

Combined Procedure for Nitrophenols Removal

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The aim of this work was to reduce the concentration of 4-nitrophenol (4-NP) and 2, 6-dinitrophenol (2,6-DNP) from synthetic solutions under the maximum limit (0.5 mg L⁻¹), admitted by international regulations. In this study the experimental methods for 4-NP and 2,6-DNP removals were: adsorption on NORIT granular activated carbon (A), electrochemical reduction on graphite cathode (R) and concurrent adsorption on activated carbon and electrochemical reduction (A+R). All the batch experiments were performed under magnetically stirring at room temperature. The remaining concentration after 120 min. of combined treatment (A+R) was close to accepted level (0.33 ÷ 0.6 mg L⁻¹). During (A+R) procedure, the total efficiencies for removal of 4-NP arrives at 96 %, comparing to the single A (87.02%) and R (65.45%) procedures. The increase in total removal yield of 2,6-DNP in (A+R) treatment is more important (98.2%).

Keywords: nitro phenols, active carbon, electrochemical reduction, adsorption

Nitrophenol (NP) derivatives are widely used in the synthesis of many chemicals, in the field of pesticides, insecticides, herbicides, such as dinosam ((*RS*)-2-(1-methylbutyl)-4,6-dinitrophenol) C₁₁H₁₄N₂O₅ and dinoseb ((*RS*)-2-sec-butyl-4,6-dinitrophenol) C₁₀H₁₂N₂O₅ and dyes. NP are present in the industrial effluents of chemical plants that manufacture explosives, dyestuffs, wood preservation agents, and products for leather treatment, as well as in agricultural irrigation effluents [1].

Nitrophenols are toxic and biorefractory compounds, and are classified as priority pollutants, dangerous for the environment, both in USA, in UESEPA list [2] and in E.U. countries [3].

Alternative treatment technologies available to remove nitrophenols from wastewater are: physical (adsorption), chemical, biological, electrochemical [4-6] and combined procedures.

In many cases, especially when the organic compound concentration is low, mass transfer would become the controlling step for electrochemical treatment. In order to improve mass transfer and enlarge specific electrode area, the fluidized bed cell is an alternative option [7].

The use of direct and mediated electrochemical oxidation for the treatment of aqueous wastes has undergone rapid development in recent years. This method can be successfully applied to the treatment of waste water containing no biodegradable organics such as phenol, chlorophenol or nitro phenol [6]. In most cases, total mineralization of the organic compounds can be achieved [8].

Recently, some new advanced Fenton oxidation process and photo Fenton have attracted much interest in the field of phenolic derivatives elimination [9]. Another new and efficient oxidative method is electro-Fenton oxidation [10].

During NP electrochemical reduction the nitro aromatic group is affected. Nitro aromatic compounds undergo reductive transformation to aromatic biodegradable amines [11]. Reduction of nitro aromatics occurred through a series of electron-transfer reactions and protonations, with nitroso compounds and hydroxylamine as highly reactive intermediates. In the case of poly nitro aromatic compounds, the location of the first nitro group reduced is influenced by regioselectivity [12].

There are many papers which refers to adsorption as physical method for NF removal [13]. Activated carbon is one widely used adsorbent in wastewater treatment [14, 15]. Many researches have been conducted to develop new adsorbent materials, such as bentonite [16], organo bentonites [17], other zeolites [18] paper mill sludge [19] and polymeric adsorbents [20]. However, activated carbon is probably still the most effective adsorbent for organic contaminants due to its high surface area, low specificity and fast adsorption kinetics [21].

If activated carbon is introduced into the electro chemical reactor, and operating in a fluidized mode, the reactor becomes a fluidized electro-chemical reactor where electro-chemical transformation (reduction or oxidation) and adsorption are both integrated in one combined procedure. Batch test are useful screening tools because they can be achieved quickly and inexpensively [22]. Care should be taken in extrapolating the results to dynamic flow conditions [23].

There are only a few reports in literature on biorefractory nitrophenol derivatives treatment by combined electro-chemical and adsorption method. Only data on 4-nitrophenol combined treatment, adsorption associated with electrochemical oxidation, have been reported [24-26].

This work present a combined procedure, electro-chemical reduction and adsorption on active carbon (A+R), aimed to reduce 4-NP and 2,6-DNP concentration from synthetic solution, and to find if there are some improvements by using the combined procedure instead of simple procedures (electrochemical reduction (R) or adsorption on active carbon (A)).

Experimental part

Reagents and solution preparation

4-Nitrophenol with purity higher than 99% (Merck, Germany), 2,6-dinitrophenol with purity higher than 95% (calculated based on dry substance), moistened with 20% H₂O (Aldrich, Switzerland), NaH₂PO₄·H₂O (monobasic) with purity higher than 99% (Fluka, Switzerland), Na₂HPO₄·2H₂O (dibasic) with purity higher than 99% (Fluka, Switzerland), NaOH with purity higher than 98% (Lachema, Czech Republic), and H₂SO₄ with purity higher than 98%, were

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Table 1
MAIN CHARACTERISTICS OF NORIT GAC 1240W

Property	Pore surface area (m ² g ⁻¹)	Micropores volume (cm ³ g ⁻¹)	Mezopores volume (cm ³ g ⁻¹)	Particle density (g cm ⁻³)	Particle porosity
Value	1062	0.38	0.45	0.485	0.77

*based on the manufacturer's catalog

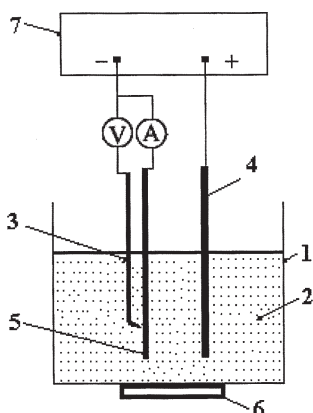


Fig. 1. Schematic diagram of the experimental set-up: (1) electrochemical batch reactor; (2) nitro phenol solution in sodium phosphate buffer and granular activated carbon in suspension; (3) reference electrode (SCE); (4) anode; (5) cathode; (6) magnetic stirrer; (7) potentiostat

used to prepare the solutions with desirable concentration for the experiments in this study. Distilled and double distilled MillyQ water was used to prepare the aqueous solutions. All chemicals were analytical grade, and were used without further purification.

Granular activated carbon type NORIT GAC 1240W, was used as adsorbent, see table 1 for characteristics. Prior to use, activated carbon was washed several times with deionized water, dried for 24 h to constant weight at 105°C, and kept in a desiccators for cooling at room temperature, to prevent the readsorption of moisture before use.

Experimental set-up

Figure 1 shows the schematic diagram of the electrochemical reactor used in this work. It consist on a glass reactor (1 L volume), a titan anode with oxide coating (grid; active surface: 47 mm x 65 mm) and a graphite cathode (active surface 47 mm x 65 mm). A known mass of activated carbon was introduced into the reactor before startup, and a magnetic stirrer was used to maintain the activated carbon in suspension (350 rpm). In each experiment was treated a volume of 0.5 L synthetic wastewater containing 10⁻⁴ moles L⁻¹ 4-NP or 2,6-DNP in sodium phosphate buffer solution, adjusted at pH 4, with H₃PO₄. Constant current density (20 mA cm⁻²) was maintained during the experiments with only minor

adjustments of the applied voltage (cell voltage was around 5 V). At appropriate time, 3 mL of sample was taken for analysis. The stirring was stopped for 5 s during the sampling, and after measurements the sample was reintroduced into the batch reactor. All the experiments were performed at constant temperature (20 ± 2 °C).

This reactor was also used for individual electrochemical reduction (R) or adsorption on activated carbon (A). In the individual electrochemical reduction experiments, no activated carbon was added into the reactor, while other experimental parameters were all the same as those in combined process (electrochemical reduction plus adsorption A+R). In the individual adsorption experiments, no current was applied in the system while other conditions were all the same as in the combined process.

Methods

Spectrophotometric determinations were made using a Unicam Helyos B spectrophotometer with the specific software VISION 32, and a quartz vat of 2 mL, with optical route of 1 cm.

TOC determinations were made using a TOC-DR2800 HACH-LANGE spectrophotometer, using Lange TOC cuvette test type LCK 385 (3 - 30 mg L⁻¹) and LCK 386 (30 - 300 mg L⁻¹).

Voltammetric measurements were made using a potentiostat-galvanostat system – AUTOLAB PG-STAT12, Eco Chemie, Netherlands, with the specific software GPES 4.9 equipped with a classic three electrodes electrochemical cell. The experimental design consist of a platinum plate as auxiliary electrode, an Ag/AgCl, KCl electrode as reference, and the glassy carbon with 0.125 cm² active surface as working electrode. The measurements were carried out without stirring, using 5.0 mL of solution. Oxygen in the system was removed by bubbling nitrogen through the solution for 15 min before each measurement. The optimized parameters in cyclic voltammetry were set up as follow: scan rate 0.1 V s⁻¹; the potential range between 0 and -1 V; the sensitivity is automatically established from a large range.

Results and discussions

UV-Visible and TOC control

In order to evaluate the advantages of adding activated carbon into electro-chemical reactor, the removal of nitrophenol derivatives by adsorption, electro-chemical

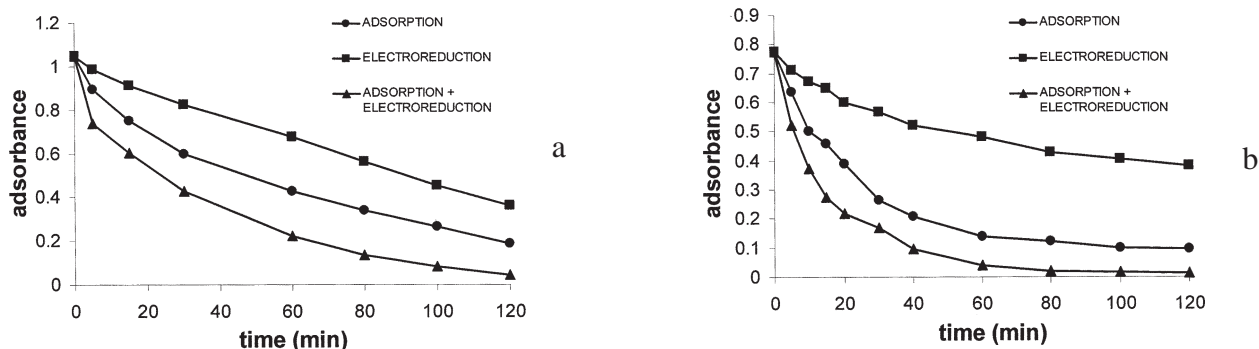


Fig. 2. Comparison of absorbance variation in time, for the: (a) 4-NP ($\lambda = 433\text{nm}$) and (b) 2,6-DNP ($\lambda = 417\text{nm}$) removal by (A), (R) and their combined process (A+R). 4-NP and 2,6-DNP initial concentration: 10⁻⁴ mol L⁻¹ in sodium phosphate buffer pH 4

reduction and their combined process were compared in the same reactor respectively.

As shown in figure 2, the decreasing of absorbance is more rapid in the combined process than of the individual processes, both for 4-NP and 2,6-NP.

The absorbance both for 4-NP and 2,6-DNP solution varies directly with the concentration, and this dependence is described by the following equations (1) in the case of 4-NP, and (2) in the case of 2,6-DNP:

$$A = 0.075 \times C; R^2 = 0.9911 \quad (1)$$

$$A = 0.042 \times C; R^2 = 0.9996 \quad (2)$$

where A is the absorbance of the solutions, and C is the concentration of the solution.

The results obtained by spectrophotometric determinations were confirmed by total organic carbon (TOC) determination. Figure 3 presents the variation of TOC values in time, in the case of 2,6-DNP removal processes by simple adsorption on active carbon, electrochemical reduction on graphite cathode, and by their combined procedure.

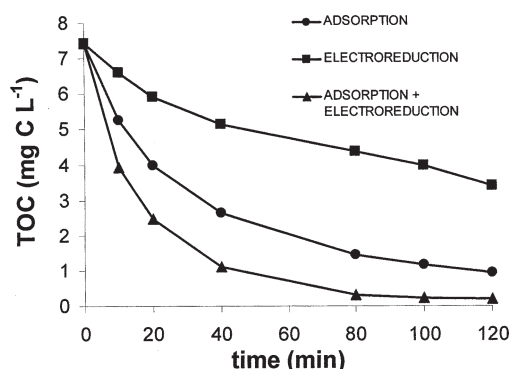


Fig. 3. Comparison of total organic carbon variation in time, for 2,6-DNP removal by: (A), (R) and their combined process (A+R)

The 2,6-DNP concentration was calculated from equation (2), and the carbon concentration (mg L^{-1}) was calculated taking in consideration the number of carbon atoms from molecular formula. As shown in figure 4, the variation of the carbon concentration determined by total organic carbon analysis is quite similar to those determined by calculation.

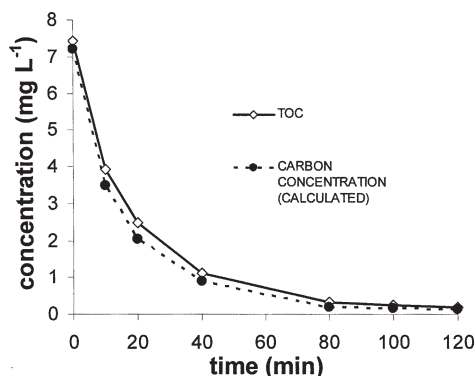


Fig. 4. Variation of carbon concentration in time, determined using TOC Lange kits (solid line) and calculated from UV-Visible measurements (dash line)

Comparing the experimental data in figure 5 we can see that in combined procedure (A+R) the 2,6-DNP concentration in remaining solution, decreased to 0.90 mg L^{-1} in 60 min and the necessary time for 4-NP to arrive at the same concentration is about 120 min. This behavior could be explain by the difference between the molar

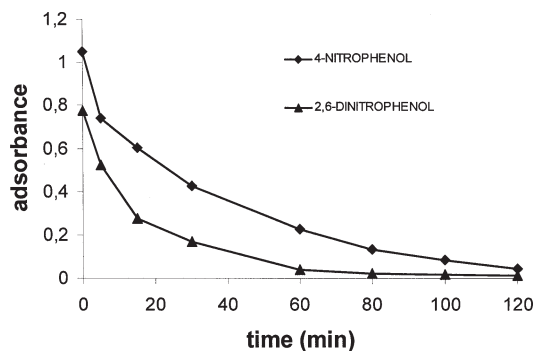


Fig. 5. Comparison of absorbance variation in time, for the 4-NP and 2,6-DNP removal by the combined process (A+R)

extinction coefficients and probably, the (A+R) treatment is more efficient for 2,6-DNP.

After 120 min of treatment, the NF concentration arrive under the maximum limit admitted by international regulations: 0.6 mg L^{-1} for 4-NP, and 0.33 mg L^{-1} for 2,6-DNP.

Voltammetric control of NF removal

In agreement with literature [1] and our results presented in previous item [27], in aqueous media, nitrophenol cyclic voltammograms, present two peaks in the reduction potentials domain, the first reversible ($E \approx 0.2 \text{ V}$) and the second irreversible (E from -0.6 to -0.8 V).

Cyclic voltammograms of 4-NP and 2,6-DNP present only one cathodic peak in the investigated potential range, figure 6. This behaviour is typical of totally irreversible systems [28, 29].

Cyclic voltammetry was applied for NF (A+R) procedure, measuring the current peak at -0.65 V vs. Ag/AgCl, KCl in the case of 4-NF, and -0.70 V vs. Ag/AgCl, KCl in the case of 2,6-DNP respectively.

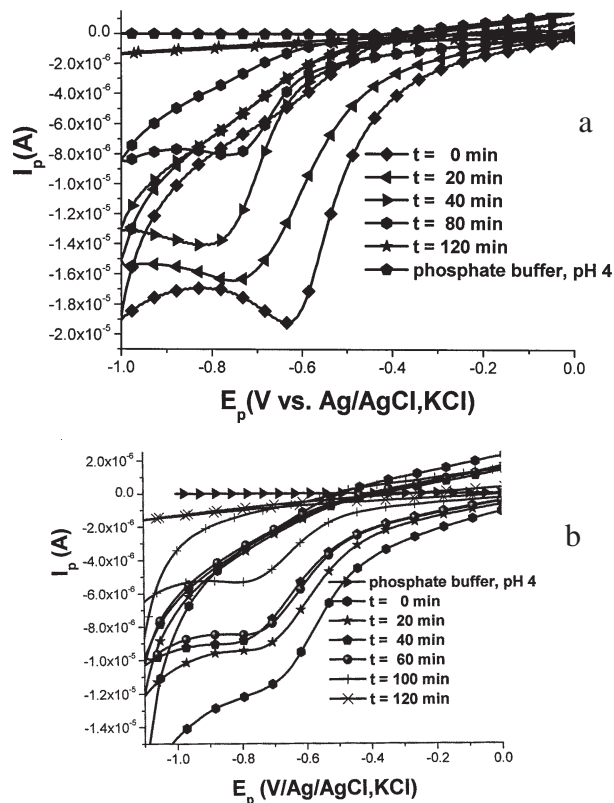


Fig. 6. Cyclic voltammetry response of: (a) 4-NP and (b) 2,6-DNP removal by combined process (A+R). The nitrophenols initial concentration: $10^{-4} \text{ moles L}^{-1}$ in sodium phosphate buffer at pH 4; scan rate: 0.1 Vs^{-1}

Table 2
SYNOPTIC RESULTS FOR TREATED NITROPHENOLS

Experimental procedure	4-nitrophenol		2,6-dinitrophenol	
	η_t (%)	η_F (%)	η_t (%)	η_F (%)
A	87.02	-	87.72	-
R	65.45	29.45	50.64	20.40
A+R	96.00	-	98.2	-

where η_t represent the total efficiency and η_F represent faradic efficiency of processes after 120 min of treatment

During the combined process (A+R), a significant decreasing in the value of the cathodic current peak was observed, both for 4-NP and 2,6-DNP, as can be seen in the figure 6.

Conclusions

Starting from the same nitro phenols initial concentration (10^{-4} mol L⁻¹), different chemical and faradic efficiencies were obtained. Combining these two reliable technologies (adsorption on activated carbon and electrochemical reduction) to treat NP, seems to promote the treatment efficiency, table 2.

Almost total removal of 4-NP (96%) and 2,6-DNP (98%) has been obtained after 120 min. of combined treatment (A+R). The final NP derivatives concentration was close to accepted level ($0.33 \div 0.6$ mg L⁻¹).

The advantages expected from the combined procedure were to enhance the nitro phenols removal efficiency and the possibility to achieve the active carbon in-situ regeneration with the aim to minimize the activated carbon consumption.

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Manuscript received: 3.02.2009