

Enhancement of methylbenzene adsorption capacity through cetyl trimethyl ammonium bromide-modified activated carbon derived from Astragalus residue

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Abstract. Activated carbon was prepared from astragalus residue by KOH and then treated with cetyl trimethyl ammonium bromide (CTAB) and used for the removal of methylbenzene from aqueous solution. The samples were characterized by FTIR, XRD, SEM and Boehm titration. The results showed that CTAB changed the physicochemical properties of activated carbon significantly. The isotherm adsorption studies of methylbenzene onto the astragalus residue activated carbon (ASC) and CTAB-modified astragalus residue activated carbon (ASC-CTAB) were examined by using batch techniques and agreed well with the Langmuir model. The maximum adsorption capacity of ASC and ASC-CTAB for methylbenzene determined from the Langmuir model was 183.56 mg/g and 235.18 mg/g, respectively. The results indicated that using CTAB as a modifier for ASC modification could markedly enhance the methylbenzene removal from water.

1. Introduction

In recent years, owing to the rapid population growth, several industries including small factories are newly opened to fulfill people's requirements and to improve their life style, the hazardous wastes from the industries and factories have started creating huge environmental issues. Organic pollution is a major global environmental issue for ecosystems since the common industrial processes require organic solvents such as methylbenzene and phenylamine [1]. These Organic matters are toxic, carcinogenic and mutagenic to humans and to the aquatic life because of refractory to biodegradation [2]. Due to the high-risk characteristics of organic matters it is necessary to remove them from wastewaters. There are several methods such as coagulation, filtration with coagulation, precipitation, ozonation, adsorption, ion exchange, reverse osmosis and advanced oxidation processes are developed to remove the organic matter from wastewater, however, these methods are limited since they often involve relatively high investment and operational cost [3].

Activated carbons are the most commonly used materials for the removal of organic matter. In most cases, activated carbon is synthesized from natural precursors, such as coal, wood and nutshells [4, 5]. Although these materials are very successful, their widespread use is restricted due to the high cost. In recent years, many researchers have focused on finding economical and available materials to prepare activated carbon especially from plant biomass and biomaterial waste, such as olive stone waste residue [6], grape bagasse [7]. To enhance the capability of activated carbon to adsorb organic matter, many functional/surface modification methods have been introduced, including chemical treatment and physical treatment et al. [8, 9]. Among these methods, various surfactants were used to



modify the surface chemical properties of activated carbon to substantially boost its adsorptive capacity for organic matter, since surfactants are amphiphilic with hydrophobic groups, making them adsorb onto activated carbon [10].

Astragalus is a traditional Chinese medicinal herb. Astragalus residue is generated in large quantities annually after the main components of astragalus are extracted and are disposed of through combustion or land filling, which produces secondary pollution and waste resources. In the present study, activated carbon was prepared from astragalus residue and cetyl trimethyl ammonium bromide (CTAB), a kind of cation surfactant, was used to modify astragalus residue activated carbon (ASC) and then the activated carbons before and after modification was applied for the adsorption of methylbenzene in aqueous media. The changes of physicochemical properties of activated carbon upon the treatment are investigated. The focus of this research is to make full use of astragalus residues in organic wastewater treatment, improve the utilization rate of resources and reduce environmental pollution and explore the use of CTAB for performance enhancement.

2. Materials and methods

2.1. Solution preparation

Methylbenzene and cetyl trimethyl ammonium bromide (CTAB) obtained from Beijing, China, were of A.R. grade. Double distilled water was used to prepare all solutions. The stock solutions were stored in a refrigerator at 4°C.

2.2. Preparation of activated carbon

Astragalus residue, obtained from a local pharmaceutical company in Ningxia, China, was used as raw material for the preparation of ASC by KOH activation. Astragalus residue was pulverized, sieved to particle size (40 mesh), washed with distilled water, and let it air-dried, then 3mL of 20wt% KOH solution was mixed with 1g astragalus residue. The resulting chemical-loaded sample was then heated in a muffle furnace (Carbolite HVT-1200, Tianjin, China) and activated at 600°C for 80 minutes, then the product was cooled to room temperature, soaked with 0.1mol/L HCl to remove the residual KOH and washed sequentially several times with distilled water until its filtrate reached neutral pH. The resulting activated carbon material was dried at 80°C for 12h and stored for subsequent use. (designed as ASC)

2.3. CTAB modification of ASC

CTAB treatment of activated carbon was carried out by dipping and heating methods. 10g of ASC was put into 1L 0.05mol/L CTAB solution for 7 hours at 70°C. The modification was conducted under stirring in a flask equipped with a stirrer and a reflux condenser and heated in a thermostat water bath. The modified ASC was washed repeatedly with distilled water until the pH of the effluent water was neutral, dried at 80°C for 12h, after the treatment the sample was cooled to room temperature and stored in a desiccator for later use (designed as ASC-CTAB).

2.4. Instruments used for characterization

The surface morphology was observed by scanning electron microscopy (SEM, HITACHI S-3400N). FTIR spectra of the astragalus residue activated carbon before and after modification were recorded in 400–4000cm⁻¹ using a Nicolet, NEXUS670 model FTIR spectrometer with KBr discs. The X-ray diffraction (XRD, Shimadzu XRD-6000) patterns were collected using Cu K α radiation. The surface areas and pore characteristics of the prepared carbons were determined by nitrogen adsorption and desorption analysis (Micromeritics, ASAP2020). The Boehm titration method [11] was carried out to identify the surface functional groups of activated carbons both qualitatively and quantitatively.

2.5. Batch experiments

Adsorption experiments were conducted in a batch mode using 15mL of an aqueous methylbenzene solution and ASC and ASC-CTAB as adsorbents. 30mg of adsorbents were added to the methylbenzene solutions. Equilibrium adsorption data of methylbenzene were obtained with an adsorption period of 1h at 25°C and a pH of 7.5. All of the adsorption experiments were conducted in triplicate. The concentration of methylbenzene in the filtrate was analyzed using UV/visible spectroscopy (UV-3600, SHIMADZU) at 206 nm. The amount of methylbenzene adsorbed (mg/g) was calculated based on a mass balance equation given below:

$$q = \frac{(c_0 - c_e)V}{m} \quad (1)$$

where q is the adsorbent capacity in mg/g; c_0 and c_e is the initial concentration and the equilibrium concentration of methylbenzene in mg/L; V is the volume of methylbenzene solution in contact with the adsorbent in L; and m is the weight of adsorbent in g.

3. Results and discussion

3.1. Characterization of adsorbents

The Boehm titration results for ASC and ASC-CTAB are shown in Table 1. It was clear that the number of phenolic hydroxyl, carboxylic, lactone groups decreased after modification by CTAB, revealing that CTAB could bring down the polarity of ASC by reducing the activated carbon acidic groups.

Table 1. The functional group content of adsorbents.

Sample	ASC	ASC-CTAB
Lactonic groups(mmol/g)	0.23	0.16
Phenolic hydroxyl groups(mmol/g)	1.07	0.74
Carboxylic acid groups (mmol/g)	0.42	0.28

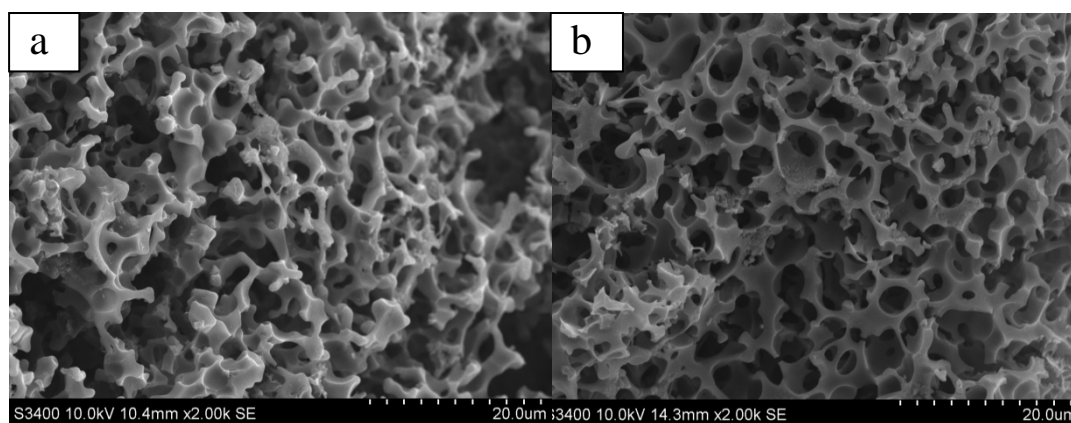


Figure 1. SEM images of ASC (a) and ASC-CTAB (b)

For the initial ASC, the BET surface area is 1519.53m²/g, which decrease to 496.88m²/g after modification. Results indicate that the pore structure of the ASC-CTAB is destroyed by CTAB and CTAB was almost uniformly deposited on the surface of ASC-CTAB, leading to pore blockage partly.

The SEM images of ASC and ASC-CTAB are shown in Figure 1. It can be seen that both of their surface present honeycomb structure, and the external surface is full of spaces, channels and cavities.

The surface of ASC-CTAB colour deepened and maybe loaded CTAB on the surface due to the adsorption after the modification.

Figure 2 shows the FTIR spectra of ASC and ASC-CTAB. The FTIR spectrum of ASC plots a band at 1575 cm^{-1} which was attributed to the double bond ($\text{C}=\text{C}$) vibrations in an aromatic system and the highly conjugated $\text{C}-\text{O}$ stretching vibration bands [12, 13]. Compared with the FTIR spectrum of ASC, It can be seen that CTAB modification can change IR adsorption peaks and produce new IR adsorption peaks. The peak occurring at 3433 cm^{-1} shows to stretching vibrations of $-\text{NH}$ [14]. The peaks observed at 2928 cm^{-1} and 2872 cm^{-1} can be attributed to the $\text{C}-\text{H}$ stretching vibrations of methyl and methylene groups [15, 16]. These spectral changes indicated that CTAB molecules have interacted with functional group of ASC in the process of modification [9]. Those results also suggested that there were more nonpolar groups in ASC-CTAB than ASC, which corresponded well with the results of Boehm titration.

The XRD spectra of ASC and ASC-CTAB are presented in Figure 3. The diffraction spectrum of ASC (Figure 3a) displayed two diffraction peaks around 26° and 43° , corresponding to the (002) and (100) diffractions of graphite [17]. The diffraction spectrum of ASC-CTAB is shown in Figure 3b. Compared with the ASC, not much has changed before and after the modification, as our results indicate, CTAB modification does not affect the crystalline structure of ASC.

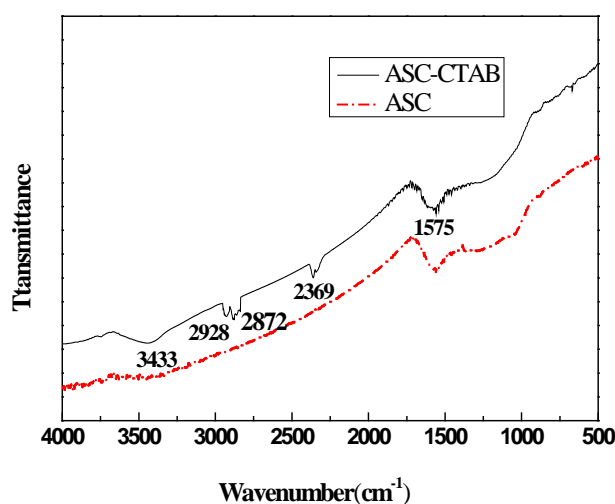


Figure 2. FTIR spectra

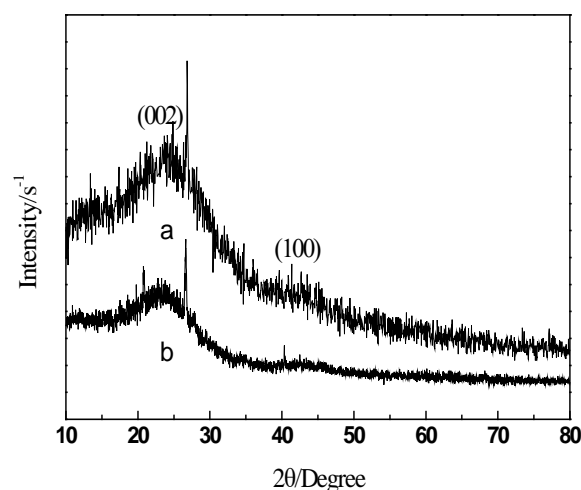


Figure 3. XRD patterns of ASC(a) and ASC-CTAB (b)

3.2. Adsorption experiments

The adsorption isotherms of methylbenzene on ASC and ASC-CTAB with the initial concentrations of methylbenzene from 100 to 500 mg/L at 25°C are shown in Figure 4. It shows that the adsorption capacity of methylbenzene on ASC-CTAB is higher than that of ASC, which is due to the oxygen-containing functional groups decreased when compared with ASC as discussed above, resulting in a reduction in surface polarity, leading to the adsorption capacity of ASC-CTAB increased for non-polar or weak-polar substance.

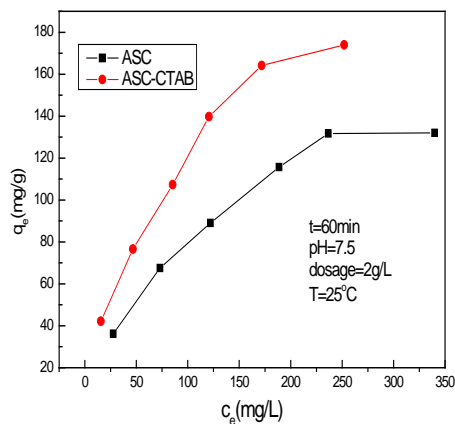


Figure 4. Adsorption isotherms

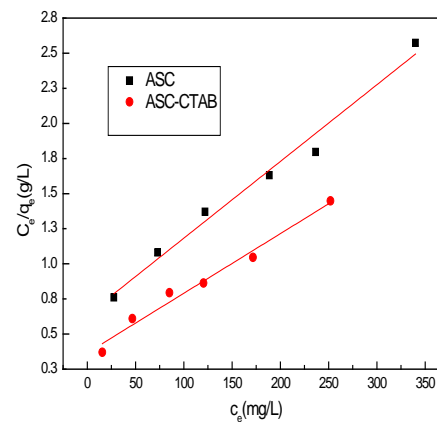


Figure 5. Langmuir plots

The equilibrium adsorption isotherm model is fundamental in describing the interactive behaviour between adsorbate and adsorbent. Analysis of isotherm data is important for predicting the adsorption capacity of the adsorbent. The experimental data of equilibrium isotherm for methylbenzene on ASC and ASC-CTAB were analyzed with the most frequently used Langmuir (Eq. (2)) isotherms [18]:

$$\frac{c_e}{q_e} = \frac{1}{q_m b} + \frac{c_e}{q_m} \quad (2)$$

where c_e (mg/L) is the equilibrium concentration of methylbenzene, q_e (mg/g) is the adsorption capacity of methylbenzene at equilibrium, q_m (mg/g) is the maximum adsorption capacity of adsorbent, and b (L/mg) is the Langmuir isotherm coefficient.

As shown in Table 2 and Figure 5, the adsorption patterns of methylbenzene on ASC and ASC-CTAB are well fitted by Langmuir model, because the correlation coefficient (R^2) is much close to 1. It implied that monolayer adsorption played a dominant role in the adsorption of methylbenzene onto the adsorbent [7, 19]. According to the Langmuir isotherm, the maximum adsorption capacities of ASC-CTAB for methylbenzene are 235.18 mg/g, which are much higher than that of ASC.

Table 2. Langmuir parameters.

Adsorbent	Langmuir		
	q_m (mg/g)	b (L/mg)	R^2
ASC-CTAB	235.18	0.012	0.9761
ASC	183.56	0.009	0.9795

4. Conclusions

In the present work, astragalus residue was used as a raw material to prepare activated carbon(ASC), and then ASC was modified by CTAB, ASC and ASC-CTAB were used to adsorb methylbenzene in simulated wastewater. The number of polar functional groups on the surface of ASC-CTAB decreased and nonpolar functional groups increased when compared to that of ASC. The FTIR spectrum of ASC-CTAB produces new $-\text{CH}_2-$ and $-\text{CH}_3$ stretching vibration peaks. Based on the SEM images, CTAB was loaded on the surface of ASC after the modification. The Langmuir model described properly the adsorption isotherm data of methylbenzene on the adsorbents. The maximum adsorption capacity of

ASC-CTAB for methylbenzene was measured up to 235.18 mg/g. The results indicated that using CTAB as a modifier for modification can markedly enhance the methylbenzene removal from aqueous solutions.

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