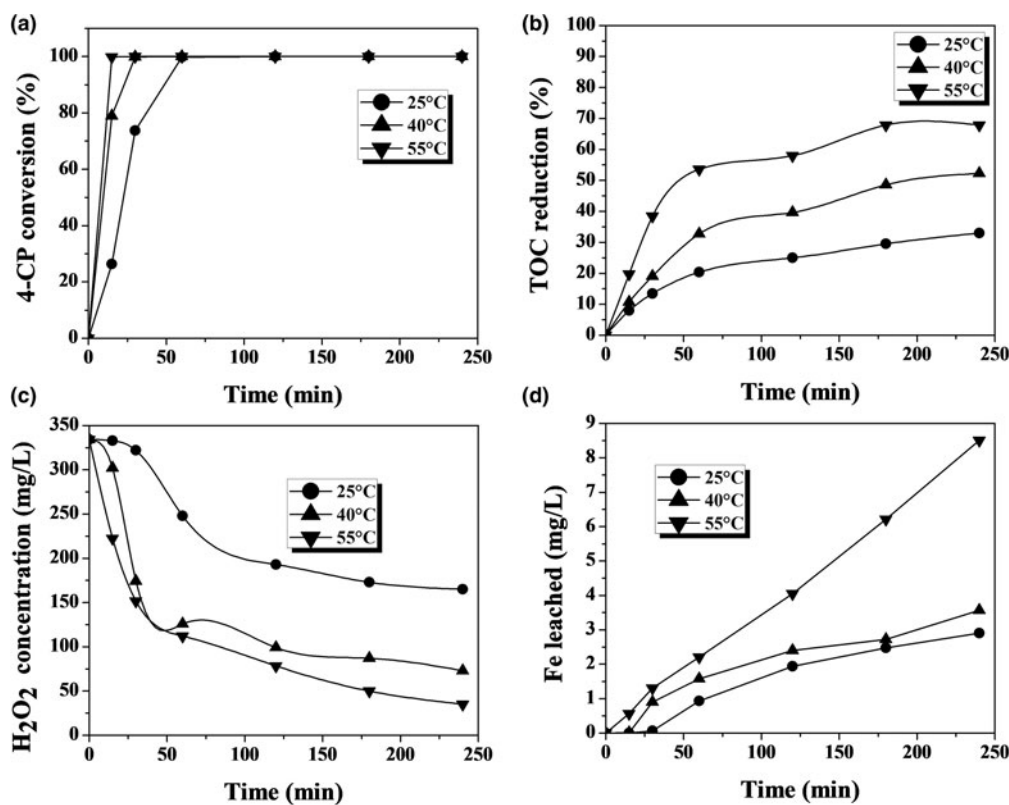
Fig. 4. CWPO of 4-CP with the Fe-KTM catalyst at various temperatures: (a) phenol conversion, (b) TOC reduction, (c) H_2O_2 concentration and (d) Fe leaching ([4-CP]$_0$: 100 mg/L; [H_2O_2]$_0$: 344 mg/L; [Fe-KTM]: 1 g/L; pH$_0$: 3.3).

Fig. 5. Time course of short-chain carboxylic acids upon CWPO at 25°C of (a) phenol and (b) 4-CP.
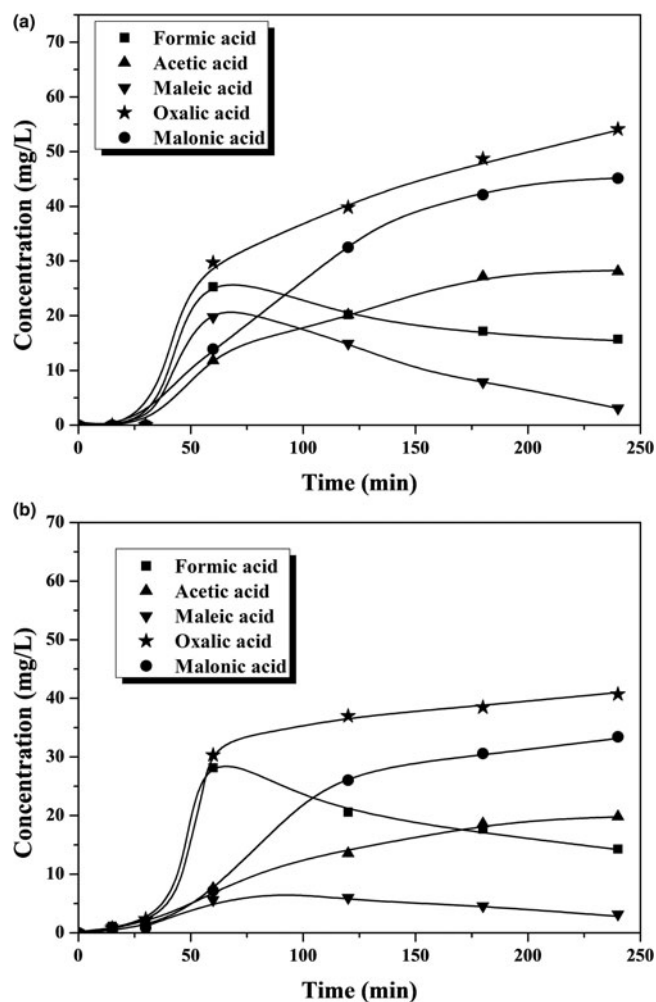

Fig. 6. Time course of short-chain carboxylic acids upon CWPO at 55°C of (a) phenol and (b) 4-CP.

stationary phase. Milli-Q water and acetonitrile (50/50 v/v) at a flow rate of 1 mL/min were used as the mobile phases. Intermediate by-products (hydroquinone, benzoquinone and catechol) in the final effluents were also analysed by HPLC, but with a different mobile phase; namely, 4 mM aqueous H_2SO_4 solution at a flow rate of 1 mL/min. Short-chain carboxylic acids were identified by anionic suppression ion chromatography (Metrohm 790 IC) using a conductivity detector. A Metrosep A Supp 5-250 column (25 cm length, 4 mm diameter) was employed as the stationary phase, while the mobile phase was a mixture of 3.2 mM Na_2CO_3 and 1 mM $NaHCO_3$ at a flow rate of 0.7 mL/min. The TOC was measured with a TOC analyser (Shimadzu, model 5000 A) equipped with an auto-sampler. The H_2O_2 and iron concentrations in the collected samples were quantified by colourimetry with a Cary 60 UV–Vis spectrophotometer (Agilent Technologies) using the titanium oxisulfate (Eisenberg, 1943) and ortho-fenantroline methods (Saywell & Cunningham, 1937), respectively.

Results and discussion

Catalyst characterization

The KT, KTM and Fe-KTM showed type IV isotherms with H3 hysteresis loops due to the capillary condensation of N_2 in mesopores

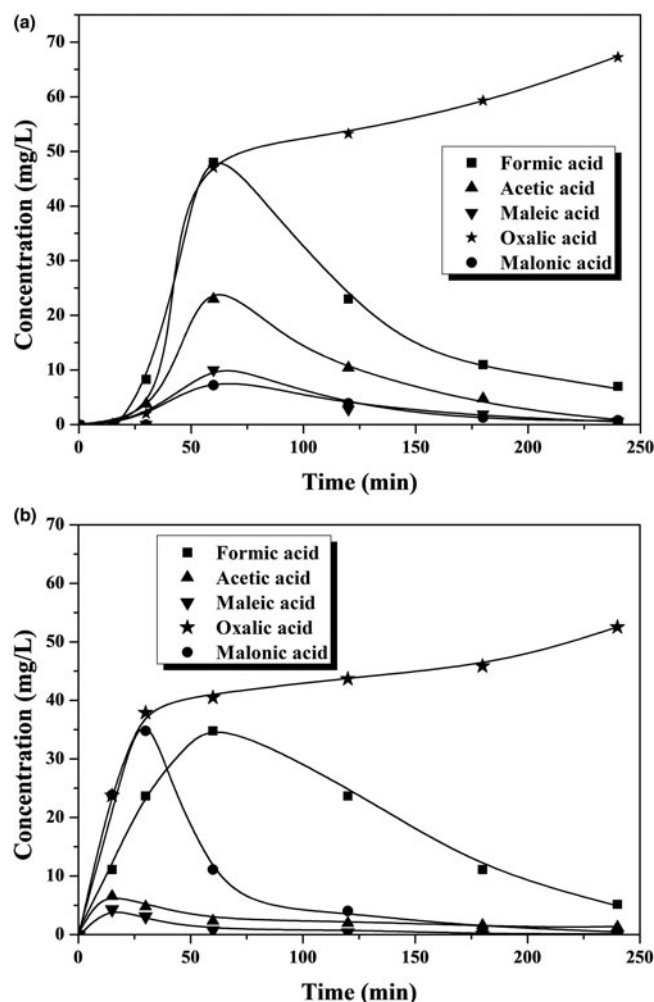(Fig. 2). This type of isotherm is typically obtained for aggregates of plate-like particles, giving rise to the slit-shaped pores typical of clay minerals (Horikawa *et al.*, 2011; Auta & Hameed, 2012).

The treatment of the starting kaolin led to an increase in pore volume and specific surface area (Table 1), mainly due to the dissolution of aluminium atoms located in the octahedral sites during the acid attack of KT after calcination (Volzone & Ortiga, 2006). Sample Fe-KTM presented the best textural properties, being characterized by a significant increase in the specific surface area (from 45 m^2/g for KTM to 106 m^2/g for Fe-KTM), with an increase in pore and micropore volumes. Development in mesopores was also observed; the hysteresis loop appears more pronounced in the case of Fe-KTM, although some contribution of microporosity may also be observed from the isotherm. The specific surface area of Fe-KTM is higher than the corresponding values reported in the literature for other iron catalysts supported on modified kaolin and also used in oxidation processes, ranging between 33 and 45 m^2/g (Ayodele *et al.*, 2012; Kosa *et al.*, 2012).

The chemical composition of these materials (Table 1) showed that the iron content of the sample increased substantially as expected from the $FeCl_3$ impregnation. In contrast, the Al/Si ratio decreased, confirming the above-mentioned dealumination during the acid attack.

Table 2. Summary of the CWPO of phenol and 4-CP with various catalysts.

Catalyst	pH_0	Temperature (°C)	Initial phenol or 4-CP concentration	H_2O_2 and catalyst initial concentrations	Efficiency (TOC, phenol and 4-CP conversions)	Metal leaching[a]	Reaction time	Reference
CWPO of phenol								
Magnetite, hematite, ilmenite	3.0	75	100 mg/L	$[H_2O_2]$ = 0.5 mg/L [Catalyst] = 2 g/L	X_{TOC} = 70% X_{ph} = 100%	0.30% 0.06% 0.03%	4 h	Munoz et al. (2017)
Ferromagnetic nanoparticles	7.0	35	94 mg/L	$[H_2O_2]$ = 40 g/L [Catalyst] = 5 g/L	X_{TOC} = 35% X_{ph} = 100%	0.10%	4 h	Zhang et al. (2009)
Al–Ce–Fe-pillared clay	3.7	25	50 mg/L	$[H_2O_2]$ = 0.2 g/L [Catalyst] = 5 g/L	X_{TOC} = 58% X_{ph} = 100%	0.60%	4 h	Sanabria et al. (2009)
Al–Fe-pillaredclays	3.7	70	50 mg/L	$[H_2O_2]$ = 6.8 mg/L [Catalyst] = 5 g/L	X_{TOC} = 50% X_{ph} = 100%	0.84%	4 h	Carriazo et al. (2005)
Fe-Cr pillared clay	3.7	30	50 mg/L	$[H_2O_2]$ = 6.8 mg/L [Catalyst] = 5 g/L	X_{TOC} = 45% X_{ph} = 100%	0.05% 9.20%	4 h	Tomul (2012)
Cu-ZSM-5	Not controlled	80	940 mg/L	$[H_2O_2]$ = 3.4 g/L [Catalyst] = 0.1 g/L	X_{TOC} not reported X_{ph} = 80%	Not reported	3 h	Valkaj et al. (2007)
Modified sludge	3.0	60	100 mg/L	$[H_2O_2]$ = 0.5 g/L [Catalyst] = 3 g/L	X_{TOC} = 65.6% X_{ph} = 98.2%	1.25%	2.5 h	Leal et al. (2018)
Perovskite LaFeO$_3$	3.1	30	940 mg/L	$[H_2O_2]$ = 23.8 g/L [Catalyst] = 5 g/L	X_{TOC} = 21% X_{ph} = 85%	1.73%	10 h	Oxana et al. (2016)
Modified kaolin	3.3	55	100 mg/L	$[H_2O_2]$ = 0.5 g/L [Catalyst] = 1 g/L	X_{TOC} = 72.3% X_{ph} = 100%	5.00%	4 h	This work
CWPO of 4-CP								
Fe$_3$O$_4$/γAl$_2$O$_3$	3.0	70	100 mg/L	$[H_2O_2]$ = 0.35 g/L [Catalyst] = 1 g/L	X_{TOC} = 84% X_{4-CP} = 100%	3.00%	4 h	Munoz et al. (2013)
Cu–Al hydrotalcite	6.8	30	250 mg/L	$[H_2O_2]$ = 1.36 g/L [Catalyst] = 1 g/L	X_{TOC} not reported X_{4-CP} = 40%	43.00%	1 h	Zhou et al. (2011)
Fe/mesoporous carbon	3.0	30	Not reported	$[H_2O_2]$ = 0.225 g/L [Catalyst] = 0.2 g/L	X_{TOC} = 47.4% X_{4-CP} = 96.1%	6.20%	4.5 h	Duan et al. (2014)
Co(II)-fly ash	3.0	50	640 mg/L	$[H_2O_2]$ = 0.35 g/L [Catalyst] = 8 g/L	X_{TOC} not reported X_{4-CP} = 59.6%	91.90%	5 h	Deka & Bhattacharyya (2015)
Al–Fe–Cu-pillared clay	Not reported	40	350 mg/L	$[H_2O_2]$ = 1.23 g/L [Catalyst] = 1 g/L	X_{TOC} = 68% X_{4-CP} = 100%	11.20%	2 h	Zhou et al. (2014)
Al–Fe-pillared clay	3.5	50	125 mg/L	$[H_2O_2]$ = 0.71 g/L [Catalyst] = 1 g/L	X_{TOC} = 60% X_{4-CP} = 100%	1.21%	4 h	Catrinescu et al. (2011)
Cu-montmorillonite	Not reported	40	128 mg/L	$[H_2O_2]$ = 0.34 g/L [Catalyst] = 0.5 g/L	X_{TOC} not reported X_{4-CP} = 52.3%	12.49%	8 h	Khanikar & Bhattacharyya (2013)
Modified kaolin	3.3	55	100 mg/L	$[H_2O_2]$ = 0.344 g/L [Catalyst] = 1 g/L	X_{TOC} = 68% X_{4-CP} = 100%	9.00%	4 h	This work

[a]Data refer to an initial catalyst concentration of 1 g/L.

Catalytic activity

The CWPO of phenol and 4-CP with the Fe-KTM catalyst at various temperatures suggests that the complete conversion of the starting compound was achieved at all temperatures (Figs 3, 4). Temperature barely affected the rate of disappearance of phenol, but it had a more significant effect on 4-CP. The latter is converted more rapidly due to the presence of the Cl atoms in its molecule, favouring the attack of the OH· radicals (present in the reaction medium from H_2O_2) on the aromatic ring of the 4-CP.

Temperature affected significantly the extent and rate of TOC reduction, with a dramatic improvement observed at 55°C compared to at ambient-like temperature (25°C). Again, a higher rate of TOC removal was observed in the case of 4-CP, although quite similar TOC removal percentages were finally achieved for both starting materials. This higher rate of TOC removal is consistent with the more rapid decomposition of H_2O_2 in the experiments with 4-CP. This may be due in part to the faster and greater iron leaching, which may lead to a somewhat greater contribution from the homogeneous reaction, which is promoted by dissolved iron. The effect is more pronounced at the highest temperature tested.

Iron leaching is a crucial issue regarding the stability of the catalyst, which is the main challenge so far in CWPO because the active catalysts developed have fairly poor durability in general. This work also showed evidence of iron leaching, which increases with temperature (Figs 3, 4). At the highest temperature tested, the iron loss was ~5% and ~9% of the initial load of the catalyst after 4 h of reaction with phenol and 4-CP, respectively. This is an important outcome, which, in previous works with various catalysts, has been attributed as a main cause of the presence of oxalic acid among the reaction products (Zazo *et al.*, 2006, 2011; Molina *et al.*, 2010, 2011; Munoz *et al.*, 2017). In our case, this acid was the main by-product remaining in the reaction medium at reasonably high concentration values (Figs 5, 6). A blank experiment carried out with only the Fe-KTM material in water did not demonstrate iron leaching.

The aromatic species commonly identified as intermediates from the Fenton process and CWPO of phenol and phenolic compounds (Zazo *et al.*, 2005, 2006) were not detected in the HPLC analyses of the final effluents in this study. Particular attention was paid to the highly toxic hydroquinone and *p*-benzoquinone, which were not detected even at the lowest temperature in the final samples after 4 h of reaction time (Figs 3, 4). In fact, even at that lowest temperature, the amount of carboxylic acids identified (Fig. 5) accounted for as much as 96% of the remaining TOC, thus indicating that the residual concentration of oligomeric condensation by-products should have been very low, if present at all. At 55°C, the amount of organic acids analysed after 4 h of experiments fitted almost completely with the residual TOC (Fig. 6). These findings are important given the very low ecotoxicity of those species (Zazo *et al.*, 2007). From the results of this work, the reaction scheme proposed for CWPO of phenol and 4-CP with catalysts based on kaolin agree with previous findings for CWPO of these compounds (Molina *et al.*, 2010; Catrinescu *et al.*, 2011), namely oxidation of phenol or 4-CP to intermediate by-products (hydroquinone, benzoquinone and catechol) and further oxidation to short-chain carboxylic acids, CO_2 and H_2O.

Finally, CWPO of phenol and 4-CP has been assessed using various catalysts and experimental conditions (Table 2). Complete phenol conversion is reached in most of these cases, while 4-CP shows conversion values of between 40% and 100%. In this work, complete conversion of both pollutants was achieved. The TOC was reduced by 20–80%, and in this work ~70% of TOC conversion was achieved with both reagents. The active-phase leaching (generally iron, but also copper or cobalt) is higher in the CWPO of 4-CP, and in previous experiments, a substantial amount of metal leaching has been reported. In this work, 5% and 9% of leached iron were quantified in the CWPO of phenol and 4-CP, respectively; these values are similar to those reported in the literature. Previous experiments on CWPO with Fe-Al_2O_3 catalysts demonstrated that iron leaching is produced mainly during the first hours of treatment (Bautista *et al.*, 2011; Munoz *et al.*, 2017). This iron leaching is associated with the weak interaction between some iron phases and the support. Therefore, modified kaolin displayed good catalytic activity compared with previous works, and its use as a support in CWPO seems to be promising due to its high availability and low cost.

Conclusions

The naturally occurring KT may be considered as a potential raw material for the preparation of inexpensive and environmentally friendly CWPO catalysts. Physical and chemical treatments, including calcination, followed by acidic and alkaline attack, allowed us to obtain a substrate with high S_{BET} (>100 m^2/g) corresponding mainly to mesopores. Further impregnation with $FeCl_3$ yielded an active material for CWPO. By using phenol and 4-CP (100 mg/L initial concentration) as target compounds, ~70% TOC reduction was achieved after 4 h of reaction time at 55°C with the stoichiometric amount of H_2O_2. At that temperature, iron leaching from the catalyst took place at moderate but significant rates (5% and 9% of the initial iron load after 4 h in the experiments with phenol and 4-CP, respectively). Further research is needed to obtain greater knowledge regarding the stability of the catalyst for improving this critical feature. In addition, experience should be gained with other hazardous target pollutants and representative industrial wastewaters so as to assess the potential application of this catalyst in CWPO.

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