2013 International Symposium on Environmental Science and Technology (2013 ISEST)

Status and development of DDNP wastewater treatment

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Abstract

It is very difficult to deal with diazodinitrophenol (DDNP) wastewater effectively. The features of current methods used to treat DDNP wastewater are summarized in this paper. Furthermore, the mechanism of supercritical water oxidation, electro-catalytic oxidation, Fenton oxidation, CPB modified zeolite, adsorption resin, white rot fungus and artificial wetland are analysed. And their features are discussed in order to find a reliable, low cost, effective and rapid way.

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Keywords: DDNP; wastewater treatment; oxidation method; micro electrolytic treatment

1. Introduction

Diazodinitrophenol (DDNP) is nitro derivatives of phenol. It is widely used in civil explosive industry as detonator primary explosive for its low mechanical sensitivity, high flame sensitivity, good initiating performance, wide source of raw materials, and low cost [1].

DDNP wastewater is reddish brown, and it contains a large number of nitrobenzene, phenol toxic, carcinogenic substances, and biological toxicity. Due to its higher density than water, nitrobenzene has high stability in water. When be entered into the water, it would sink to the bottom and keep long time [2]. Also since it has certain water solubility, the water pollution will last for quite a long time. If wastewater directly discharged without treatment, it would cause serious pollution of water environment.

Sodium salt method is often used to prepare DDNP as shown in Fig. 1 and it has the following characteristics:

- Large quantity. About 200 kg wastewater will be produced by 1 kg DDNP;
- Complex composition. The wastewater contains a large number of diazo, nitro, nitroso and other nonbiodegradable compounds;

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• High chroma. DDNP wastewater has heavy nitrogen and washing wastewater are dark red, dark red yellow and orange;
• Toxic. With a strong acid or strong alkali, it contains more toxic and harmful pollutants.

Fig. 1. The preparation process of DDNP and the source of wastewater.

2. DDNP Wastewater Treatment Methods

By good DDNP wastewater treatment methods and reliable technologies, the efficiency of DDNP wastewater treatment could be improved, and processing costs reduced, while the COD, BOD, SS and chroma could be reduced in the specified range of national emission standard. So far, there are many methods to treat DDNP wastewater.

2.1. Oxidation method

2.1.1. Supercritical water oxidation

By using supercritical water (such as \( T=374 \, ^\circ C, \, P=22.1 \, MPa \)) as medium, oxidant or catalyst could decompose organic matters. Under supercritical condition, the physical properties of the fluid are between the gas and liquid. It not only has the same diffusion coefficient as gas, but also has the same density as liquid and dissolving capacity. Supercritical water is a good solvent for organic matter and oxygen. Organic matters are oxidized in the oxygen-rich homogeneous condition, and the reaction will not be limited by phase transfer. The main features of supercritical water oxidation method are:
• Homogeneous reaction;
• High processing efficiency;
• No secondary pollution;
• Energy saving;
• Separating with salt easily.

Based on the above characteristics, the technology is known as clean technology, and has great potential for application\[3,4\].

The methods developed by Yang et al. [5] consider that the order of the main factors, which affect the
treatment, was temperature > residence time > the peroxide amount > pressure. Supercritical water oxidation method is an efficient organic technology, the removal rate of COD can reach above 99%, and the chroma removal rate could be 100%. The optimum reaction conditions are: \( T = 600 \degree C, P = 24 \) MPa, and the amount of excess oxygen is 0.8 MPa. With the increasing reaction temperature, pressure, residence time and increase of oxygen concentration, COD removal rate will increase.

### 2.1.2. Electro-catalytic oxidation

The new type of Boron-doped diamond (BDD) electrodes has been used for treating DDNP industrial wastewater by electro-catalytic oxidation process. BDD thin film electrode has high oxygen evolution potential (3 V), and it can directly oxidize hydroxyl to oxygen free radicals, ozone, hydrogen peroxide and hydroxyl free radical. There are a lot of refractory organic matters in organic wastewater. They can be decomposed to \( CO_2 \) or other simple compounds via BDD thin film electro-catalytic oxidation, so as to achieve the purpose of degradation of COD [6,7]. The main features of the method are [7]:

- Diamond membrane water treatment process does not produce anode sludge. Diamond film electrode is superior to soluble anode.
- Electrode thickness is not reduced with the electrolytic process. The chemical characteristics of the diamond film is relatively stable, and redox reaction would not occur in the electrolysis process. Therefore, the thickness of diamond film will not be reduced with electrolytic process.
- No electrode poisoning phenomenon.

With the increase of cell voltage, removal rate of COD will continue to improve. The smaller the plate spacing is, the higher the removal efficiency is. However, the small plate spacing leads to the decline of removal rate of COD, due to adsorption and the existence of side reactions caused by electrode clogging [7-9]. The initial high COD of wastewater will be detrimental to the catalytic reaction. The increasing electrical conductivity of the solution has no effect on electro-catalytic oxidation efficiency. Under experimental conditions, the optimal concentration of NaCl was 1 g/L. The results by Wang et al. [8] reveal that DDNP production wastewater degradation by electro-catalytic oxidation follows the first order kinetics under a certain cell voltage or an initial COD. But the total reaction rate equation shows that the degradation rate is related to the 1.4th power of the bath voltage and -0.24th power of initial COD, so it is clear that the effect of bath voltage is more significant.

### 2.1.3. Fenton oxidation

Fenton reagent which mixes hydrogen peroxide \((H_2O_2)\) and \(Fe^{2+}\) is a strong oxidant. Fenton reagent has a good effect on the oxidation of a variety of organic compounds, especially on some difficult biodegradable toxic organic wastewater which contains nitrobenzene, aromatic amine and various phenolic compounds [10,11]. Main features of Fenton method are [12]:

- Fenton reagent is environment friendly, and it has very strong oxidizing effect. The oxidation does not produce secondary pollution, and pollutants in wastewater can be oxidized to water, \( CO_2 \) or salt.
- Fenton reagent can degrade organic pollutants rapidly. It not only can be used as a separate process for wastewater treatment, but also can match with other processes such as biochemical pre-treatment and after-treatment, and both of them can effectively reduce processing cost and improve the processing efficiency.
- By free radical reaction, it can improve the ability of biological degradation of organic pollutants.
- Run stably and operate easily.
- Poor controllability. The reaction rate is difficult to control since the reaction cannot stop until the reactant is consumed wholly. And the acidity of solution is required harsh, that is pH value generally
being less than 4.

- Reaction reagent has storage and transportation problems. H$_2$O$_2$ and ferrous salt belong to the unstable reagents, and they are perishable during storage, and at the same time H$_2$O$_2$ is a strong oxidizing agent, so transportation also exist certain risk.

The results of Niu [12] show that when pH value was 4.0, the dosage of H$_2$O$_2$ was 40 mL/L, the dosage of FeSO$_4$$\cdot$7H$_2$O was 2.502 g/L and the reaction time was 4 h, under normal temperature, the COD of DDNP wastewater after the treatment was 1386 mg/L; the removal rate of COD was 66.68%; the color of DDNP wastewater declined 2700 times; the removal rate of color was 89.20%.

2.2. Micro electrolytic treatment

Micro electrolytic treatment is a physical and chemical process for wastewater treatment using Fe/C galvanic cell reaction principle, and also be known as internal electrolysis. The method mainly uses electrochemical oxidation and reduction principle, through the iron filings on floc electrical agglomeration, coagulation, adsorption, filtration and the combined effects of waste water treatment. Iron and carbon are mixed and then added to the wastewater. Since iron and carbon have different electrode potentials, they will form a primary battery when immersed in the electrolyte solution. Scrap iron is negative electrode, and carbon is positive electrode [13]. The basic principles are: (1) Iron is an active metal, in acidic aqueous solution can occur following reaction: Fe-2e=Fe$^{2+}$; (2) When the water in the presence of oxidants, Fe$^{2+}$ can be further oxidized to Fe$^{3+}$. The nitro in the structure of nitrobenzene can be reduced to amino, and the color of reduced amine is light, and susceptible to microbial decompose, and chroma will be reduced. Cast iron is an alloy of iron and carbon, and is composed by pure iron, Fe$_3$C and some impurities. Cast iron is a very small particle and be dispersed in the iron. Therefore, when the iron is immersed in the waste water, it will form many small micro batteries. Pure iron is anode and carbonized iron and impurities become cathode. There are two basic reactions:

$$\text{Fe-2e}\rightarrow\text{Fe}^{2+} \quad (1)$$

$$2\text{H}^{+}+2\text{e}\rightarrow2\text{[H]}\rightarrow\text{H}_2 \quad (2)$$

The main features of the method are simple device structure, convenient operation, low cost, wide application range, good treatment effect, and long service life [14,15].

The study of Ai et al. [15] show that under acidic conditions, the optimum process condition is: pH=4; $T$=25 $^\circ$C; reaction time was 2 d; and $V_{Fe}/V_C$ was 1.2. Under the optimum acidic condition, the removal rate of COD was 85.65% and S$^{2-}$ removal rate was 91.03%. Under alkaline conditions, the optimum process condition is: pH=10; $T$=25 $^\circ$C; reaction time was 2 d; and $V_{Fe}/V_C$ was 1.2. Under the optimum alkaline condition, the removal rate of COD was 90.13% and S$^{2-}$ removal rate was 91.60%.

2.3. Adsorption method

2.3.1. CPB modified zeolite

Zeolites are zeolite group minerals in general which have porous framework structure containing aluminum silicate minerals. Cationic surfactant of cetyl pyridinium (CPB) is used to modify natural zeolite so as to improve the porosity and surface activity obviously. Thus, the adsorption, ion exchange property and exchange capacity, catalytic performance are all enhanced, and the practical value of natural zeolite is also improved [16]. The natural zeolite can be modified by the cation surfactant of CPB, and its adsorb ability is strengthened after being modified. On the one hand, ion exchange, namely electrostatic attraction makes negative ions move to the modified zeolite surface, then replace outer anion with balance function of aggregate; On the other hand, the o xoacid anions form ion complex precipitation and be
removed in the modified zeolite surface. Surfactant can not enter the zeolite cavities inside due to its larger molecules, so reaction occurs only in the zeolite surface, and zeolite still retains the ion exchange capability, so it can exchange heavy metals in wastewater [17].

The optimum adsorbing temperature of CPB modified zeolite for treating DDNP wastewater is 35 °C, the optimum adsorbing time is 1 h. When the volume of wastewater is 5 mL, the modified zeolite's consumption is 4 g [17].

2.3.2. Adsorption resin

Resin adsorption can treat wastewater in pharmaceuticals, fuel, chemical and other fields. Moreover, it can be desorbed well, and solve the problem of regeneration of adsorbent. Here are the characteristics [18,19]:

- Chemical properties are very stable, and adsorption resin is insoluble in acids, alkalis and organic solvents.
- The intermolecular force can enrich, separate and recovery organic matter from water solution.
- Adsorption resin has a narrow pore-size distribution, good mechanical strength, easy desorption characteristics compared with activated carbon.

The study of Zhang [20] show that when controlled the COD being 200 mg/L, its optimum operations are as follows: the desorption solution volume is 7 BV; adsorption flow rate is 3 BV/h; pH is 7.0-9.0; adsorption temperature is room temperature; the regenerant is alcohol; desorption flow rate 1.5-1.3 BV/h. Under the optimum operation conditions, COD can reach the national discharge standard, and COD desorption efficiency is above 95%. The stability tests demonstrate that the recycling property is satisfactory.

2.4. White rot fungus

White rot fungus is a kind of white filamentous fungi which can cause wood rot. The degradation mechanism of white rot fungi is very complex including biological mechanism and chemical processes. It can be divided into intracellular process and extracellular process, and mainly extracellular oxidation process. Compared to other technologies, degradation technology of white rot fungi has its unique advantages [21,22]:

- Without specific preconditions, it can completely mineralize certain low concentrations of contaminants.
- Kinetic advantages. White rot fungi can reduce pollutants to near zero.
- To other microorganisms, it has antagonistic action.
- Extracellular degradation. It can degrade toxic pollutants, and does not poison the cell body.
- To degrade various structures of different chemical compounds, even degrade all kinds of mixed pollutants.
- It can be applied in solid and liquid systems, and has a more extensive practical application.

The experiments of Ling [21] show that after five steps of treatment, which were neutralization and explosion elimination, hydrolytic acidification, Fe-C micro-electrolysis, regulating the influent concentration of biochemical treatment (diluted five times), and treatment by immobilized White rot fungi, the color of DDNP wastewater was down to 100 times from 62500 times; decolorization rate was 99.9%; COD down to 129.9-180.9 mg/L from 29481.6 mg/L of the raw water; COD removal rate could reach 99%. The effluent quality (pH=6) could meet the explosive wastewater discharge standards (GB 14470.2—2002).
3. Conclusions

The paper discusses methods of dealing with DDNP industrial wastewater in recent years, and each of them has advantages and disadvantages, and some of the methods need further verification. People are exploring a kind of processing method which has the advantages of simple process, convenient operation, thorough treatment, energy saving and low cost in the existing science and technology foundation. To develop methods making the processing and recycling processes together, we explore the best treatment to reduce or avoid the secondary pollution.

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