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Enhanced adsorption of atrazine on a coal-based activated carbon modified with sodium dodecyl benzene sulfonate under microwave heating

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A B S T R A C T

The concentrations of sodium dodecyl benzene sulfonate (SDBS), modification time and temperature were considered to be the specific factors that influence the SDBS-modified coal-based activated carbon (SCACs). The superior properties of the SCACs were assessed through the adsorption amount of atrazine under same conditions. The adsorption capacity of optimal sample (SCAC-10) that the CAC was modified in 50 ml of 0.6 mmol/l SDBS aqueous solution for 10 min under microwave heating (MWH) is superior. Compared with the CAC sample, the acidic functional groups of the SCAC-10 sample were reduced, thereby resulting in the increasing pH_{pzc} value, the pore volume and specific surface area, and the elemental analysis results exhibited the O/C ratio of the SCAC-10 sample decreased from 0.41 to 0.38, which is consistent with X-ray photoelectron spectroscopy analysis results. The kinetics of adsorption fitted with pseudo-second-order model perfectly, and the Langmuir model was suitable for the SCAC-10 samples with a maximum capacity of 222.22 mg/g. Results exhibited the modification of CAC by SDBS with MWH can effectively improve the adsorption capacity of the samples for atrazine.

1. Introduction

Atrazine, which is a triazine herbicide, has been extensively applied since the 1950s and selected to increase the production of corn because of its low cost and high efficiency. Over the past decades, the consumption of atrazine was in the tens of thousands of tons around the world [1]. As atrazine is a kind of endocrine disrupting, potentially carcinogenic and toxic chemical and it easily migrates, has long residue, and natural stability [2,3], it was frequently detected in soils, groundwater and surface water, and its residues can be found in animals and foods, thereby influencing human health and ecological environment. Although atrazine had been banned by European countries, and the World Health Organization established drinking water standards for priority pollutants, it is still extensively utilized globally, thereby resulting in serious problems of water environment. So the research and development of highly effective and economic techniques for removing atrazine have been always encouraged.

Various technologies and processes including advanced oxidation processes [4], biodegradation [5] and photocatalytic [6] have been explored for removing atrazine from water. Nevertheless, adsorption is consistently recognized as one of the most effective techniques for water treatment, because of its high removal efficiency, simple operation and absence of by-products [7]. Atrazine can be efficiently removed from wastewater by using a wide variety of adsorbents, therein activated carbons (ACs) have been usually extensively to clean up atrazine around the world, which is attributable primarily to the superior properties in the surface area, porosity, functional groups and surface activity [8–10]. Furthermore, the adsorption capacity of the modified ACs was promoted to a certain extent because of the superior properties to absorb the target pollutants. Atrazine is hydrophobic and non-polar because it possesses a heterocyclic aromatic ring and a nonpolar aromatic compound [10]. It is an appealing proposition to develop a highly selective sorbent for adsorption atrazine. ACs have been modified by different regents to improve the structure and chemical properties and enhance the adsorption capacity for removing atrazine [3,10]. Recently, Lupul et al. discussed the effects of the modification by N_2, HNO_3 and NH_3 on the adsorption of atrazine onto the

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Table 1
Textural characteristics evaluated by the N_2 adsorption–desorption isotherms at 77 K of the samples.

Parameters	CAC	SCAC-5	SCAC-10	SCAC-15
BET specifics surface area (m²/g)	960.295	898.267	992.984	934.268
Micropore specifics surface area (m²/g)	748.914	697.745	772.378	720.011
External specifics surface area (m²/g)	211.381	200.522	220.606	214.257
Total pore volume (m^3/g)	0.382	0.360	0.405	0.383
Micropore volume (cm³/g)	0.294	0.272	0.305	0.282
Average pore size (nm)	0.601	0.599	0.582	0.586

hemp stem-based ACs. Their results suggested that the increase in the C–C group led to an increase in the $\pi-\pi$ interactions between ACs and atrazine, thereby improving the adsorption amount of atrazine onto ACs [3]. Tan et al. reported that the corn straw-based biochar modified by Na_2S and KOH was effective in the adsorption of atrazine [10]. It was demonstrated that the differences in the types and concentrations of the surface functional groups of sorbents may affect the adsorption mechanism of biochar for pollutants. Currently, several surfactant-modified ACs can effectively improve the adsorption capacity of sorbents for pollutants. Ahn et al. reported that the ACs modified by sodium dodecyl sulphate (SDS) exhibit the significantly high adsorption capacity for heavy metal [11]. Moradi also reported that ACs modified by SDS are good adsorbent for the removal of MB dye [12]. However, it is little known about enhancing adsorption of atrazine onto the ACs modified by anionic surfactant.

Previous studies reported that the superior coal-based activated carbon (CAC) was prepared from the coal produced in Xinjiang region of China [13] and microwave heating (MWH) was proved to be an efficient and rapid method for modifying ACs [14], as the temperature rising fast and uniform temperature distribution of CAC by microwave thermal, and microwave thermal can save energy compared with traditional heating. In this paper, the modification of CAC by anionic surfactant SDBS under MWH to bring about highly efficient adsorbent performance for removing atrazine was an important innovation and interesting exploration. Meanwhile, the relationship between the structure and properties of the modified CACs and the adsorption mechanism of atrazine are very worthy of interpretation. This study could develop an effective method to remove harmful pesticides, particularly for atrazine, and provide a comprehensive reference for other studies.

2. Materials and methods

Details of the preparation and characterization means of SCACs, the effects of different modification and adsorption conditions on the adsorption of atrazine onto the materials were given in the Supplementary file.

3. Results and discussion

3.1. Characterization

3.1.1. BET analysis

The nitrogen adsorption–desorption isotherms of the samples are shown in Fig. 1. According to IUPAC classification states that all the adsorption isotherms of N_2 on the samples are type-I, which tend to be stable at high P/P_0 and increase substantially at low P/P_0 [15]. These isotherms clearly exhibit the mainly microporous nature of carbon materials. The conclusions are similar to the results reported by Wibowo et al. [16]. The textual properties of CAC and SCACs modified for different times are listed in Table 1. It can be seen that the modified time affects the pore size distribution, the BET specific surface area and total pore volume. The optimal modified time was demonstrated to be 10 min and the SCAC-10 sample is better than other adsorbents in the above properties.

Although the specific surface area and total pore volume of SCAC-5 and SCAC-15 are smaller than that of CAC, which may have caused the main pore channels to be obstructed. The adsorption amounts of atrazine onto SCAC-5 and SCAC-15 are higher than that onto CAC. Obviously, the new functional groups built in SCAC-5 and SCAC-15 brought about the changing in the surface properties. As compared with the adsorption of CAC, the adsorption amount of SCAC-10 for atrazine is higher, since the increase of its micropore volume and specific surface area. The results are consistent with the influence of the modified time on the adsorption, shown as Fig. S1. Tan et al. have illustrated that the superior porous structure and BET specifics surface area play the important role in the adsorption of atrazine onto biochars [10]. Liu et al. studied the porous structure and BET specific surface area of the biochars from two different feedstocks (peanut shell-PB; wheat straw-WB) were lower than the samples in this paper, so the adsorption capacity of their samples for atrazine isn't superior [17]. Furthermore, the results reported by Chingombe et al. had showed that adsorption of organic molecules with low molecular weight was more suitable for the microporous region [18].

3.1.2. Elemental analysis

After the modification, the C content increased from 68.03% to 69.39%, while the O content decreased from 28.16% to 26.75% (see Table 2). The decrease of the oxygen content of the SCAC-10 led to the reduction of its polarity [19]. In addition, the O/C and $(O+N)/C$ ratio decreased from 0.41 to 0.38 and 0.42 to 0.39, respectively, which suggested that the increase of hydrophobicity of material and the reduction of polar groups of material would be benefit for the adsorption of atrazine. Similar conclusions had been derived by Tan et al. [10]. What's more, the H/C values of samples are less than 1.0, indicating that the samples are highly carbonized and exhibits a highly aromatic structure [20]. And the increase of H/C value of SCAC-10 is in favor of adsorption of atrazine as demonstrated by Chingombe et al. [18].

3.1.3. Surface acidity and basicity, surface functional groups and pH_{pzc}

The pH_{pzc}, the surface acidity, surface basicity and compositions of the surface functional groups of CAC and SCAC-10 are listed in Table 2. The pH_{pzc} value increased because of the decrease in carboxyl, lactone, and phenol in the modification process [21], which was also demonstrated by the XPS analysis (shown in Fig. S3) and the elemental analysis. Chingombe et al. indicated that the reduction of acidic oxygen-containing functional groups of adsorbent is conducive for the adsorption of atrazine [17].

With the introduction of SDBS into SCAC-10, the hydrophobicity and the degree of carbonization increased, leading to reduction of acidic functional groups and the enhancement of π electron density [2]. Thus the $\pi-\pi$ interactions between SCAC-10 and atrazine were enhanced and the reduction of acidic oxygen-containing functional groups, resulting in promoting the adsorption capacity of absorbent.