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Adsorptive desulfurization using different passivated carbon nanoparticles by PEG-200

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ABSTRACT

Carbon nanoparticles dispersed in aqueous phase (CNPs) were synthesized using different poly(ethylene glycol) (PEG 200) assistant solution methods including microwave pyrolysis and alkali-assisted heating, ultrasonication, and refluxing. The CNPs (<5 nm) were used for the selective removal of sulfur thiophenic compounds (benzothiophene (BT), dibenzothiophene (DBT) and dimethyldibenzothiophene (DMDBT)) from liquid model fuels including aromatic compounds (naphthalene (NP) and 1-methylnaphthalene (MNP)). The presence of PEG in the preparation procedure of CNP was crucial and adsorption capability was related to the passivation by PEG. The decomposition of PEG at high temperature introduced more acidic functional groups on the carbon framework and also promoted the formation of porous CNP nanostructures because of hydrophobic PEG aggregations. Adsorption experiments showed the order for CNPs with different method as: microwave irradiation > heating > refluxing > ultrasonication. The highest efficiency of CNPs by microwave-assisted technique for sulfur removal was examined due to the higher decomposition of PEG and more porosity of CNP nanostructures which were produced at higher temperature. Moreover the CNPs were regenerable by a solvent-washing process. This study showed that passivated CNPs are very effective for rapid desulfurization of liquid fuels, operating at ambient conditions with the ease of separation and regeneration.

1. Introduction

The harmful effects of sulfur oxide (SOx) pollution on environment have imposed stringent sulfur regulation on automotive fuels globally [1]. Thus, in recent years the reduction of the sulfur content in fuel to reach a sulfur level of less than 10 ppm has received much attention in many countries. The demand for producing low-sulfur fuels imposes significant challenges to current desulfurization methods and the development of new technologies. To reach this low level, it is required that the highly refractory S-containing compounds, such as benzothiophenes and most refractory substituted dibenzothiophenes (e.g. 4,6 dimethyldibenzothiophene) are removed from fuels [2–4]. Sulfur removal from various liquid hydrocarbon fuels has conducted by the catalytic hydrodesulfurization (HDS) process at 300–400 °C and high hydrogen pressure with high hydrogen consumption in refineries. Unfortunately, when this level of deep desulfurization is attempted, the catalytic hydrodesulfurization process conditions become very severe, leading to increased process cost [5,6].

Various new approaches to deep desulfurization of liquid hydrocarbon fuels have been reported in the literature [5,7–9]. Adsorption by novel adsorbents due to their high capacity and selectivity has highly attracted researchers [10–14]. Plenty of research has been conducted to find adsorbent materials that are highly selective towards sulfur compounds, in the presence of coexisting aromatic hydrocarbons and olefins that account for a large excess in the fuel. Activated carbon [11,15,16], zeolite [13,17] and mesoporous materials [6] are the well-known adsorbents. Nano-adsorbents such as nano γ-alumina [18,19] and loaded nanoparticle adsorbents [20] have been recently reported for the removal of organosulfur compounds.

Carbon nanoparticles (CNPs), a novel class of recently discovered nanocarbons, consist of discrete, quasispherical nanoparticles with sizes below 10 nm [21]. CNPs have attracted considerable attention because of their abundant photo-physical or chemical properties, low cost and good water-solubility. During the past few years, much progress has been made in the synthesis, properties and applications of CNPs. CNPs have been synthesized by various methods such as the candle soot oxidation, carbohydrate carbonization, thermal decomposition of small molecules, pyrolysis of polymers, microwave-based assisted pyrolysis and electrochemical methods [22].

The strong and tunable fluorescence, capable surface functionalities, and the variety of simple, fast and cheap synthetic routes promotes the wide application of CNPs in catalysis, bio-imaging, optoelectronics, sensors, surface-enhanced Raman scattering and as replacements for toxic metal-based quantum dots (QDs) and photoactive nanocatalysts [21,23]. Han et al. have successfully constructed different complex

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Table 1
Adsorbents synthesis: method preparation, optimized conditions and materials used.

Adsorbents	Method preparation	Optimized conditions		Materials used			
		Time (min)	Power/temperature	Glucose	Distilled water (mL)	Sodium hydroxide	PEG 200 (mL)
Micr.$_{\text{GHP-9 min}}$	Microwave irradiation	9	600 W and 2450 Hz	1 g	5	–	15
Micr.$_{\text{HP-9 min}}$	Microwave irradiation	9	600 W and 2450 Hz	–	5	–	15
Micr.$_{\text{HPN-5 min}}$	Microwave irradiation	5	600 W and 2450 Hz	–	5	Basic solution	15
Micr.$_{\text{HPN-9 min}}$	Microwave irradiation	9	600 W and 2450 HZ	–	5	Basic solution	15
Heating$_{\text{GHPN-1.5 h}}$	Heating in water bath	90	90 °C	0.7 g	5	Basic solution	15
Refluxing$_{\text{HPN-6 h}}$	Heating with refluxing	360	120 °C	–	10	3 g	50
Ultrasonic$_{\text{GHPN-4 h}}$	Sonication in ultrasonic bath	240	150 W	10 mL of glucose solution (1 M)	–	10 ml of NaOH solution (1 M)	60

photocatalysts such as TiO_2/CQDs, SiO_2/CQDs, Fe_2O_3/CQDs, ZnO/CQDs, and Cu_2O/CQDs, and applied these in organic contaminant photodegradation with visible or near infrared light excitation [23].

The application of CNPs as an adsorbent for fuel was first reported by our research group [24,25]. In our previous work we demonstrated the efficiency of CNPs for the adsorption of thiophenic sulfur compounds from simulated model diesel fuel. Because of the immiscibility of CNPs aqueous solution in organic phase, it can be used as an adsorbent for removal of sulfur compounds from liquid fuel. Due to the presence of carboxylic acid groups at the surface of CNPs, they have excellent water solubility and suitability for subsequent functionalization with various organic, polymeric, inorganic, or biological species [21].

In our previous works, the synthesized CNPs in aqueous media were presented as a novel adsorbent for the removal of sulfur from liquid fuel and the importance of presence of PEG in preparation of carbon nanoparticles which have capability for desulfurization was not clear. In the present study, it is found that only CNPs that are produced in the presence of PEG can remove the organosulfur compounds. To further clarify the dominant role of PEG in the production of nanoparticles with desulfurization ability and the adsorption mechanism of sulfur compounds by CNPs, we synthesized CNPs by different, rapid and low cost methods. The applied methodologies were microwave pyrolysis [26], alkali assisted heating [22], alkali assisted ultrasonication [27] and alkali assisted refluxing [28]. The synthesized CNPs were then used for the adsorption of the thiophenic compounds benzothiophene (BT), dibenzothiophene (DBT), 4,6-dimethyldibenzothiophene (DMDBT), naphthalene (NP) and 1-methylnaphthalene (MNP) from

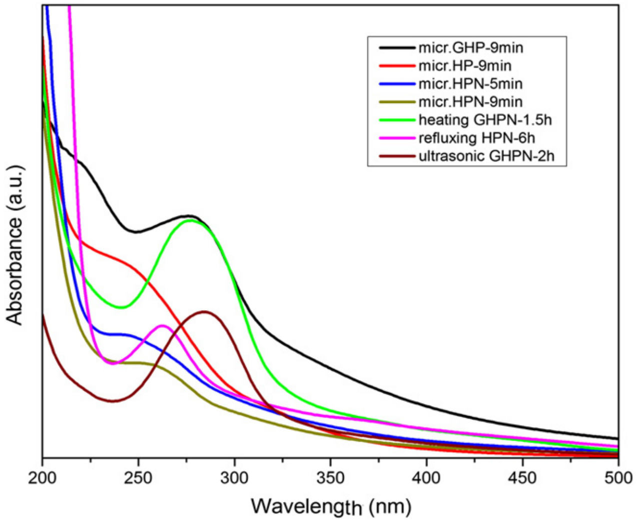
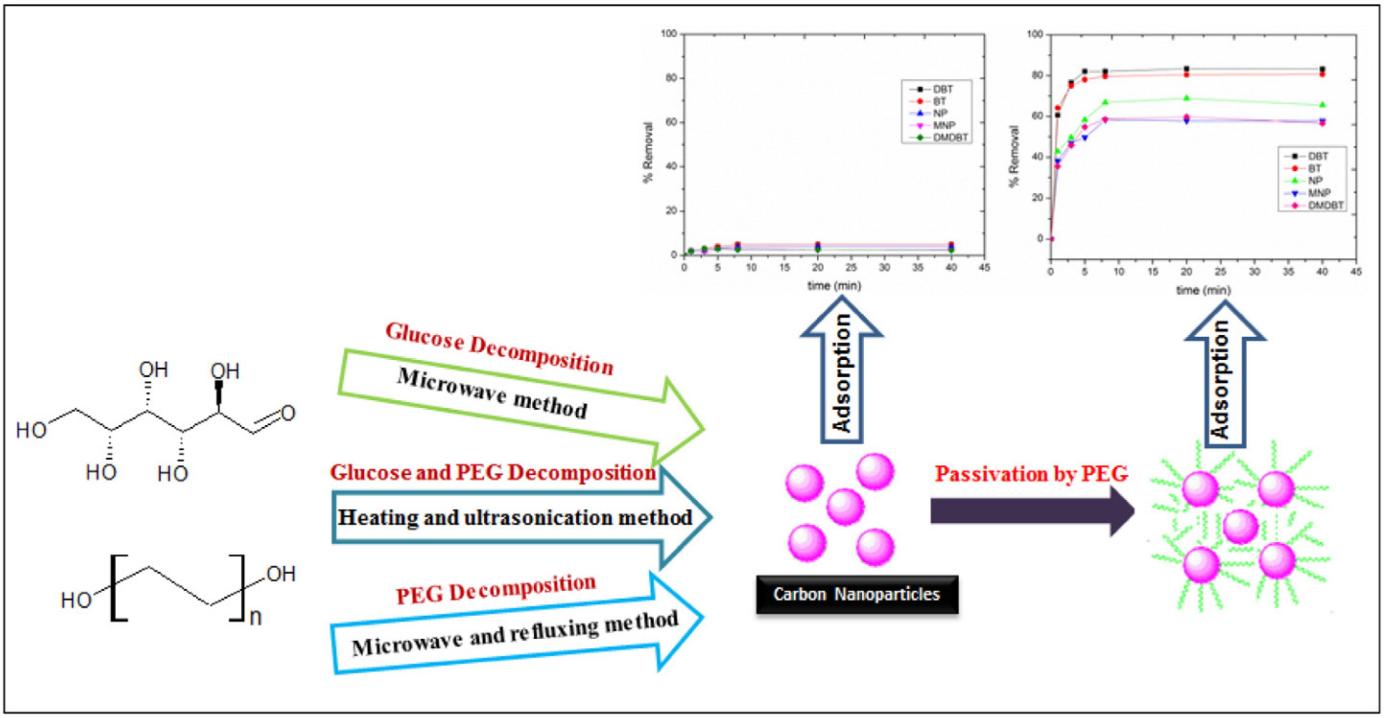


Fig. 1. UV/Visible absorption spectra of different CNPs.



Scheme 1. The preparation, passivation and adsorption process by CNPs.