

Removal of tannins and polyhydroxy phenols by electro-chemical techniques

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Abstract: The removal of tannins and their basic molecules such as catechol, pyrogallol, phloroglucinol and resorcinol was studied by electro-flotation and electro-oxidation techniques. Iron rods and triple oxide ($\text{TaO}_2/\text{RuO}_2/\text{IrO}_2$) coated titanium rods were used as electrodes for electro-flotation and electro-oxidation respectively. Interaction of tannins and polyhydroxy phenols with iron oxy-hydroxide formed by anodic dissolution of iron was studied by UV-Visible, FT-IR and zeta-potential measurements. GC-MS was used to identify the intermediate compounds formed during electro-oxidation. Catechol, pyrogallol, phloroglucinol and resorcinol were found to be mineralized in the presence of triple oxide ($\text{TaO}_2/\text{RuO}_2/\text{IrO}_2$) coated titanium electrodes. Catechol and pyrogallol were found to form insoluble organo-metal complexes while resorcinol and phloroglucinol were found to adsorb on iron oxy-hydroxide. The sludge thus formed was simultaneously separated from the aqueous phase by hydrogen bubbles. It was observed that the power consumption is relatively high for electro-oxidation compared with electro-flotation. The effects of pH and reaction time on their removal were also studied and the results are discussed.

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Keywords: electro-oxidation; electro-flotation; tannins; catechol; pyrogallol; phloroglucinol; resorcinol

INTRODUCTION

Tannins are extensively used in the leather industry to convert hides and skins into leather. Skins are tanned to achieve the desired flexibility in the dried condition and to protect them from microbial attack or hydrolysis when moist. Tannins are defined as polyphenols with molecular weights ranging from 500 to 20 000 which are capable of precipitating gelatin, certain proteins and alkaloids. Depending on the structure and action towards hydrolytic agents, tannins are usually classified into two broad categories, namely hydrolysable and condensed tannins. Hydrolysable tannins are characterized by a sharp distribution of molecular weight around 2000. Condensed tannins are characterized by a wide molecular weight distribution, a flavonoid structure with mainly phenolic reactive groups, and polymerization occurring under the action of acids to yield amorphous tannin red. Tannins are used as antioxidants and stabilizers and also as depressants in mineral-processing operations. Purification of tannery wastewaters containing tannins, sulfonates, ethoxylates, fatty acids, dyes, proteins and soluble carbohydrates has long been a problem owing to their toxicity. Extensive exposure of skin to hydroxy phenols may cause discoloration, local irritation, eczema or even death due to absorption. Hence it is important to remove these tannin compounds from wastewater.

In recent years, electro-chemical techniques have been applied both in the purification of drinking water and in the treatment of various industrial effluents that are not easily biodegradable. Electro-coagulation¹ was suggested for potable water production wherein the Mo content was decreased from 9.95 to 0.006 ppm and Fe from 130 to 0.015 ppm. Nearly 99% of suspended solids were removed from surface water by adopting a three-stage process comprising electro-coagulation, flotation and micro-filtration.² Electro-coagulation and flotation techniques were reported for the separation of oil from emulsions,³ the purification of urban and restaurant wastewater,⁴ and textile wastewater,⁵ the removal of latex particles,⁶ metal ions⁷ and sulfur species⁸ from aqueous suspensions and for the treatment of industrial liquid waste.⁹ Szpyrkowicz *et al* have suggested the use of Ti/Pt/Ir as anode for the removal of nitrogen from industrial wastewater.¹⁰ Mraz and Krysa¹¹ have attempted to improve the efficiency of the process and the life of the electrodes by incorporating surface modifications to the electrodes. Electro-chemical oxidation was extensively studied for the treatment of wastewaters containing phenolic compounds.^{12–15} The present study was aimed at understanding the mechanism of tannins removal from tannery effluents by electro-flotation and electro-oxidation. Accordingly, pure compounds of resorcinol, pyrogallol, catechol and

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phloroglucinol were selected since most of the tannins are polymers of these compounds. The chemistry of these compounds is similar to that of phenol, though the reactivity in terms of electrophilic and nucleophilic substitution reactions is different.

EXPERIMENTAL

Chemicals

Synthetic tannins manufactured by M/s Bayer chemicals AG and M/s BASF AG, Germany, were used in this study. The purity of resorcinol, pyrogallol, catechol and phloroglucinol obtained from M/s SD Fine Chem Ltd, Mumbai, India is above 98%. All the other chemicals used in the study are of analytical grade and were procured from Merck.

Electro-chemical cell

An electro-chemical cell (15 cm length, 15 cm width and 15 cm height) fabricated out of Perspex was used in the present study. The effective volume of the cell was about 3.0 L. Rods of iron and triple oxide ($\text{TaO}_2/\text{RuO}_2/\text{IrO}_2$) coated titanium with a length of 11 cm and diameter of 0.6 cm were used as electrodes. A set of electrodes consists of seven rods, each of anode and cathode assembly arranged parallel to each other in the same plane. The surface area of the set of anodes and the connecting lead was calculated to be 170 cm^2 . The entire electrode assembly was placed on the non-conducting wedges fixed to the bottom plate of the cell. In order to avoid short-circuiting, spacers were provided between anode and cathode rods. The gap between anode and cathode was maintained at 0.2 cm to minimize the ohmic loss. The schematic diagram of the complete system along with an isometric view of the electro-chemical cell and electrode assembly is shown in Fig 1.

Methods

For each experiment, a known quantity of tannin sample was weighed and dissolved in a known quantity of double distilled water. Sodium chloride (0.014 M) was added to achieve the desired conductivity. The synthetic effluent thus prepared was transferred into the electro-chemical cell. The anode and cathode leads were connected to the respective terminals of the rectifier. Electric power was supplied by a stabilized power source through a DC rectifier fitted with digital ammeter and voltmeter. After passing the required current for a desired duration, the floated material was scooped out and collected in a separate tray. Treated effluent sample was withdrawn from the outlet of the cell for characterization.

Chemical analysis

Standard methods prescribed by American Public Health Association¹⁶ were adopted for quantitative estimation of Chemical Oxygen Demand (COD), H_2O_2 and chlorine.

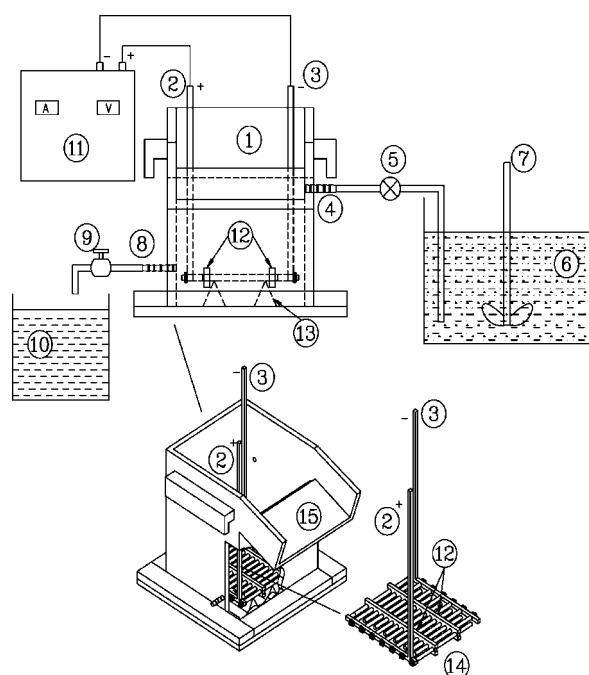


Figure 1. Schematic diagram of electro-chemical cell.

(1) Electro-chemical tank, (2) lead to anode, (3) lead to cathode, (4) inlet, (5) peristaltic pump, (6) conditioning tank, (7) stirrer, (8) outlet, (9) discharge valve, (10) discharge tank, (11) DC power supply, (12) spacers, (13) wedge, (14) electrode assembly, (15) froth lip.

Spectral analysis

The resultant aqueous solutions of electro-flotation were analysed using a Shimadzu UV-Visible recording spectrophotometer (model UV-160A, Japan). The solid precipitates formed during electroflotation were dried at 100°C for a period of 8 h and analysed using a Nicolet-740 GC FT-IR spectrometer. Ten mg of the sample was dispersed in 200 mg of spectroscopic grade KBr to record the spectra. Fifty scans were collected on each sample at a resolution of 4 cm^{-1} . The aqueous solutions resulting from electro-oxidation were analysed using GC-MS (HP 6890 attached with GC-MSD). The electro-oxidized aqueous sample was withdrawn from the electro-chemical cell and its pH was adjusted to 3.0 with HNO_3 . The sample was transferred into a separating funnel and 5.0 mL of diethyl ether was added to the aqueous phase. The organic and aqueous phase was thoroughly shaken for a period of 15 min and then allowed to separate into organic and aqueous phases. A $1.0 \mu\text{L}$ aliquot of ether phase was injected into a GC-MS system equipped with a DB-5 capillary column. The oven temperature was programmed to remain at the initial 60°C for 1.0 min and automatically increased to 300°C at a rate of 10°C per minute and finally 10 min at 300°C . The automatic injection system was kept at 250°C while the mass detector temperature was held at 280°C . The reaction products were identified with the help of the Wiley database.

Zeta-potential measurements

Zeta-potential measurements were conducted using Zeta meter3+. The iron oxy-hydroxide precipitate

formed during electro-flotation was siphoned out into a beaker and equilibrated with respective solutions of resorcinol, catechol, pyrogallol and phloroglucinol for a period of 30 min. The equilibrated suspension was injected into the micro-electrophoresis cell using disposable syringes. A minimum of three readings with a standard deviation of <2% was taken and the average value was reported. Prior to each measurement, the electrophoresis cell was thoroughly washed and rinsed with de-ionized water followed by rinsing with the sample solution to be measured.

RESULTS AND DISCUSSION

Removal of commercial tannins

Aqueous solutions of six different synthetic tannins generally used in tanning of skins and hides were taken and subjected to electro-flotation and electro-oxidation. Three different materials, viz aluminium, iron and triple oxide ($\text{TaO}_2/\text{RuO}_2/\text{IrO}_2$) coated titanium were used as anodes. A constant current of 7.5A (47 mA cm^{-2}) was applied over a period of 900 s and the resultant aqueous solutions were analysed for chemical oxygen demand (COD). The results thus obtained along with the initial COD of the respective solutions are shown in Table 1. From the results, it is evident that 75–99% of COD could be removed by using either aluminium or iron as anode. While the removal of COD was better when using iron and aluminium electrodes it was negligible in the presence of triple oxide ($\text{TaO}_2/\text{RuO}_2/\text{IrO}_2$) coated titanium electrodes. The poor removal of tannins by electro-oxidation may be attributed to the refractive nature of the molecules and insufficient oxidation time. The power consumption was calculated to be 1.9 Wh g^{-1} . It is evident that the commercial tannins could be effectively removed from tannery wastewater by electro-flotation using aluminium or iron as electrodes.

Table 1. Effect of anodic material on the removal of commercial tannins

Tannin	Manufacturer	Initial COD (ppm)	COD removal (%) after electrolytic treatment		
			Al	Fe	Ti
Syantn GF	Bayer Chemicals AG	704	94.3	95.7	2.6
Syantn GDC	Bayer Chemicals AG	1055	75.7	90.0	2.3
Syantn RT	Bayer Chemicals AG	1339	74.7	88.3	0.4
Syantn Relugan RR	BASF AG	596	99.5	81.7	2.7
Syantn Relugan RE	BASF AG	763	74.3	96.5	0.5
Syantn Relugan RF	BASF AG	803	86.3	89.8	0.4

Conditions: current density: 47 mA cm^2 , treatment duration: 900 s, tannin concentration: 2000 ppm, anode: Fe, cathode: Fe.

Removal of polyhydroxy phenols

Since tannins are polymers of hydroxy phenols, pure compounds of resorcinol, catechol, pyrogallol and phloroglucinol were used in further studies. Aqueous solutions of these compounds with known concentration were processed by using iron and triple oxide-coated titanium electrodes.

Effect of pH

A fixed quantity of resorcinol solution with an initial concentration of 100 ppm was taken into the electro-chemical cell comprising iron electrodes. The pH of the solution was adjusted to a desired value using either HCl or NaOH. A fixed current density of 47 mA cm^{-2} was applied for a period of 900 s. Depending on the initial pH of the solution, the pH was found to shift towards the basic range (9.5–11.5) during electro-flotation. This phenomenon, however, was not observed when the separate solutions of hydroxy phenols and ferrous sulfate solutions with similar pH values were mixed together. The shift in pH during electro-flotation may be due to disproportionate electro-chemical reactions on anode and cathode. The electrode surface will be affected either due to surface coating or due to passivation. In the present investigation, pH was maintained constant by the continuous addition of dilute HCl. After the experiment, a portion of the aqueous suspension was centrifuged and the COD of the supernatant solution was analysed. The experiment was repeated at various pH conditions. Similar tests were repeated on catechol, pyrogallol and phloroglucinol. The results obtained are presented in Fig 2. It is evident that the maximum removal of hydroxy phenols was observed in the pH range 8.0–9.0. It may be noted that the

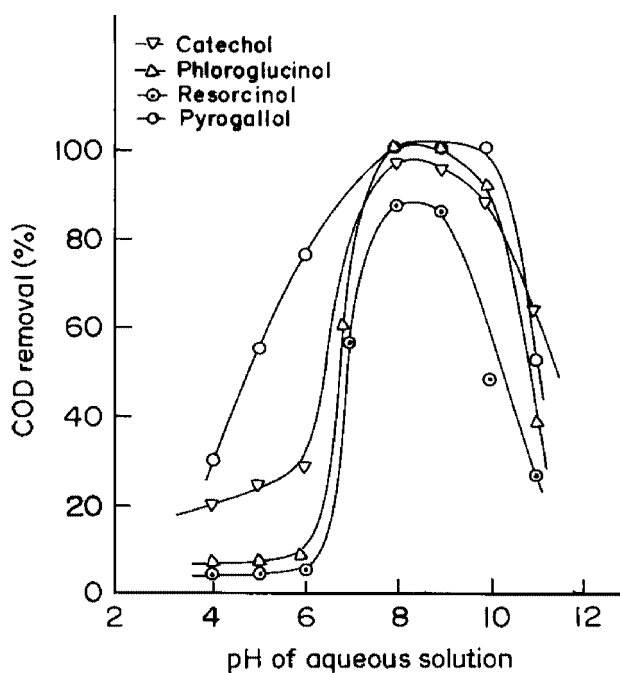
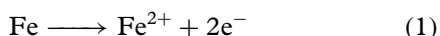
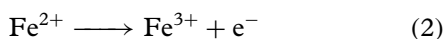


Figure 2. Effect of pH on the removal of catechol, pyrogallol, phloroglucinol and resorcinol by electro-flotation using iron electrodes.

respective metal ions are released while using soluble anodes such as Fe and Al whereas oxygen bubbles are generated by using stable anodes such as triple oxide-coated titanium. Anodic dissolution of iron could be represented as



Fe^{2+} ions thus released into aqueous solution may partly be converted to Fe^{3+} ions either by anodic oxidation or under an oxidizing environment.



The ions thus released into aqueous solution form oxy-hydroxy species in aqueous solution. The hydroxy species have a pronounced tendency to undergo polymerization due to interaction between hydroxyl groups of adjacent molecules. In the case of iron, it is well known that species such as FeOH^{2+} , $\text{Fe}(\text{OH})_2^{+}$, $\text{Fe}(\text{OH})_2$, $\text{Fe}(\text{OH})_3$, $\text{Fe}(\text{OH})_4^{-}$ and $\text{FeO}(\text{OH})$ are formed. Depending on the pH of the aqueous solution a particular species will be dominant compared with other species. $\text{Fe}(\text{OH})_2$, $\text{Fe}(\text{OH})_3$ species will be predominant between pH 8.0 and 9.0.¹⁷ In other words maximum removal of COD is taking place in the presence of $\text{Fe}(\text{OH})_2$, $\text{Fe}(\text{OH})_3$ precipitate. It could be attributed to the dissociation of the protons associated with the hydroxyl groups of the ligand in the presence of metal hydroxides. The density of the OH sites will be very high on the surface of the metal hydroxide precipitate compared with the bulk aqueous solution. Hence deprotonation of the ligand could be achieved easily on the surface of the metal hydroxide. A similar phenomenon was observed while adsorbing catechol on alumina.¹⁸ Maximum adsorption, observed around pH 9.0, was explained as being due to the formation of an inner sphere complex between the metal ion and hydroxy groups of the phenolic molecule. Other examples include adsorption of catechol on the surface of TiO_2 ¹⁹ and on copper.²⁰ In all the cases, maximum removal of hydroxy phenol was observed at a point of maximum metal hydroxylation. Maximum removal of hydroxy phenols also coincides around the $\text{p}K_a$ values of hydroxy phenols. The respective $\text{p}K_a$ values for pyrogallol, phloroglucinol, catechol and resorcinol are 8.94, 8.45, 9.40 and 9.3. Maximum adsorption of catechol on copper around pH 4.5–6.0, however, clearly illustrates the importance of metal hydroxy species in the adsorption process. If the $\text{p}K_a$ values influence the adsorption, maximum adsorption should take place at the pH where the proton attached to the reactive group of the ligand is dissociated. Thus the $\text{p}K_a$ values of the polyhydroxy phenols had little influence on the interaction process. In order to establish the mechanism of interaction between iron hydroxide and the hydroxy phenols, both the supernatant solution and the precipitate were analysed by UV-Visible and FT-IR spectroscopic techniques respectively.

Interaction of hydroxy phenols with iron oxy-hydroxides
Pure aqueous solutions of resorcinol, catechol, pyrogallol and phloroglucinol and their reaction products with Fe^{2+} , Fe^{3+} ions released from the anode were scanned from 200 to 800 nm using a UV-Visible spectrophotometer. With the UV-Visible spectra it is possible to distinguish the organic ligand and the metal–ligand complex. Depending on the unsaturated ring bonds and the hydroxyl groups attached to the ring, most phenols have their maximum absorption intensity around 275 nm. The UV-Visible spectra of catechol, pyrogallol and phloroglucinol and their reaction products with the Fe ion along with the spectra of pure ferrous sulfate and ferric chloride are shown in Fig 3. It is interesting to note that all the pure compounds have exhibited absorption maxima

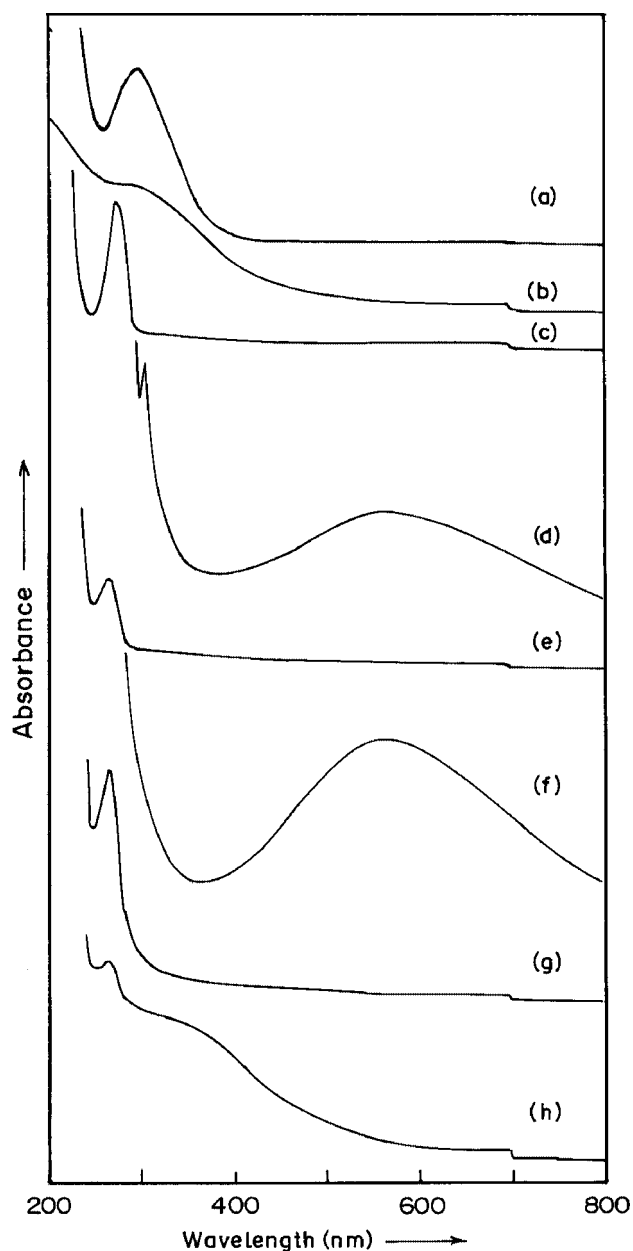


Figure 3. UV-Visible spectra of (a) ferric chloride, (b) ferrous sulfate, (c) catechol, (d) reaction product of catechol with Fe, (e) pyrogallol, (f) reaction product of pyrogallol with Fe, (g) phloroglucinol, (h) reaction product of phloroglucinol with Fe.

around 274 nm. This band in the region of 269–275 for these ligand molecules could be attributed to ligand $n-\pi^*$ and $\pi-\pi^*$ transitions. During the initial phase of the experiment aqueous solutions of catechol and pyrogallol were turned to a blue colour. This blue solution could be attributed to the metal–ligand complex. These solutions have exhibited a broad band around 570 nm, which could be assigned to charge transfer between ligand and metal ion. In the case of phloroglucinol, broad peaks at 250 nm and 347 nm appeared in addition to the original peak at 275 nm. It may be attributed to either complex formation or to the formation of polymers and their respective quinonic intermediates. No additional peak, however, was observed in the solutions of resorcinol in the presence of Fe ions released from the anode. The results clearly indicate that catechol and pyrogallol form metal complexes whereas no such complexes were observed in the case of resorcinol and phloroglucinol. Earlier researchers^{21,22} have demonstrated the complexation of pyrogallol and catechol with Cu^{2+} and Fe^{3+} ions. Hydroxy phenols bearing different environment on the benzene ring showed that the presence of two hydroxyl groups in the *ortho* position was essential for complexation. Thus catechol and pyrogallol, which have *ortho* hydroxy groups, only can form complexes.

FT-IR spectra of iron oxy-hydroxide formed by anodic dissolution of iron anode and the precipitates formed in the presence of resorcinol, catechol, pyrogallol and phloroglucinol during electro-flotation along with individual FT-IR spectra of pure resorcinol, catechol, pyrogallol and phloroglucinol are presented in Fig 4. Iron oxy-hydroxide exhibits a very strong and broad peak around 3420 cm^{-1} , and a low intensity peak at 1625 cm^{-1} . These peaks are due to stretching vibrations of OH and HOH bending modes of free water. The peak at 1625 cm^{-1} can be specifically ascribed to water adsorbed within the colloids. The sharp nodes associated with a broad peak at 3420 cm^{-1} could be due to stretching vibrations of OH groups with different environment. Low intensity bands at 1339 cm^{-1} and 1198 cm^{-1} are also attributed to OH bending. The weak transitions at 870 cm^{-1} and 775 cm^{-1} are probably due to FeO vibrational modes. A band with moderate intensity around 1029 cm^{-1} and a low intensity band at 717 cm^{-1} indicate the presence of $\gamma\text{-FeOOH}$ and Fe_2O_3 respectively. Identification of iron oxides by FT-IR spectra was studied by various authors.^{23–25} The FT-IR data suggest the formation of different iron oxides during electro-flotation. X-ray diffraction of iron oxides formed during electro-flotation also confirms the presence of different iron oxides.⁸ The FT-IR spectra of resorcinol, catechol, pyrogallol and phloroglucinol are also presented in Fig 4. It is apparent that all the compounds have exhibited a broad and intense band in the region of $3200\text{--}3400\text{ cm}^{-1}$. This band is attributed to stretching vibration of hydroxyl groups. It has split into three bands in the case of pyrogallol and phloroglucinol, which have three hydroxyl groups.

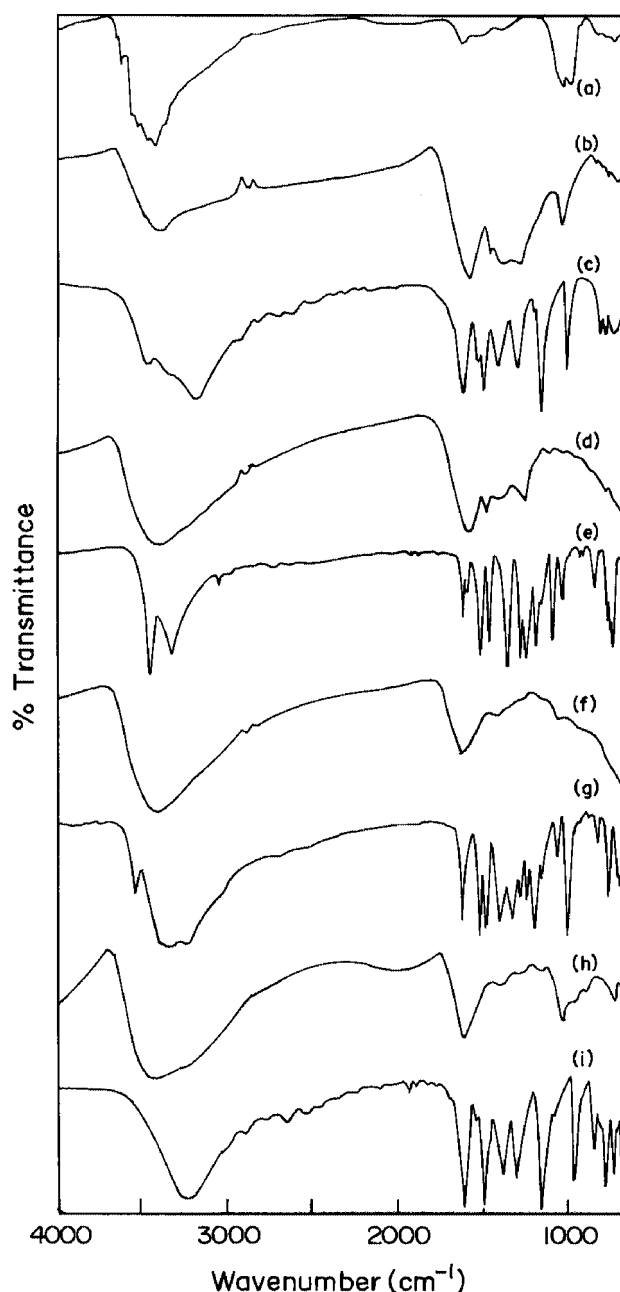


Figure 4. FT-IR spectra of (a) iron oxy-hydroxide precipitate, (b) reaction product of pyrogallol with Fe, (c) pyrogallol, (d) reaction product of catechol with Fe, (e) catechol, (f) reaction product of phloroglucinol with Fe, (g) phloroglucinol, (h) reaction product of resorcinol with Fe, (i) Resorcinol.

Catechol exhibits two characteristic bands at 3327 and 3452 cm^{-1} , consistent with previous work.^{26,27} Splitting of the band, is however, negligible in the case of resorcinol. The sharp and intense band observed around 1621 cm^{-1} in the spectrum of catechol, pyrogallol and phloroglucinol is attributed to stretching vibrations of C–C bonds and in-plane vibrations of the benzene ring. In the case of resorcinol the same was observed at 1610 cm^{-1} . The sharp band at 1521 cm^{-1} could be attributed to stretching vibrations of C–C and C–O. The sharp bands around 1485 , 1418 , 1365 , 1330 , 1190 , 1150 , 1000 , 840 , 770 and 730 cm^{-1} are explained as being due to

C–C, C–H, C–O and ring vibrations. The above data are consistent with the vibration spectrum of pyrogallol published earlier.²⁸ The FT-IR spectra of co-precipitated hydroxy phenols in the presence of iron oxy-hydroxide are also shown in Fig 4. It is interesting to note that bands in the region of 3450–3650 cm^{-1} ascribed to surface hydroxyls are absent. Also, there is no splitting of the broad band in the region of 3200–3500 cm^{-1} observed in the spectra of pure hydroxy phenols. Instead, a unique broad band exactly at $3420 \pm 5 \text{ cm}^{-1}$ was observed in all the spectra. This clearly indicates the interaction between OH groups of both iron oxy-hydroxide and hydroxy phenols. The low intensity broad band at 1625 cm^{-1} observed in the original spectrum of iron oxy-hydroxide was absent in the presence of pyrogallol and catechol and slightly shifted to 1617 cm^{-1} in the presence of phloroglucinol and resorcinol. This clearly suggests that the water adsorbed within the colloids of iron oxy-hydroxide was eliminated in the presence of pyrogallol and catechol. High intensity bands at 1029 and 980 cm^{-1} attributed to $\gamma\text{-FeO (OH)}$ were absent in the spectra of the reaction products. Instead, a new band at 1583 cm^{-1} was observed which could be attributed to Fe–catechol and Fe–pyrogallol complexes. The FT-IR studies on a titanium–catechol system have shown a similar band at 1585 cm^{-1} , which was interpreted formation of a Ti–catechol complex.²⁹ The intensity of the other bands attributed to stretching, bending vibrations of C–C, C–H, C–O, etc. are very weak in the spectra of reaction products of pyrogallol and catechol. From the above data it could be inferred that the hydroxy phenols are interacting with iron oxy-hydroxide during the electro-flotation process.

The interaction of resorcinol, phloroglucinol, pyrogallol and catechol with iron oxy-hydroxide was further established by zeta-potential measurements. The zeta-potentials of iron oxy-hydroxide formed during electro-flotation and also in the presence of resorcinol, phloroglucinol, pyrogallol and catechol were separately measured and the results are shown in Fig 5. The isoelectric point (iep) of iron oxide is observed at pH 8.5. From the results shown in Fig 5, a shift in iep towards acidic pH was observed in the presence of pyrogallol and catechol. It was also observed that as the concentration of hydroxy phenol increases, the iep was found to shift further towards acidic pH values. This shift in iep is generally attributed to chemical interaction. Such chemical interaction however, was not clear in the case of resorcinol and phloroglucinol. The positive charge of the particles was slightly decreased and the iep of the iron oxy-hydroxide remained the same. It could be attributed to the electrostatic interaction between the ligand and iron oxy-hydroxide. Thus, the interaction of hydroxy phenols with iron oxy-hydroxide was clearly established by zeta-potential measurements.

Generally, molecules having oxygen atoms can share the lone pair of electrons with most of the d-block elements, facilitating coordinate covalent bonds. The

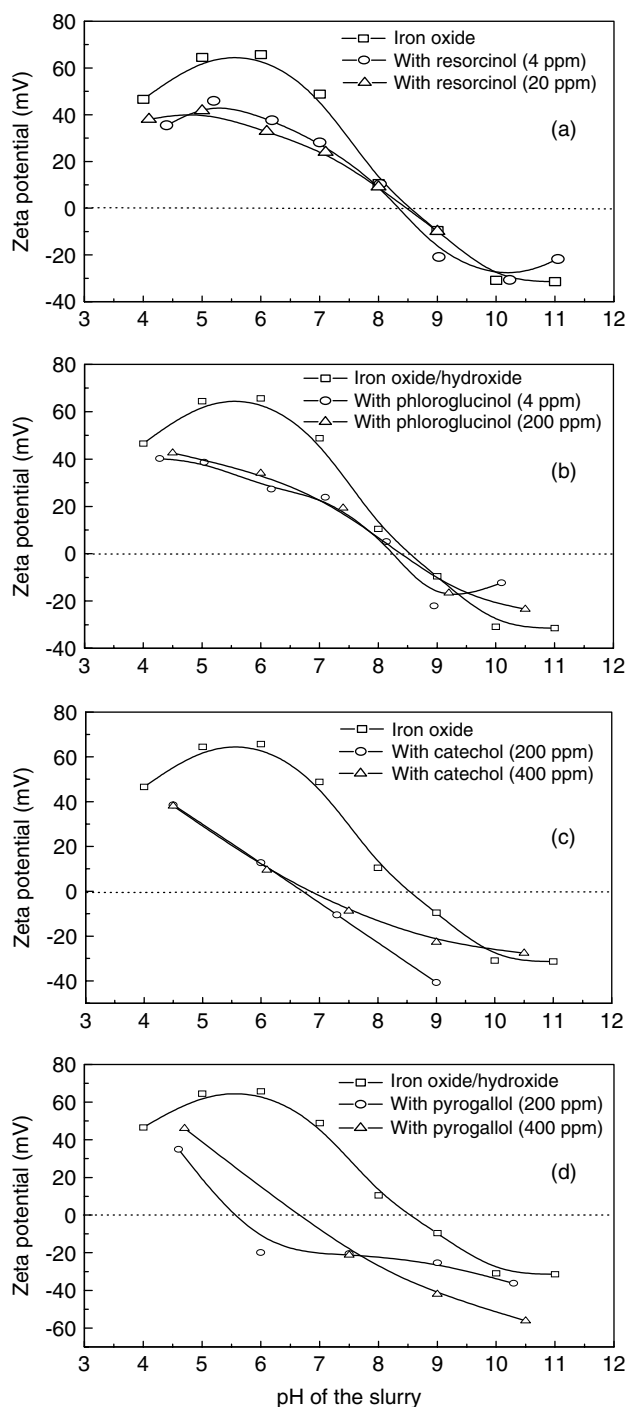


Figure 5. Zeta-potential measurements of iron oxy-hydroxide in the presence of different concentrations of (a) resorcinol, (b) phloroglucinol, (c) catechol and (d) pyrogallol with reference to pH.

position of oxygen atoms in the organic molecule, however, is paramount to achieve such chemical bonding. Hydroxyl groups in pyrogallol and catechol are situated in adjacent carbon atoms (*para* position) of the benze ring, whereas in the case of resorcinol and phloroglucinol they are situated on alternate carbon atoms (*meta* position) of the ring. The chemical interaction is favourable only with the molecules having adjacent oxygen atoms. The driving force of the reaction is the conformational stability of a five-membered ring formed between Fe^{3+} and the

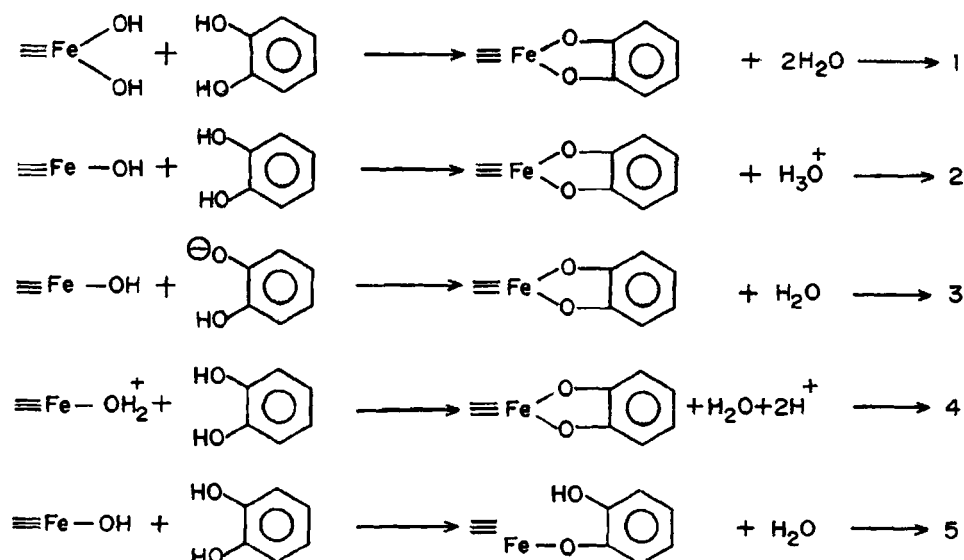


Figure 6. Possible reaction schemes of interaction of hydroxy phenols with iron oxy-hydroxide.

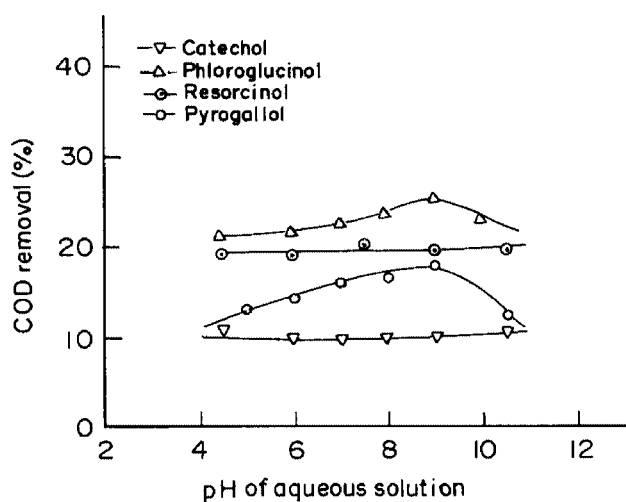


Figure 7. Influence of pH on the removal of catechol, phloroglucinol, resorcinol and pyrogallol by electro-oxidation.

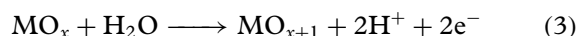
hydroxy phenol. The possible reaction schemes of complex formation are given in Fig 6. The possibility of reaction schemes 2 and 4 were found to be remote, as the pH of the suspension remained intact. Further, if reaction scheme 5 is possible, resorcinol and phloroglucinol also should react with hydroxylated iron. Zeta-potential measurements and UV-Visible spectra, however suggest no such chemical interaction.

Electro-oxidation

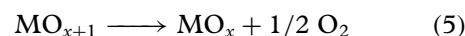
The electro-chemical oxidation of hydroxy phenols using titanium electrodes coated with oxides of Ta, Ru and Ir was studied. The effect of pH on the oxidation of resorcinol, phloroglucinol, pyrogallol and catechol was studied and the results are shown in Fig 7. The results clearly indicate that the influence of pH on the degradation of these compounds is marginal. Maximum removal of COD was observed at the slightly alkaline pH of 8.5–9.0. Earlier studies³⁰ by Beltran *et al*, have reported that near neutral

conditions are the best for the effective degradation of organics. The observed decrease beyond pH 9.0 can possibly be attributed to the oxidation of hydroxyl ions and low solubility of ozone. It was reported that the dissolved ozone concentration was about 0.43 millimoles at pH 4.0 and 0.15 millimoles at pH 10.0.³¹

The degradation of organics by electro-oxidation will take place both on electrodes and in solution. Anodic oxidation of organics on metal oxide electrodes involves three different reactions.³² The first reaction, an electro-chemical one, leads to the formation of the active species (MO_{x+1}) by physically-adsorbed hydroxy radicals or chemisorbed active oxygen. The physisorbed hydroxy radical causes the complete combustion of organic compounds and the chemisorbed active oxygen participates in the formation of selective oxidation products. In general the hydroxy radical is more effective for pollutant oxidation.



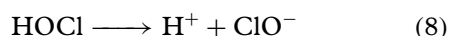
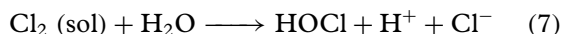
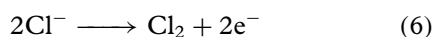
where MO_x is metal oxide. The MO_{x+1} species is considered to be the active species responsible for both organics oxidation and oxygen evolution. Thus there is a competition between the reaction of organics oxidation and side reaction of oxygen evolution:



(R is an organic molecule)

These two reactions are important in the oxidation of organics and oxygen evolution with regeneration of the metal oxide MO_x that is oxidized to the higher oxide MO_{x+1} . Polyhydroxy phenols might have been oxidized indirectly by nascent chlorine, oxygen and H_2O_2 generated as secondary reaction products. After electro-oxidation, the aqueous solution was analysed for hydrogen peroxide and chloride. Formation of

H_2O_2 at the rate of 10–15 ppm and disappearance of chloride was detected during electro-oxidation:



Electro-oxidation experiments were conducted at a constant current density of 47 mA cm^2 . These anodic reactions occurred simultaneously with the following primary cathodic reaction:



Nascent chlorine in turn forms HOCl in an acidic environment and ClO^- in basic conditions. Though these radicals are short-lived, they can oxidize even refractive organic molecules. Various intermediate species formed during electro-oxidation of pyrogallol, phloroglucinol, resorcinol and catechol were analysed by GC–MS and the results were incorporated in

Table 2. Intermediate reaction products of catechol, pyrogallol, phloroglucinol and resorcinol formed during electro-oxidation (samples analysed after 30 min of electro-oxidation)

Catechol

- (1) Dichloroethanoic acid
- (2) Dichloromethane
- (3) 1,2,4-Cyclopentanetrione
- (4) 2-Hydroxy-1-methylcyclopenten-3-one
- (5) 1,2-Benzene dicarboxylic acid, bis (2-ethylhexyl) ester
- (6) 1,2-Benzene dicarboxylic acid diethyl ester
- (7) Hexanedioic acid, mono (2-ethylhexyl) ester

Pyrogallol

- (1) 1,2-Benzene dicarboxylic acid, bis (2-ethylhexyl) ester
- (2) 2-Hydroxy-3-methyl-2-cyclopenten-1-one
- (3) Dihydro-5-isopropyl furanone
- (4) 2,4-Dimethyl-3-hexanone

Phloroglucinol

- (1) 1,1,3,3-Tetrachloroacetone
- (2) Dichloroacetic acid
- (3) Dichloromethane
- (4) Propanedioic acid, hexyl-diethylester
- (5) 2-Ethylbutanol
- (6) Di (2-ethylhexyl) adipate
- (7) 2-Hydroxy-1-methylcyclopenten-3-one
- (8) 1,2-Benzene dicarboxylic acid, bis (2-ethylhexyl) ester
- (9) 1,2-Benzene dicarboxylic acid, bis (2-methoxyethyl) ester

Resorcinol

- (1) 1,2-Benzene dicarboxylic acid dibutyl ester
- (2) 1,2-Benzene dicarboxylic acid, bis (2-methylpropyl) ester
- (3) 4-(1,1,3,3-Tetramethyl) butyl phenol
- (4) 3,4-Dichloro-2-naphthol
- (5) 1,2-Benzene dicarboxylic acid diethyl ester
- (6) 4,6-Dichloro resorcinol
- (7) 2,5-Dichloro-*p*-benzohydroquinone
- (8) 4-Chloro-1,3-benzenediol
- (9) 1,1,1,2-Tetrachloroethane
- (10) 1,2-Benzene dicarboxylic acid, bis (4-methylpentyl) ester
- (11) 1,2-Benzene dicarboxylic acid, bis (1-methylethyl) ester

Table 2. From the results, it is apparent that the oxidation of resorcinol and phloroglucinol results in more chlorinated products whereas intermediates which resulted from the oxidation of catechol and pyrogallol are free from chlorinated products. Polymeric esters such as 1,2-benzene dicarboxylic acid, bis (2-ethylhexyl) ester, 1,2-benzene dicarboxylic acid diethyl ester, hexanedioic acid, mono (2-ethylhexyl) ester, 1,2-benzene dicarboxylic acid, bis (2-methoxyethyl) ester, 1,2-benzene dicarboxylic acid, bis (4-methylpentyl) ester, and 1,2-benzene dicarboxylic acid, bis (2-methylpropyl) ester, were observed as oxidation products. After 2 h of electro-oxidation of catechol, however, simple molecules such as dichloroethanoic acid and dichloromethane were observed. Such polymeric derivatives were observed while subjecting phenolic wastewater to electro-chemical oxidation.³³ Anodic oxidation of phenol in the presence of NaCl has led to organochlorinated compounds, which were further oxidized to volatile CHCl_3 . Although chlorophenols are formed in the initial stages they were eventually converted to polymeric compounds free from chlorine.

Effect of reaction time

Removal of hydroxy phenols by electro-flotation and by electro-oxidation techniques was studied with reference to time. Samples were collected at different time intervals and the COD was estimated. The results are plotted in Figs 8 and 9. It is apparent that the catechol, pyrogallol and phloroglucinol could be effectively removed within a short period of 5 min whereas it took 10 min in the case of resorcinol by electro-flotation. The slow rate of removal of catechol and pyrogallol in the initial stage could be attributed to poor coagulation. The Fe ions released from the anode are initially consumed for complexation with organic molecules. The insoluble complex thus generated is colloidal in nature and hence not amenable to flotation. Generally the size of the particles and the

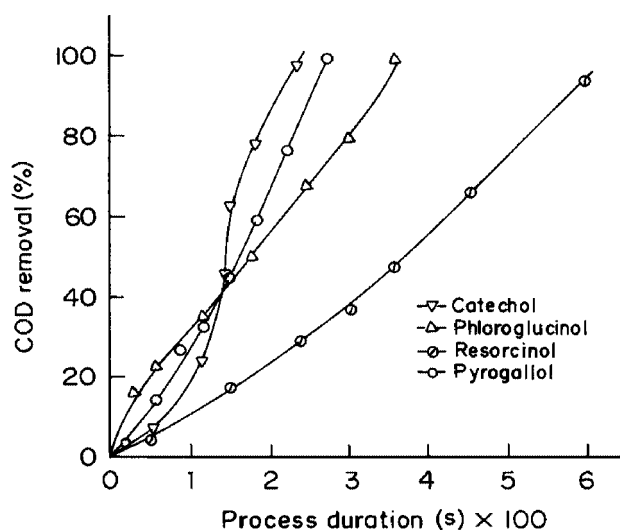


Figure 8. Effect of electro-flotation time on the removal of catechol, phloroglucinol, resorcinol and pyrogallol.

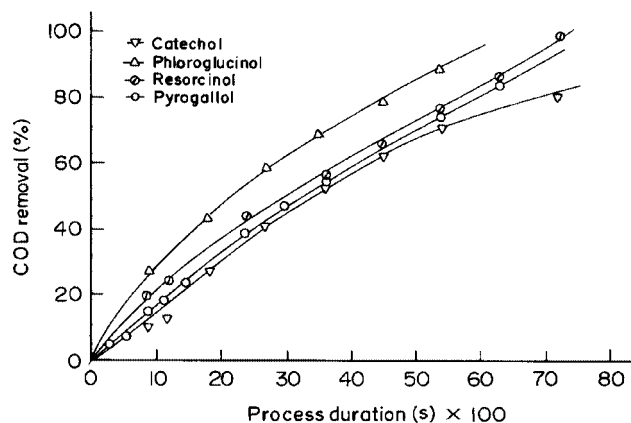


Figure 9. Effect of electro-oxidation time on the removal of catechol, phloroglucinol, resorcinol and pyrogallol.

bubbles should be in the same order for effective flotation.³⁴ The size of the hydrogen bubbles resulting from water electrolysis was reported to be in the range of 15–80 μm , depending on the pH and current density.³⁵ As the electro-flotation time is extended, the excess Fe ions released from the anode aids the coagulation of colloidal particles.³⁶ The coagulated particles are simultaneously removed from the aqueous part by hydrogen bubbles. The high rate of removal at the later stage could be attributed to the onset of the coagulation process. This phenomenon is particularly evident in the removal of catechol and pyrogallol, which form metal complexes. The power consumption was estimated to be 18.5 Wh g^{-1} for the removal of catechol, pyrogallol and phloroglucinol. The removal rate of hydroxy phenols by electro-oxidation was observed to be very slow. It requires more than 2.5-h to achieve above 80% removal. Energy consumption for the electro-oxidation process was estimated to be 555 Wh g^{-1} , which is nearly 30 times more compared with the electro-flotation process. The advantage of electro-oxidation is that the pollutants are converted to CO_2 and H_2O and sludge generation could be totally avoided. It is also apparent that the degradation of resorcinol and phloroglucinol is better compared with catechol and pyrogallol by electro-oxidation.

CONCLUSIONS

Electro-flotation and electro-oxidation techniques were found to be effective for the removal of tannins and hydroxy phenols from aqueous solutions. Maximum removal was observed in the pH range 8.0–9.0, coinciding with the hydroxylation of iron oxy-hydroxides and acid dissociation constant of hydroxy phenols. Catechol and pyrogallol were observed to form a metal complex with iron oxy-hydroxides by a condensation mechanism. The chemical interaction of these compounds was substantiated by UV-Visible, FT-IR and zeta-potential measurements. The removal rate of catechol and pyrogallol by electro-flotation was better than that of phloroglucinol and resorcinol. The latter compounds however are easily

mineralized by electro-oxidation. The energy consumption was observed to be very low (18.5 Wh g^{-1}) for electro-flotation compared with electro-oxidation (555 Wh g^{-1}). Polymeric esters such as 1,2-benzene dicarboxylic acid, bis (2-ethylhexyl) ester, 1,2-benzene dicarboxylic acid diethyl ester, hexanedioic acid, mono (2-ethylhexyl) ester, 1,2-benzene dicarboxylic acid, bis (2-methoxyethyl) ester, 1,2-benzene dicarboxylic acid, bis (4-methylpentyl) ester, and 1,2-benzene dicarboxylic acid, bis (2-methylpropyl) ester, were observed as intermediate products during electrooxidation. Although hydroxy phenols are ultimately mineralized by electro-oxidation, chlorinated intermediates were observed in the case of phloroglucinol and resorcinol.

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