Selective Adsorption for Toluenediamine Recovery from TDA Tar through Surface Modification of Activated Carbon

Dongliang Wang*, Wei Wang, Wenliang Meng, Guixian Li, Yong Yang

School of Petrochemical Engineering, Lanzhou University of Technology, Gansu Lanzhou 730050, China
wangdl@lut.edu.cn

Toluenediamine (TDA) tar, as the heavy fraction from the dinitrotoluene hydrogenation to produce the important product of TDA, contains significant amounts of meta-TDA of 10 - 30 wt.% and is currently incinerated as waste at great cost. In this paper, the adsorption separation technology was adopt for the recovery of meta-TDA from TDA tar with some porous adsorbent materials. The activated carbon has the highest adsorption ratio for ethanol solution of meta-TDA. After treatment by HNO_3 or CH_3COOH, the modified activated carbon has the slightly decreased adsorption capacity for TDA tar of 238.8 $mg \cdot g^{-1}$ or 243.3 $mg \cdot g^{-1}$ with the meta-TDA selectivity of 96.36 % or 98.15 %. While the activated carbon modified by NaOH or $NH_3 \cdot H_2O$ leads to the higher adsorption capacity of 287.9 $mg \cdot g^{-1}$ or 261.2 $mg \cdot g^{-1}$ for TDA tar with relative lower meta-TDA selectivity of 90.10 % or 96.02 %. The FT-IR and BET results confirm that surface oxygen-containing groups can be created through the acid or alkali modification, which result in enhancing the adsorption selectivity of meta-TDA. The proposed selective adsorption based on modified activated carbon would be an efficient and low-cost separation technology for TDA recovery from TDA tar.

1. Introduction

Toluenediamine (TDA) is the important intermediate for the production of toluene diisocyanate (TDI) which is the raw materials for the preparation of polyurethane. During the hydrogenation of dinitrotoluene (DNT) to obtain TDA, the low-boiling constituents are removed overhead in the rectification column, the bottoms comprise 2,4-TDA, 2,6-TDA and oligomer mixture, called as TDA tar. TDA tar contains significant amounts of meta-TDA (10 - 30 wt.% of 2,4-TDA and 2,6-TDA) in order to keep it pumpable or flowable. TDA tar is classified as hazardous waste due to its toxicity. The disposal or incineration of TDA tar leads to a waste of the desired TDA and is not environmental friendly.

Several technologies have been developed to recover meta-TDA from TDA tar. BASF (China) Company Ltd. Shanghai Branch proposed the thin-film evaporator process with a rotary scraper film (Yu et al., 2012). Beckhaus et al. (1998) raised a rectification process with ortho-TDA as the entrainer to reduce meta-TDA content in TDA tar. After the treatment, meta-TDA content is generally below 10 wt.%. Brady et al. (2002) added a stripping column in the Beckhaus process, and at least 97 wt.% up to 99.8 wt.% of meta-TDA presenting in the original mixture could be recovered. Monobasic alcohol such as cyclohexanol, dibasic alcohol, or ethylene glycol were also used as entrainer (Lai et al., 2016). Oliveira et al. (2019) invented the hydrogenation process of TDA tar with a heterogenous catalyst comprising at least one metal with Ni, Co, Ru, Pd, Pt on the support of carbon, TiO_2 or ZrO_2. The selective adsorption is an alternative method for TDA recovery due to its mild conditions. The 13X molecular sieve was used as adsorption material to recycle meta-TDA from TDA tar, and the yield of meta-TDA can achieve 70.56 wt.% (Li et al., 2009). Su et al. (2013) used resin adsorbent to separate meta-TDA from TDA tar. The choice of these adsorption materials is derived from practical experience in industrial production, and there is no clear theoretical basis. Activated carbon is attractive adsorbent due to its wide availability, high thermal stability, low cost, and low sensitivity to moisture (Rashidi et al., 2013). Activated carbon was used to remove astaxanthin from microalgae (Casella et al., 2020). In this study, the activated carbon with abundant surface oxygen-containing groups was found to be beneficial for the recovery of meta-TDA. The acid

modification and alkali modification were adopted to create oxygen-containing groups, and the surface of the adsorbents were analyzed to reveal their influence on the adsorption capacity and selectivity.

2. Experiment method

The effect of five adsorbents on the absorption performance for meta-TDA were firstly investigated. Because the adsorption performance was better than other adsorbents, the activated carbon was modified with acid or alkali to test the adsorption for meta-TDA in TDA tar. The adsorption ratio was measured using a UV/VIS spectrophotometer at the maximum absorption wavelength.

2.1 Selection of adsorbent

Activated carbon, diatomite, ZSM-5 molecular sieve and permutite were chosen as adsorbents to study the adsorption performance for the meta-TDA.

- Four groups of 100 mL ethanol solution wtih 0.1 mol/L meta-TDA were placed in three-necked flask (250 mL).
- Then, 1 g adsorbent was added into each solution, keeping stirring conditions for some time.
- Samples were centrifuged at 4,000 rpm and the concentrations of the supernatants were determined by UV/VIS spectrophotometer to analyze the adsorption performance.

2.2 Acid or alkali modification of selected adsorbent

Nitric acid, acetic acid, NaOH and ammonia were used to modify the activated carbon to create oxygen-containing groups.

- Activated carbon was grinded and sifted to powders of 100-mesh. Four equal parts of the powders were placed in four conical flasks.
- 100 mL solution of 0.1 mol·L^{-1} nitric acid, acetic acid, NaOH or ammonia water were added into each conical flasks under the ultrasonic treatment for 12 h at 25 °C.
- The modified powders were recovered through filtration. Each filter cake was washed with distilled water until the pH of filtrate was 7, and the filter cake was dried for 24 h at 110 °C.

2.3 Adsorption performance of modified adsorbent

Adsorption performance of the different modified activated carbons were studied.

- Four groups of TDA tar (1 g) were dissolved in 20 mL anhydrous ethanol in four three-necked flasks.
- 1 g modified activated carbon was added into each three-necked flask under stirring condition for some time.
- Four samples were filtered and dried for 24 h at 110 °C. Unit adsorption amount was measured for each sample.
- The dried activated carbons were desorbed in 10 mL anhydrous ethanol at 50 °C under stirring for 3 h.
- The GC internal standard method was used to determine the composition of desorption ethanol solution, in which the internal standard substance is p-nitrotoluene.

2.4 Calculation of adsorption ratio and quantity

The solution concentration was measured using a UV/VIS spectrophotometer at the maximum absorption wavelength (meta-TDA at 212 nm). The adsorption ratio and meta-TDA mass (m_{m-TDA}) were calculated according to Eq(1) and Eq(2).

$$\text{Adsorption ratio \%} = (1 - C_t/C_0) \times 100 \text{ \%} \tag{1}$$

$$m_{m-TDA} = C_{m-TDA} \times V \tag{2}$$

where C_0 and C_t were the initial and final concentration of meta-TDA in ethanol solution. C_{m-TDA} was the mass concentration of meta-TDA, mg·L^{-1}. V was the volume, L.
Meta-TDA content of the desorption ethanol solution could be determined by the GC internal standard method.

3. Results and discussion

The Influence of surface chemistry for the four adsorbents and the enhanced adsorption of the modified activated carbon were discussed in detail.

3.1 Influence of adsorbent surface

The adsorption performances of meta-TDA for activated carbon, diatomite, ZSM-5 molecular sieve and permutite are showed in Figure 1. It can be seen that activated carbon has the best adsorption effect on meta-TDA. With the increase of adsorption time, the adsorption ratio of activated carbon also increased more significantly than that of the other three adsorbents.
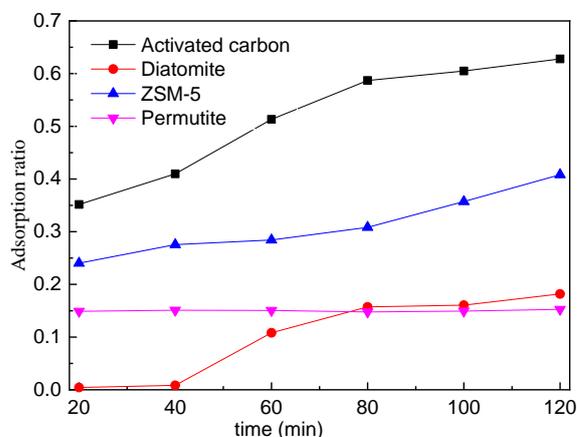
Figure 1: Effect of different adsorbents on the adsorption of meta-TDA
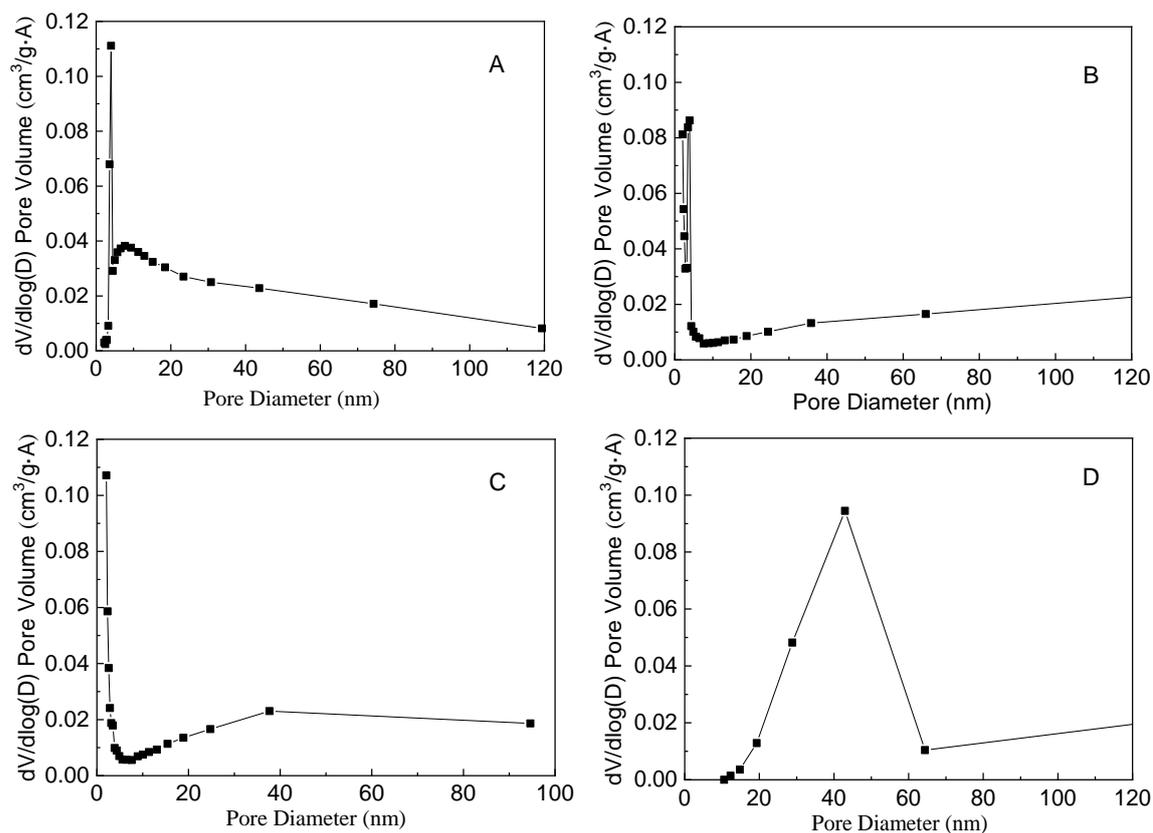
Figure 2: Characterization of pore size distribution of (A) activated carbon; (B) diatomite; (C) ZSM-5; (D) permutite (inset: N_2 physical adsorption / desorption curve)

The N_2 adsorption/desorption isotherms of adsorbents are shown in Figure 2. The pore size distribution chart shows that there are two distinct peaks at 4 nm and 7.7 nm for activated carbon in Figure 2(A), indicating that the pore size is mainly centered at 4 nm with mesopores of a diameter about 2 - 10 nm. The diatomite has a strong peak at 4.19 nm in Figure 2(B) because of the collapse for pore structure after high-temperature calcination to form amorphous silica. The pore size of ZSM-5 is generally below 2 nm, so there is no obvious

strong peak in the range of mesopores and macropores in Figure 2(C). Permutite has a strong peak at 42.92 nm with a distribution ranging from 10 nm to 60 nm in Figure 2(D). The surface area and pore structure of different adsorbents were summarized in Table 1. The specific surface area of activated carbon is relatively small, but the pore size of activated carbon is suitable for the adsorption of meta-TDA molecules. Appropriate pore size is beneficial for the adsorption of meta-TDA.

Table 1: Surface area and pore structure of different adsorbents

No.	Adsorbents	Surface area ($m^2 \cdot g^{-1}$)	Pore volume ($cm^3 \cdot g^{-1}$)	Pore size (nm)
A	Activated carbon	21.5	0.052	8.9
B	Celite	522.4	0.044	5.4
C	ZSM-5	296.8	0.043	1.9
D	Permutite	2.9	0.041	45.0

The FT-IR spectrums of diatomite, ZSM-5 and permutite mainly show the vibration peak of the skeleton of the materials themselves in Figure 3. The difference between activated carbon and other silica-alumina-based framework adsorption materials is the surface acid group. Although these functional group peaks are weak for activated carbon, they have an important influence on the adsorption of meta-TDA.
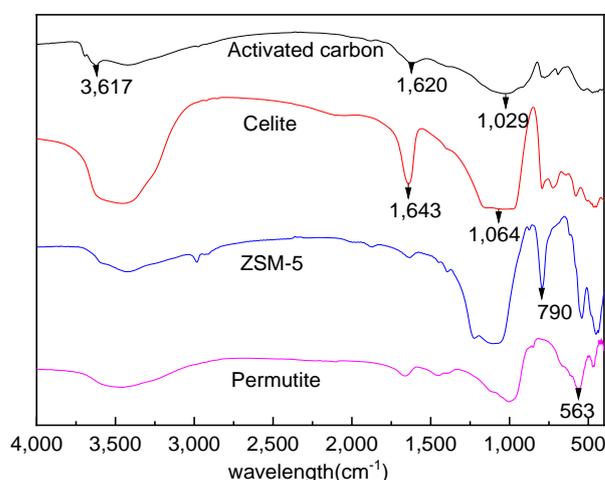
Figure 3: FT-IR spectrums of different adsorbents

3.2 Influence of activated carbon modification

After the acid or alkali modification, the adsorption effect of activated carbon can be seen in Table 2.

Table 2: Adsorption capacity of modified activated carbon

Modification method	Adsorption capacity for TDA tar ($mg \cdot g^{-1}$)	Adsorption capacity for meta-TDA ($mg \cdot g^{-1}$)	Adsorption selectivity for meta-TDA (%)
Unmodified	252.9	153.4	60.66
HNO_3	238.8	230.1	96.36
CH_3COOH	243.3	236.6	98.15
NaOH	287.9	259.4	90.10
$NH_3 \cdot H_2O$	261.2	250.8	96.02

For unmodified activated carbon, the adsorption capacity per unit mass adsorbent for TDA tar is 252.9 $mg \cdot g^{-1}$, for meta-TDA is 153.4 $mg \cdot g^{-1}$, and the adsorption selectivity is 60.66 %. After acid modification by HNO_3 or CH_3COOH, the unit adsorption capacity of activated carbon for TDA tar decreases slightly to 238.8 $mg \cdot g^{-1}$ or 243.3 $mg \cdot g^{-1}$, while the adsorption capacity for meta-TDA has improved to 230.1 $mg \cdot g^{-1}$ or 236.6 $mg \cdot g^{-1}$ regarding the special selectivity obviously up to 96.36 % or 98.15 %. After NaOH or $NH_3 \cdot H_2O$ modification, the unit adsorption capacity increases both for both TDA tar and meta-TDA with adsorption selectivity of 90.10 %

or 96.02 %. The weak acid modification is more conducive to improve the adsorption selectivity of activated carbon for meta-TDA.

Figure 4 shows the FT-IR spectrums of different modified activated carbons that represent the characteristics of the functional groups on the surface of the activated carbon. It can be seen that the unmodified activated carbon has few weak peaks. The activated carbon modified with HNO_3 is similar to the surface characteristic peak of unmodified activated carbon in Figure 4(B). The stretching vibration of C-O bond at 1,026.0 cm^{-1} can been seen after the CH_3COOH, NaOH or $NH_3 \cdot H_2O$ modification. The activated carbon modified with CH_3COOH has a strengthened stretching vibration of C-O at 1,322.8 cm^{-1} and the absorption peak of carbonyl group at 1,622.1 cm^{-1}, which indicates that the carbonyl group number of oxygen-containing groups has increased significantly. The surface oxygen-containing groups can be created through the acid or alkali modification, which may result in enhancing the adsorption selectivity of meta-TDA.
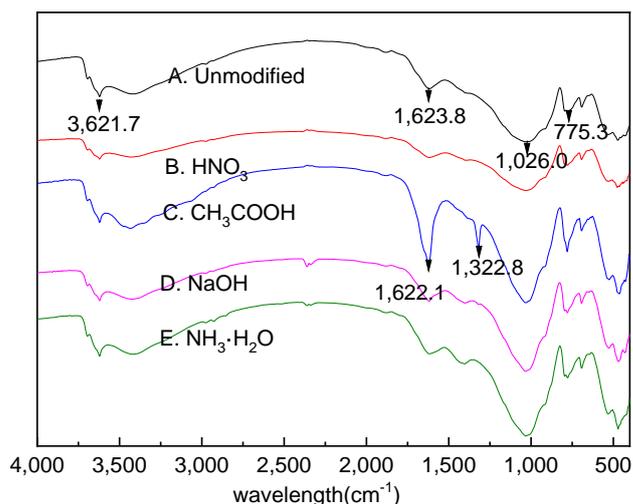
Figure 4: FT- IR spectrum of different modified activated carbons

3.3 Analysis of the desorption product

Activated carbon containing adsorbed TDA tar was desorbed in 10 mL anhydrous ethanol at 50 °C under stirring for 3.0 h. The desorption liquid was analyzed with a Fourier infrared analyzer. The FT-IR spectrum of the desorption product was compared with the meta-TDA of 2,4-TDA in Figure 5. It can be seen that stretching vibrations of N-H at 3,422.0 cm^{-1} and 3,351.7 cm^{-1} represent the primary amine groups in the mixture. These characteristic peaks indicate that the desorption product consists mainly of 2,4-TDA.
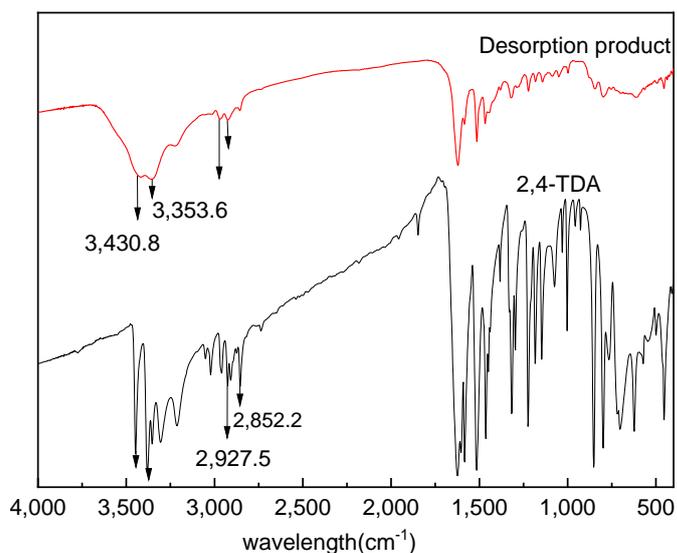
Figure 5: FT-IR spectrum of the desorption product
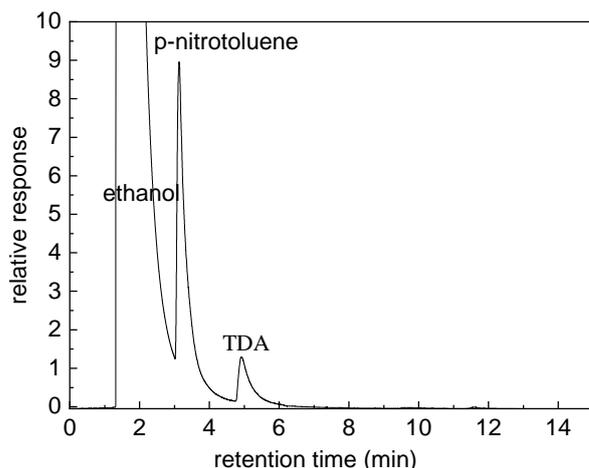
Figure 6: The desorption product gas chromatogram using internal standard method

4. Conclusions

The proposed selective adsorption has demonstrated excellent adsorption performance for TDA recovery from TDA tar. Due to the suitable pore size, highest pore volume and typical surface chemistry, the activated carbon has the highest adsorption ratio. The surface oxygen-containing groups of activated carbon can be created through the acid or alkali modification, which may result in enhancing the the adsorption selectivity of meta-TDA. After acid modification by HNO_3 or CH_3COOH, the unit adsorption capacity of activated carbon for TDA tar remains at 238.8 mg·g^{-1} or 243.3 mg·g^{-1} corresponding to the selectivity for meta-TDA of 96.36 % or 98.15 %. While NaOH or NH_3·H_2O modification leads to the higher adsorption capacity of 287.9 mg·g^{-1} or 261.2 mg·g^{-1} for TDA tar with relative lower selectivity for meta-TDA of 90.10 % or 96.02 %. Adsorption separation technology based on modified activated carbon would be an efficient and low-cost method for TDA recovery from TDA tar. Besides meta-TDA, the identification and recovery of other components in TDA tar should be focused in furure, and the adsorption equipment should also be investigated for the development and application of this TDA recovery technology.

Acknowledgements

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