catalysts

MDPI

Supplementary Material

Text S1

The energy cost in the electrochemical oxidation system can be calculated according to Eq. (S1):

$$E_{\mathrm{EO}} = \frac{SjUt}{Vlog(C_0 / C)} \quad \text{(S1)}$$

where E_{EO} is the electric energy consumed to degrade the concentration of NB by one order of magnitude in 1 L solution (Wh L^{-1}); S, j, U and V are the anode surface area (cm^2), applied current density (mA cm^{-2}), average voltage (V), and the volume of the reaction solution (mL); C_0 and C are the initial and finial concentrations of NB (mg L^{-1}); t is the time (min) needed to degrade NB from the initial concentration to the final concentration.

Text S2

Hydroxyl radicals (•OH) produced by the electrodes are determined with Salicylic Acid (SA) as a radical scavenger. The hydroxylated products of 2,3-dihidroxybenzoic Acid (2,3-DHBA) and 2,5-dihydroxibenzoic Acid (2,5-DHBA) were analyzed by HPLC (Dionex U3000, USA), equipped with an WpH C18 column (4.6 nm × 250 mm, 5 μm) The UV detector at λ=320 nm. The mobile phase was a mixture of Milli-Q water with 1% phosphoric acid (A) and acetonitrile (B) (70:30, V: V) at a flow rate of 1.0 mL min^{-1}. The injection volume was 20 μL and the total analysis time was 18 min. During the electrochemical oxidation process, only the hydroxylated product 2,5-DHBA was detected. Thus the concentration of •OH is equal to the concentration of 2,5-DHBA according to the reaction stoichiometry. The apparent rate constant of •OH production on the anode could be expressed as $k_{[\bullet OH]}$ (mM/(min·m^2)), which was calculated as follows:

$$k_{[\bullet \mathrm{OH}]} = \frac{dC(\bullet \mathrm{OH})}{Sdt} \quad \text{(S2)}$$

where $k_{[\bullet OH]}$ is the apparent rate constants of •OH production (mM/(min·m^2)), i.e. the concentration of •OH yield per min per unit anode area. S is the anode surface area (m^2). C(•OH) is the concentration of •OH trapped by SA (mM), and t is the reaction time.

Text S3

Titanium sheets (purity 99.9%, 50 mm × 50 mm × 1 mm) were sanded with 200, 400 and 600 grit sandpapers to remove surface oxide layer, then immersed in 10% NaOH solution for 60 min and etched with 5% oxalic acid solution at 95° C for 120 min to gain a gray surface with uniform roughness. The middle layer (SnO_2-Sb) was prepared by the sol-gel technique with a coating solution containing ethylene glycol, citric acid, $SnCl_4 \cdot 4H_2O$ and $SbCl_3$ with a molar ratio of 140: 30: 9:1. The sol-gel solution was covered on the Ti sheets by the dip-coating method. Then, the Ti sheets were dried at 145° C for 10 min and sintered at 500° C for 10 min in a muffle furnace. This procedure was repeated 20 cycles, and the last cycle was annealed for 2 h at 500° C to obtain Ti/SnO_2-Sb. The Ce-PbO_2 layer was acquired by electrodeposition with Ti/SnO_2-Sb as the anode and two Ti plates as the cathodes. The electrodeposition was conducted under 20 mA cm^{-2} for 60 min, and the electrolyte consisted of 0.1 M HNO_3, 200 g L^{-1} $Pb(NO_3)_2$, 0.4 g L^{-1} $Ce(NO_3)_3$, and 0.5 g L^{-1} NaF.

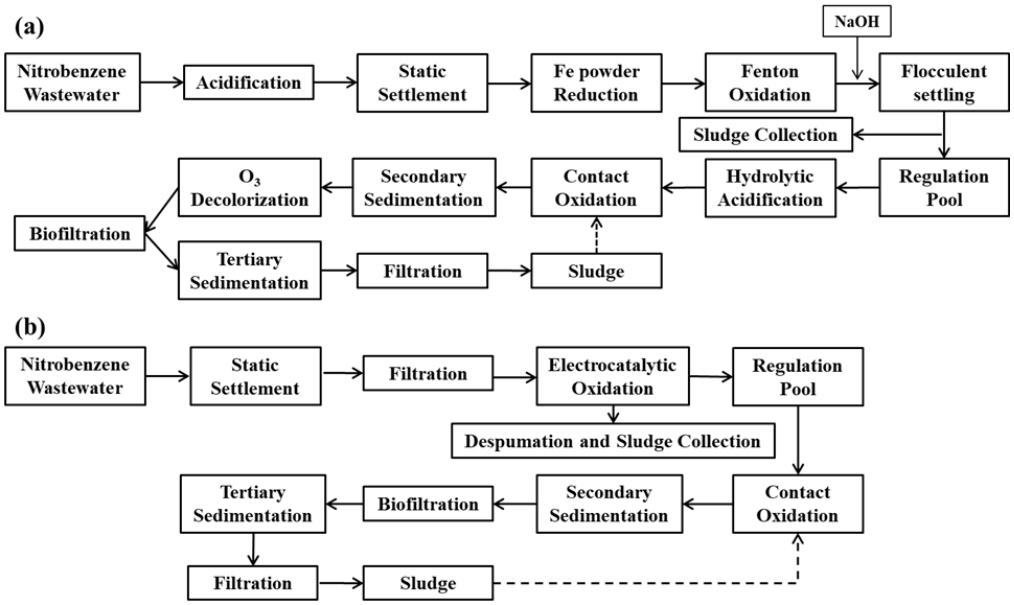


Figure S1. The flowcharts of the wastewater treatment processes before (**a**) and after (**b**) reform in the chemical plant.

Table S1. Intermediates of NB identified by GC-MS/MS in electrospray ionization positive mode.

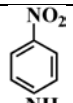
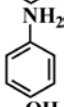
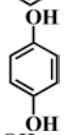
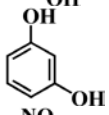
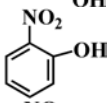
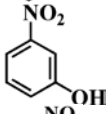
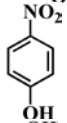
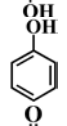
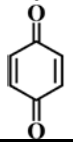
Compound	Molecular weight	Molecular structure	Retention time (min)
Nitrobenzene	123.11		8.13
Aniline	93.13		9.14
Hydroquinone	110.11		8.42
Resorcinol	110.11		8.84
o-Nitrophenol	139.11		9.26
m-Nitrophenol	139.11		14.17
p-Nitrophenol	139.11		14.63
Phenol	94.11		7.54
Benzoquinone	108.10		7.35

Table S2. The operating costs of electrochemical oxidation unit and the replaced Fenton-flocculant precipitant process.

Item	Operating costs（Yuan/ton）	
	Fenton-flocculant precipitant	**Electrochemical oxidation**
Energy cost	7	19.95
Agent fee	239	5
Sludge disposal	1600	300
Equipment maintenance	50	30
Total	1896	355