Short Communication

Propellants, Explosives, Pyrotechnics

DOI: 10.1002/prep.202000166

Research on Regenerating Activated Carbon in 2,4,6-Trinitrotoluene (TNT) Explosives Manufacturing Industry by Microwave Radiation and Ionized Nitrogen

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Abstract: Currently, 2,4,6-trinitrotoluene (TNT) explosive plants often apply activated carbon to treat aromatic nitrogen compounds in wastewater, so finding optimal measures to regenerate activated carbon is essential. The method of using microwave radiation in combination with the ionized current of nitrogen was studied. The results showed that the application of the above method helped the regeneration efficiency of activated carbon reach 95.26 % after 60 minutes of treatment. The optimum conditions were given with an microwave power of 500 W, a nitrogen pressure of 0.015 MPa. The above method has a high environmental significance when the effluent after regeneration has a chemical oxygen demand (COD) of 130 mg/l, allowing it to be discharged into the environment. The method also makes economic sense when activated carbon can be regenerated many times.

Keywords: Activated carbon · 2,4,6-Trinitrotoluene · Microwave radiation · Ionized nitrogen · Regeneration

1 Introduction

The production of organic compounds began in the beginning of the 19th century. Subsequently, nitro aromatic explosives such as 2,4,6-trinitrotoluene and 2,4,6-trinitrophenol (picric acid) were synthesized and widely applied, especially for military purposes because of their properties: highly explosive, thermally stable and insensitive to collision and friction [1,2]. In addition, they have been used in civil industries as raw materials to produce pesticides, herbicides, pharmaceutical products, dyes and explosives [3,4].

After 1940, the proportion of TNT production in different countries increased exponentially [5]. Therefore, the widespread use of the military with improper handling of explosives and their modified products has led to an increase in environmental pollution, especially soil, sediment, and surface water and groundwater to the extent of threatening human health. Over the years, this situation has escalated, thus it requires attention to the research community [6].

Studies have shown that TNT can cause many adverse effects on different ecosystems, namely microorganisms such as Escherichia coli K-12 strain AB1157, luminescent bacteria (*Salmonella typhimurium TA1535 / pTL210*), algae, plants, invertebrates, some vertebrates and humans [7]. Other studies done on animals such as dogs, mice, frogs, and humans have shown that TNT and its conversion products are teratogenic, cytotoxic, and possibly mutagenic. [8,9].

Due to the ecological toxicity and durability of TNT and its modified products in the environment, there are many treatment methods studied by scientists around the world such as liquid phase oxidation under high temperature and pressure [10], the enhanced oxidation method uses H_2O_2, O_3, Fenton, TiO_2 combined with UV [11–14], the adsorption method with different materials [15–17], biological method using microorganisms capable of decomposing TNT [18,19].

The method of using activated carbon is widely applied in many production facilities for treatment of large volumes of wastewater with low TNT concentration. One of the disadvantages of the above method is the ability to regenerate activated carbon for further application, if activated carbon after use is not recycled or used for other purposes, it will cause a huge source of environmental pollution [20–22]. Therefore, it is necessary to find method to regenerate activated carbon after use for all industrial plants that use activated carbon to treat pollutants.

There are several methods to regenerate activated carbon that scientists have researched and proposed such as using heat, ultrasonic waves and chemicals. However, the use of heat to regenerate activated carbon will destroy the structure, and it causes air pollution [23], the method of using ultrasonic waves must be done with high frequency and it will cause minor disruption of activated carbon [24], while the method of using chemicals is costly and it creates secondary waste water which makes treatment difficult [25]. Several studies have shown that nitroaromatic compounds

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will gradually be destroyed and transformed into simpler forms under the influence of microwave radiation and ionizing current [26,27].

The objective of this study was to combine microwave radiation and ionized nitrogen for desorbing TNT from saturated activated carbon, also to find the optimal conditions of this process.

2 Experimental Section

2.1 Materials and Chemicals

Activated carbon (AC) in the form of cylindrical particles about 2 ÷ 3 mm long, diameter of about 1 mm saturated with nitroaromatic compounds and TNT-containing wastewater were provided by Z113 Chemical Engineering Co., Ltd (Figure 1).

Toluene, acetone, iodine solution, $Na_2S_2O_3$, NaOH (China), starch (Vietnam) are used immediately without refining.

Figure 1. Saturated activated carbon.

2.2 Desorption Diagram of AC by Microwave Radiation and Ionized Current

Ionization device: uses high voltage to ionise nitrogen molecules (Figure 2) consisting of an inner copper neutral conductor (1.0 mm i.d., 5.0 mm o.d.) and an outer gas conduction device made of polytetrafluoroethylene (PTFE) (diameter of 7 cm and length of 30 cm). The nitrogen gas is affected by an applied high voltage of 9 kV to form an ionic flow that exits the device.

Microwave generator: It consisted of a 0.9 kW microwave generator (GA0.9SC20A01A2, National Electronics) with a 2.45 GHz microwave magnetron head (TMO1.2V52) connected to a sliding short. Power was monitored using a dual directional coupler with 60 db attenuation, two power sensors (E9320 Peak and Average Power Sensors), and a dual-channel microwave power meter (N1914A).

Desorption device: is made of stainless steel with diameter of 15 cm and length of 40 cm (useful length of 30 cm).

Ionization device and desorption device will be combined to form a complete desorption system as shown in Figure 3.

TNT-saturated activated carbon will be loaded into the device through the inlet. The system is started by turning on a microwave generator at a certain power. After that, the gas ionizing device will be turned on, the flow of nitrogen from the compressed air tank will be opened and blown through the ionizing device with the pressure adjusted appropriately.

2.3 Study on Factors Affecting Regeneration of AC by Microwave Radiation and Ionized Nitrogen Current

2.3.1 The Effect of Different Working Regimes on the Efficiency of Regeneration of AC

Regeneration efficiency of AC of the system was studied on 3 modes:

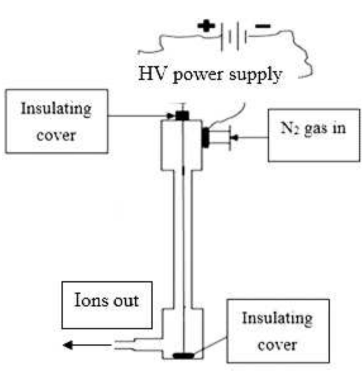

Figure 2. Ionization device.

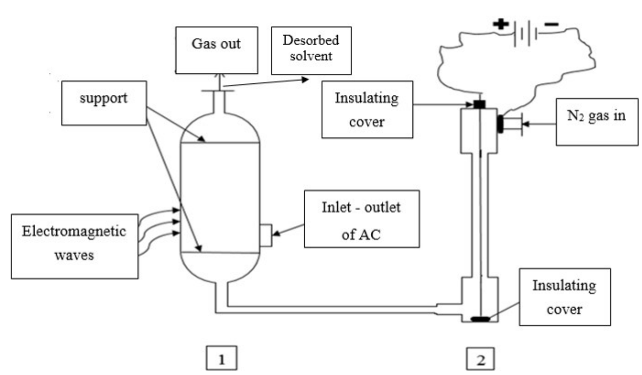

Figure 3. Complete desorption system.

- Mode 1: The system after loading 3.5 kg of AC will only turn on the microwave generator at the power of 500 W, the ionizing device and the nitrogen tank will not turn on
- Mode 2: The system after loading 3.5 kg of AC will turn on the microwave generator at the power of 500 W and the nitrogen tank at a pressure of 0.015 MPa
- Mode 3: The system after loading 3.5 kg of AC will turn on the microwave generator at the power of 500 W, the ionizing device at 9 kV and the nitrogen tank at a pressure of 0.015 MPa

The efficiency of regeneration of AC was determined after 60 minutes.

2.3.2 The Effect of Microwave Power

The power of the microwave generator varies with 300, 400, 500 and 600 W.

2.3.3 The Effect of Nitrogen Pressure

The pressure of nitrogen flow changes 0.005, 0.01, 0.015, and 0.02 MPa.

2.4 Evaluation of the Efficiency of Experimental System

2.4.1 Investigation of Re-Adsorption Ability of AC

To evaluate the re-adsorption ability of the activated carbon, the method of independent comparison of Berberin adsorption ability between reused activated carbon and new activated carbon under the same conditions was used. First, the calibration curve for UV-spectroscopic analysis of Berberin was constructed at wavelength of 421 nm. Based on this, amounts of Berberin adsorbed by re-adsorbed activated carbon and new activated carbon were obtained. Then, the re-adsorption ability of activated carbon was calculated by the formula:

Re-adsorption ability of AC (Regeneration performance H, %) $= (m_1/m_2)*100\,\%$

m_1 – amount of Berberin adsorbed by re-adsorbed activated carbon

m_2 – amount of Berberin adsorbed by new activated carbon

2.4.2 Investigation of Times of Regenerations of AC

AC after desorption was dried and re-adsorbed with TNT-containing wastewater of Z113 Chemical Engineering Co., Ltd. The activated carbon column (diameter of 10 cm and length of 50 cm) was used to adsorb TNT from wastewater. After every 2 h, the solution through the column was analyzed by sodium sulfites spectrophotometry [28]. When there was no change in the concentrations of TNT in the wastewater after going through the activated carbon column, it means that activated carbon was saturated with TNT. When the activated carbon was saturated with TNT, it was regenerated by using above desorption system. 8 cycles of desorption↔re-adsorbed were performed to evaluate the possibility of regenerations of AC.

2.4.3 Iodine Number of Activated Carbon

Iodine Number of Activated Carbon is determined according to ASTM D4607 – 14 "Standard Test Method for Determination of Iodine Number of Activated Carbon". The measurement of Iodine Number of Activated Carbon is carried out 3 times to get an average value.

2.4.4 Specific Surface Area of AC by BET Method

The specific surface area of AC is determined by the N2 adsorption-desorption isothermal method at a temperature of 77 K on the US TriStar-3000 measuring device at VietNam Academy Of Science And Technology.

2.4.5 Determination of COD of the Desorbed Solvent from AC

The COD of the desorbed solvent from AC is determined according to TCVN 6491: 1999 - Water quality – Determination of the chemical oxygen demand.

3 Results and Discussion

3.1 Factors Affecting Regeneration of AC by Microwave Radiation and Ionized Nitrogen Current

3.1.1 The Effect of Different Working Regimes on the Efficiency of Regeneration of AC

AC regeneration system can work in 3 different modes. Each mode will correspond to different regeneration conditions. Mode 1 corresponds to regeneration of AC by microwave radiation, mode 2 incorporates additional pressure from the nitrogen gas stream, while mode 3 is a complete combination of microwave radiation and the pressure of ionized nitrogen gas. Each mode will give different performance of regeneration of AC (Table 1).

If using only microwave radiation to regenerate AC, the efficiency is not high, the decomposition rate of organic compounds is slowly, thus mode 1 has relatively low regeneration performance of 38.83 % and Iodine Number of 432 mg/g, while the COD of the desorbed solvent is quite

Table 1. The influence of different working modes on the efficiency of AC regeneration after 60 minutes of treatment.

Mode	Regeneration performance H, %	Iodine Number, mg/g	COD, mg/l
1	38.83	432	450
2	56.15	474	435
3	95.26	687	130

high of 450 mg/l. In the presence of pressure from the inert nitrogen gas (mode 2), the regeneration efficiency increases significantly to 56.15 %, but Iodine Number is still quite low (474 mg/g) and only COD of the desorbed solvent is still high (435 mg/l). Thus, it can be seen that the effect of the microwave and the pressure from the inert nitrogen gas can only separate the organic compounds associated with AC not too tight, and the microwave partially decomposed organic compounds. The difference in mode 3 can be seen clearly, under the effect of microwave radiation and ionized nitrogen flow, the regeneration efficiency of AC is almost absolute after 60 minutes (95.26 %), the Iodine Number is close to that of new AC (687 versus 732 mg/g), and the COD of the desorbed solvent is only 130 mg/l.

After passing through the ionization device, the nitrogen gas is transformed into an activated (ionized) gas stream and passed through an desorption device. Here, the gas stream will interact with the organic solvents adsorbed on AC. Under the influence of the microwave, the ionized gas flow and the pressure, the organic solvents will easily be separated from the activated carbon and decomposed into simple substances.

3.1.2 The Effect of Microwave Power

Power is a very important factor when studying the effect of microwave radiation on regeneration of AC. The higher the power of microwave radiation, the easier it is to separate the organic solvents from the AC. In other words, the higher the power of microwave radiation, the faster the interaction between ionized gas and adsorbed organic solvents takes place, thus the decomposition of organic solvents is faster.

When the power of microwave radiation increases from 300 to 500 W, the regeneration efficiency of AC increases linearly (53.5–95.26 %), at the same time Iodine Number also increases linearly (462–687 mg/g), while the COD of the effluent after desorption decreases from 198 mg/l to 130 mg/l (Table 2). It is obvious that microwave power has a great influence on the regeneration efficiency of AC of the experimental system. However, when the power of microwave radiation increased to 600 W, the regeneration efficiency of AC does not increase further, so the system reached the limit of efficiency at the power of microwave radiation of 500 W.

Table 2. The effect of microwave power on the efficiency of AC regeneration after 60 minutes of treatment, nitrogen pressure of 0.015 MPa.

Power, W	Regeneration performance H, %	Iodine Number, mg/g	COD, mg/l
300	53.5	462	198
400	75.13	571	164
500	95.26	687	130
600	95.82	691	125

3.1.3 Effect of Nitrogen Gas Pressure

Another important factor affecting the regeneration efficiency of AC by microwave radiation and ionized nitrogen flow is the pressure of nitrogen gas. The pressure of nitrogen gas has two effects: one is to create a pressure that makes the process of separating organic solvents from AC easier; the second is to increase the amount of ionized nitrogen which helps to decompose organic compounds faster.

When the pressure of nitrogen gas increases from 0.005 to 0.015 MPa, the regeneration efficiency of AC increases from 71.11 to 95.26 %, Iodine Number also increases from 504 to 687 mg/g, while the COD of the effluent after desorption does not change much. If the pressure of nitrogen gas continues to increase to 0.02 MPa, the regeneration efficiency and Iodine Number of AC do not increase much, but the COD of the effluent after desorption increases greatly (from 130 mg/l to 225 mg/l) (Table 3). This is explained that when the pressure of nitrogen gas increases too high, it will create a great pressure to push organic compounds out quickly, the interaction time between ionized nitrogen and organic compounds reduces, thus organic compounds will not have enough time to decompose into simpler compounds. Therefore, the pressure of nitrogen gas of 0.015 MPa is optimal for the regeneration of AC.

Table 3. The effect of nitrogen gas pressure on the regeneration efficiency of AC after 60 minutes of treatment, the power of microwave radiation of 500 W.

Pressure of nitrogen gas, MPa	Regeneration performance H, %	Iodine Number, mg/g	COD, mg/l
0.005	71.11	504	128
0.01	83.24	592	124
0.015	95.26	687	130
0.02	98.75	704	225

3.2 Reusability Assessment of AC after Regeneration Process by Experimental System

In order to evaluate whether the system of the regeneration of AC using microwave radiation and ionized current is valid and effective, the reusability and the number of reuse of AC after regeneration must be assessed. The results of 5 times of the regeneration of AC are given in Table 4.

Based on the results of Table 4, it can be seen that after 5 times of the regeneration, the regeneration efficiency and Iodine Number of AC are reduced but still at high values and activated carbon can continue to be used. Regeneration efficiency drops from 95,26 % to 80.12 % while Iodine Number drops from 687 mg/g to 509 mg/g. The decrease in regeneration efficiency and Iodine Number of AC may be due to the surface area of AC that has been reduced after each regeneration time. Under the influence of microwave radiation and the pressure of ionized nitrogen gas, the unstable capillaries of AC may be broken, after the 1st regeneration, the surface area of AC is 681.1 m^2/g (compared to 774.8 m^2/g of new AC), after the 3rd regeneration, there is 605.2 m^2/g, and after 5th regeneration, surface area of AC is only 561.2 m^2/g.

4 Conclusion

A good way to regenerate activated carbon in the 2,4,6-trinitrotoluen explosive industry is to use microwave radiation in combination with ionized nitrogen. The method helps the regeneration efficiency reach 95.26 % after 60 minutes of desorption under conditions of microwave power of 500 W, and pressure of nitrogen flow of 0.015 MPa. Activated carbon can be regenerated many times by experimental system.

Acknowledgements

This research was supported by Viet Tri Industrial University.

Table 4. Reusability assessment of AC after regeneration process by experimental system.

Regeneration times	Regeneration performance H, %	Iodine Number, mg/g	Surface area, m^2/g
New	–	732	774.8
1	95.26	687	681.1
2	92.87	637	–
3	89.01	598	605.2
4	84.43	542	–
5	80.12	509	561.2

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Manuscript received: July 2, 2020
Revised manuscript received: October 27, 2020
Version of record online: December 16, 2020

