Research Article

Electro-combustion of Pyridazine using a Boron-Doped Diamond Anode

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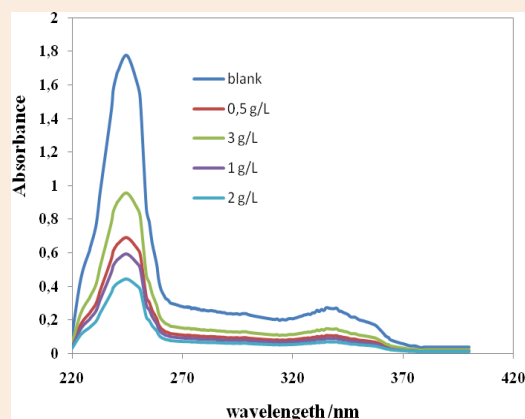[2]Chemistry Department of, College of Science, King Khalid University, Abha, Saudi Arabia
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Abstract

Disposal of industrial wastewater containing pyridazine compound by electrochemical methods has been studied in this paper. It was found that only a small fraction of the organics was oxidised by direct electrolyses, while complete mineralisation of the organics was obtained with the indirect process, electrogenerating hypochlorite from chloride oxidation. The effects of operating factors, such as concentration of pyridazine, current density and chloride concentration, were also investigated. The experimental data suggested that the Boron-Doped Diamond Anode (BDD) had the highest electrocatalytic activity and increasing the chloride concentration in the electrolyte resulted in an increasing of COD and electro- oxidation removal.

Keywords: pyridazine, electro oxidation, BDD, electrochemical

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Introduction

In recent years there has been increasing interest in environmental damage and human injury by industrial pollution, and the relevant legislation is always being made harsher. In this framework electrochemical methods offer a good opportunity to prevent and remedy pollution problems due to the discharge of industrial and sewage effluents. Various innovative technologies have been proposed for the removal of pesticides from water. There are many treatment processes that have been used or investigated extensively to treat agriculture wastewaters such as biological treatment [1], photo catalytic oxidation [2], ozonation [3], Fenton's reaction [4] and electrochemical methods [5-13].

In this framework electrochemical methods offer a good opportunity to prevent and remedy pollution problems due to the discharge of industrial and sewage effluents. In recent years, electrochemical methods are drawing attention and starting to substitute traditional processes due to the advantages such as high efficiency, ease of operation and environmental compatibility [15-17]. The electric current induces redox reactions resulting in the transformation/destruction of the organic compounds and their virtually complete oxidation to CO_2 and H_2O. For electrochemical treatment of dyeing wastewater, direct and indirect oxidation processes are being employed. In a direct oxidation process, pollutants are first absorbed on the anode surface and then destroyed by the electron transferring reaction. In an indirect oxidation process, strong oxidants, such as hydrogen peroxide, metal peroxide, hypochlorite, chlorine, ozone and Fenton reagents, are electrochemically generated [16] and then destroy the pollutants by the oxidation reactions. All of the oxidants are generated in situ and are utilized immediately [17]. Direct oxidation method employed for the complete degradation of organics can obtained with high efficiency using high oxygen over-potential anodes such as PbO_2, SnO_2, diamond and boron-doped diamond (BDD) electrodes [18,19].

In recent studies Errami and co-workers studied the electrooxidation of various groups pesticides bupirimate [10,12-14]; methidathion [14] in brine solution using BDD and SnO_2 anodes. The authors studied the electrooxidation of various organic compound by Bonfatti and co-workers, organic substrates [20]. The nitrogenous heterocyclic compounds, such as Pyridazine (fig.1) are frequently found in surface and groundwater sources in the Europe and other parts of the world. Pyridazine presence in the environment is due to their widespread use as solvents and pesticide, paint stripping, in the dry cleaning industry and in various household products.
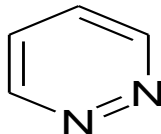

Figure 1 Chemical structure of pyridazine.

Experimental

Materials and Reagents

Electrochemical measurements were performed using a computer controlled by Potentiostat/Galvanostat model PGZ 100 associated to "Volta-Master 4" software. A conventional three electrodes cell (100 cm^3) thermo regulated glass cell was used (Tacussel Standard CEC/TH). The anode was a square plate of BDD electrode with effective surface area of 1 cm^2, whereas the cathode was a platinum electrode, and the gap between electrodes was 1cm. A saturated calomel electrode (SCE) was used as a reference. Galvanostatic electrolysis was carried out with a volume of 75 cm^3 aqueous solution of initial COD_0 (60 mg/L). The range of applied current density was 5 to 30 mA/cm^2 and samples were taken, at predetermined intervals during the experiment, and submitted for analysis. All tests have been performed at different temperature in magnetically stirred and aerated solutions. In all cases sodium chloride was added to the electrolytic cell, at different concentrations. The chemical oxygen demand (COD) is measured according to the standard methods for examination of water and wastewater [11]. The Chemical Oxygen Demand (COD) values were determined by open reflux, a dichromate titration method. The UV–Vis spectra of pyridazine were recorded in 200–400 nm range using a UV–Vis spectrophotometer (UV-1700 Pharmaspec, Shimadzou) with a spectrometric quartz cell (1 cm path length). The Chemical Oxygen Demand (COD) values were determined by open reflux, a dichromate titration method. All chemicals used in the experiments were of analytical pure grade and used without further purification. All measurements were repeated in triplicate and all results were observed to be repeatable within a 5% margin of experimental error.

Results and Discussion

Effect of supporting electrolytes

The investigation of the mediator concentration effect has been performed in the range 0,5 –3 g /L for concentration of NaCl. As shown in Fig. 2, the electro-oxidation of the organic substrate is achieved at reasonable rates only in the presence of the mediator and is higher at higher NaCl concentrations, up to values around 2 g /L. Further increase above this limit causes inversion of the trend. Possibly, when the chloride concentration becomes sufficiently high, a decrease of the anode potential takes place, due to the potentiostatic buffering by the ClO^- evolution reaction.

Kinetic studies were carried out to determine the COD reduction efficiency for electrooxidation pyridazine at different concentration supporting electrolyte NaCl. For this purpose, the removal rate of COD was assumed to obey a first-order kinetic as follows [10, 12, 14]. The values of rate constant for different supporting electrolyte concentration are summarized in **Table 1**.
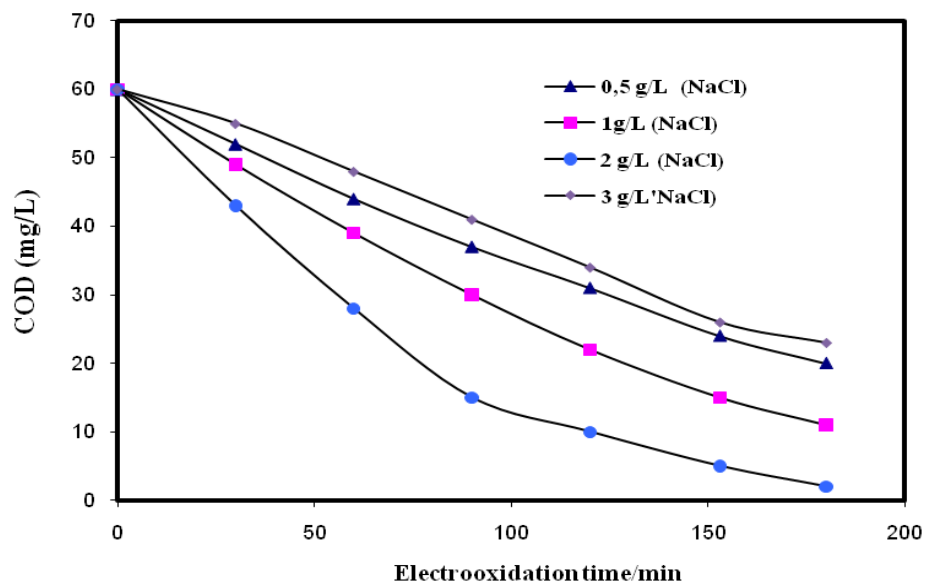
Figure 2 Influence of supporting electrolytes on the decay of COD during electro-oxidation of 60 mg/L pyridazine on BDD anode. Conditions: Current density 25 mA.cm^{-2}; T: 25°C.

Table 2 Effect of the NaCl concentration on the values of the rate constant and the %COD

Concentration of NaCl (g/L)	Rate constant, K (min^{-1})	COD removal (%)
0 ,5	5 ,8.10^{-3}	66
1	8,8.10^{-3}	81
2	1,68.10^{-2}	96
3	5,6.10^{-3}	61

In order to have an idea about the nature of the formed species during the electrolyses, UV-vis spectra of the solution samples were taken. **Figure 3** exemplifies the behaviour observed for all the electrolyses performed. The first spectrum at *blank* corresponds to the original solution and it is in agreement with the same kind of spectra presented by without electrolysed. For the samples corresponding to the different electrolysis of different concentration NaCl two bands can be observed: the first at 245 nm usually associated with the π-π^* electronic transition of C=C and N=N. groups and the second at 340 nm associated to the n-π^* electronic transition for group C=N.

It is observed that the absorption of the bands decreases with time and almost disappears 2 g/L of NaCl concentration resulting in the complete degradation of the solution. The absorbance at 245 nm decreases rather slowly. The slower decrease of this absorbance can be related to the formation of intermediates resulting from the electrooxidation of the pyridazine.
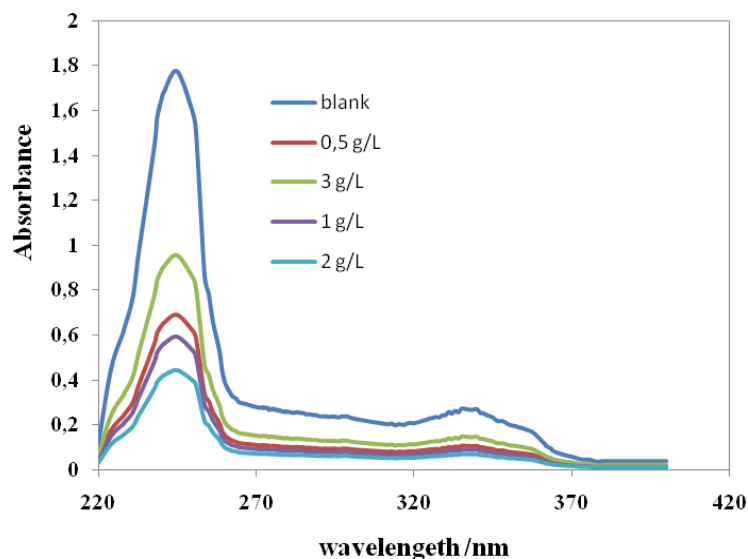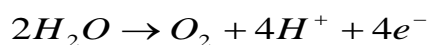
Figure 3 UV spectra of the degradation solution which was diluted to 6 times at different concentration of NaCl at current density of 25 mAcm^{-2}, pyridazine concentration of 60mgL^{-1}.

Effect of current density

The efffect of the current density on the COD removal during the electrooxidation of pyridazine at the anode is shown in **Figure 4**. Increasing the current density until 25 mA.cm^{-2} resulted in an enhancement of the oxidation rate. After 180 min time of electrolysis, the COD percent removal increased from (44 ± 4.4) % to (96 ± 5) % when the current density increased from 5 to 25 mA.cm^{-2}. This behavior indicates that in these experimental conditions, the oxidation of nitrogen compound is completely under mass transport control and an increase of the applied current favors only the secondary reaction of oxygen evolution:

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^-$$

The % COD of pyridazine was observed to fall with pseudo first-order kinetics on the entire surface studied (**table 2**).

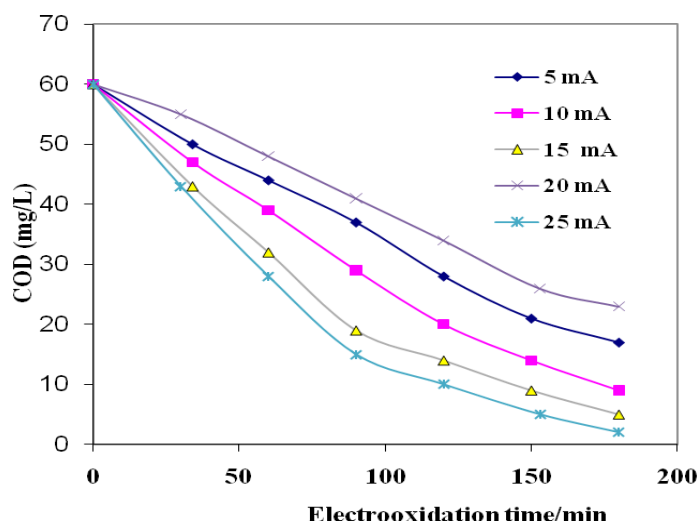**Figure 4** Influence of current density on the decay of COD during electro-oxidation of 60 mg/L pyridazine on BDD anode. Conditions: T= 25 °C, 2 g/L of NaCl.

Table 2 Effect of the current density on the values of the rate constant and the %COD

Curent density (mA/cm²)	Rate constant, K (min⁻¹)	COD removal (%)
5	$(1.32 \pm 0.22) \times 10^{-3}$	$(44 \pm 5{,}2)$
10	$(5.82 \pm 0.16) \times 10^{-3}$	(60 ± 5.7)
15	$(8.53 \pm 0.33) \times 10^{-3}$	(72 ± 6.2)
20	$(0.32 \pm 0.23) \times 10^{-2}$	(82 ± 5.4)
25	$(1{,}68 \pm 0.33) \times 10^{-2}$	(96 ± 3.4)

The results of UV-spectra of pyridazine at different curent density after 180 min of electrooxidation time are shown in **Figure 5**. As it can be seen that at 25 mA after 180 min of treatment, the UV-spectrum changed greatly and had a weak absorbance at 245 nm. The absorbances at 345 nm also decreased much. These results confirmed that obtained with COD removal for pyridazine under different Curent density.
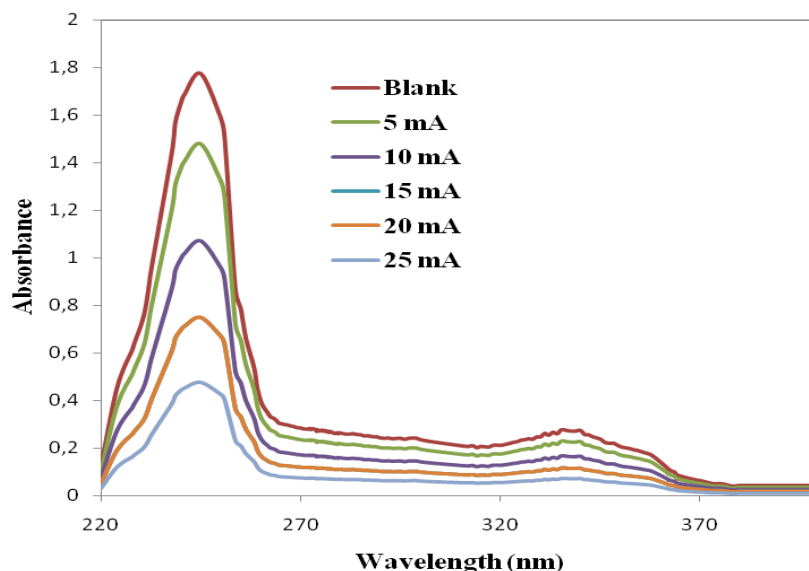

Figure 5 UV spectra of the degradation solution which was diluted to 6 times at different concentration of NaCl at current density of 25 mAcm⁻², pyridazine concentration of 60 mgL⁻¹.

Effect of initial concentrations of pyridazine

The initial concentration of organic coumpound is always an important parameter in wastewater treatment. Figure 6 shows the effect of different initial nitrogen's compound concentrations on the rate of pyridazine degradation and corresponding concentration removal during electrolysis at temperature of 25 °C and using a current density of 25 mAcm⁻² and concentration 2g/L of NaCl.

The influence of the initial concentration of organic compound on its degradation was studied in the concentration range between 25 and 80 mg/L. Figure 6 shows the influence of the initial concentration of pyridazine on the COD removal. Here increasing the initial concentration showed a increase in the percentage of COD; however,

the net amount of COD removal increased. For example, the COD removal values were 66.7, 91 and 99% for 80, 60 and 25 mg/L Pyridazine concentrations with net amounts of COD removal of 30, 5 and 1mg/L, respectively.
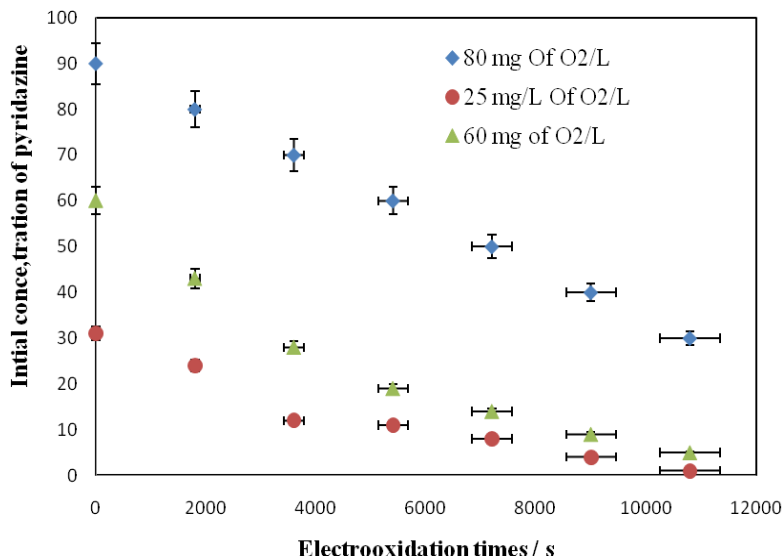

Figure 6 Effect of the initial concentration of pyridazine on the removal of COD (conditions: initial chloride concentration = 2 g/L, current density =25 mA/cm^2, and T=25°C).

Conclusion

The electrochemical approach is a novel process for effective removal of organic compound. This work is a first attempt to investigate the degradation of the nitrogen compound in electrochemical treatment. In the present study, effect of current density, effect of NaCl concentration, initial pyridazine concentration on the performance of pyridazine electrolysis were investigated using BDD anodes.

The experimental results allowed us to draw the following conclusions:

The best results were obtained when electrolyses were carried out at high densities, 25 mA.cm^{-2}, and in the presence of supporting electrolyte 2g/L of NaCl concentration.

The removal rate of COD increases with applied current density until 25 mAcm^{-2} due to the increase of the mass transport caused by oxygen evolution reaction, but decreases for higher values due to the improvement of this reaction.

The UV–Vis spectral studies confirmed that the proposed electrochemical degradation process is an effective method for the degradation of nitrogen's compound such as pyridazine.

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