Journal of
Chemical Engineering & Process Technology

Patil, J Chem Eng Process Technol 2013, 4:3
DOI: 10.4172/2157-7048.1000151

Research Article Open Access

Ultrasound-Assisted Desulfurization of Commercial Kerosene by Adsorption

Mahesh Shantaram Patil*

Vishwakarma Institute of Technology, Department of Chemical Engineering, Pune, India

Abstract

Sorption of hexyl mercaptan sulfur onto carbon-based adsorbents (activated carbon and carbon nanotubes) by ultrasonic irradiation was investigated. The adsorptive capacity was examined. Carbon nanotubes show higher adsorptive capacity. The experimental data were fitted to the Langmuir and Freundlich adsorption isotherm model.

Keywords: Ultrasound; Hexyl mercaptan sulfur; Adsorption; Activated carbon; Carbon nanotubes

Introduction

The topic of research deals with removal of sulphur from commercial kerosene by adsorption “concerned with the desulphurisation” from a hydrocarbon strea. In 2006 the EPA reduced the allowable sulphur levels in liquid fuels. Gasoline sulphur limit was reduced from 300 ppmw to 30 ppm and diesel fuel sulphur limit was reduced from 500 ppmw to 15 ppmw [1]. Deep desulfurization of liquid hydrocarbon fuels is becoming an important subject worldwide. The desulfurization performance of sold super acid type adsorbent (sulphated alumina) for commercial kerosene was evaluated on batch system and on continuous flow system [2]. The removal of sulphur components from gasoline by carbon nanotubes for use as support in catalysis was conducted in batch conditions [3]. A novel approach to ultra-deep desulfurization of transportation fuels by sulphur-selective adsorption for pollution prevention at the source studied [4]. The mercaptan in kerosene is partially oxidized and the remaining was removed by a carbon impregnated with an oxidation catalyst [5]. Hexyl mercaptan was selected as a solute (adsorbate) since this mercaptan was present in substantial amount in typical naphtha [6].

Experimental

Materials

Hexyl mercaptan, activated carbon and carbon nanotubes were procured from Sigma Aldrich.

Preparation of carbon adsorbents

The activated carbon and carbon nanotubes were then washed with acidified distilled water to remove the greasy material and dust and then washed with distilled water till the washing give a clear transparent liquid free from turbidity. Usually 8-10 times of washings are required for this cleaning operation. The washed carbon adsorbents were dried in an oven for 24 hrs at 100-110°C.

Properties of commercial kerosenes

Table 1 shows sulfur contents of Thiophene type and benzothiophene type of kerosene A and kerosene B were 2.8 mass ppm (mg-sulfur/kg-kerosene) and 4.7 mass ppm respectively [2].

Apparatus and procedure

Sono-sorption batch experiments were performed using ultrasonic bath with frequency of 22.5 kHz and a nominal power of 120 Watt (ULTRASONICS LABLINE CL 500).

Properties	Commercial kerosene A	Commercial kerosene B
Total sulfur content [mass ppm]	5.6	6.4
Sulfur content of TP type and BT type [mass ppm]	2.8	4.7
Boiling point range [^{0}C]	146.5-278.0	158.0-271.5
Density at 15^{0}C [g/m*l*]	0.794	0.7940
Aromatics content [vol%]	17.8	16.9

Table 1: Properties of Commercial Kerosenes.

The stock solution of hexyl mercaptan in kerosene was prepared (10 g/l) and further diluted to desired concentrations. The hexyl mercaptan solution (100 ml) in Kerosene was taken in the ultrasonic bath. The initial hexyl mercaptan concentration was taken in the range of 100-4000 mg/l. The solution containing hexyl mercaptan in kerosene and carbon adsorbents was irradiated for 10 min and 1 h to reach equilibrium.

FTIR TEM UV spectroscopic and X-ray diffraction spectroscopy: Powder XRD grams of activated carbon and carbon nanotube were recorded by means of X-ray diffractometer (Brucker D8). Fourier transform infrared ray (FTIR) spectroscopic measurement was performed on a spectrometer (FTIR-8400; Shimadzu) with a resolution of 4.00 cm^{-1}. The adsorbent materials were characterized by Fourier transform infrared (FTIR) spectroscopy in KBr phase. Infrared spectra were recorded in the range 3800-600 cm^{-1}. Transmission electron microscopy (TEM) image was taken on a 120 kv JEOL1210 equipped with EDS analyzer Link QX-2000.

UV–VIS spectrophotometer (SHIMADZU 160A model) was used for determination of Hexyl mercaptan concentration .The wavelength of maximum absorbance of hexyl mercaptan was 230 nm.

Results and Discussion

FTIR spectra of activated carbon and carbon nanotubes in the re

***Corresponding author:** Mahesh Shantaram Patil, Vishwakarma Institute of Technology, Department of Chemical Engineering, 666, Upper Indira Nagar, Pune-411037, India, Tel: 91-09422581310; E-mail: patil.mahesh.mahesh29@gmail.com

Received December 04, 2012; **Accepted** December 28, 2012; **Published** December 31, 2012

Citation: Patil MS (2013) Ultrasound-Assisted Desulfurization of Commercial Kerosene by Adsorption. J Chem Eng Process Technol 4: 1501doi:10.4172/2157-7048.1000151

region of 600-3800 cm^{-1} are shown in figure 1. Sharp peaks are observed in activated carbon and carbon nanotubes. To characterize the functional elements absorbed by activated carbon and carbon nanotube, FTIR is used. FTIR of a) shows sharp peak at 900, 1000, 1200, 1500, 1790 and 2800 cm^{-1} which corresponds to hydroxyl, carbonyl, aliphatic, ethers, aromatic C=C stretching and carboxylic groups respectively. FTIR of b) shows dominant peaks at 800, 900, 1250, 1500, 1600, 1800, 2800 and 3300 cm^{-1} which corresponds to Si-O, C-N, N-CH_3, CNT, C-O, and C-Hx respectively. The nanometric length of the carbon nanotubes was found in the range of 100 nm (Figure 2) [7].

X-ray diffraction patterns activated carbon and carbon nanotubes are reported in figure 3. It was observed as a broad intense peak in the case of activated carbon and a small peak in the case of carbon nanotubes. X-ray studies have shown that many so-called amorphous substances have crystalline characteristics even though they may not show certain features such as crystal angles and faces usually associated with crystalline state. Although interpretation of the X-ray diffraction patterns is not free from ambiguities there is general agreement that amorphous carbon consists of plates in which the carbon atom are arranged in a hexagonal lattice each atom except those at the edge being held by covalent linkages to three other carbon atom.

The time versus concentration data has shown in figure 4. The equilibrium reaches within 20 min for both adsorbents.

Figure 5 shows the effect of different initial concentrations of hexyl mercaptan in kerosene ranging from 100 to 4000 ppm. The mixture of hexyl mercaptan in kerosene and 0.5 g adsorbent was irradiated to ultrasound. It is clearly shows that activated carbon affect the adsorption for higher range of hexyl mercaptan concentration.

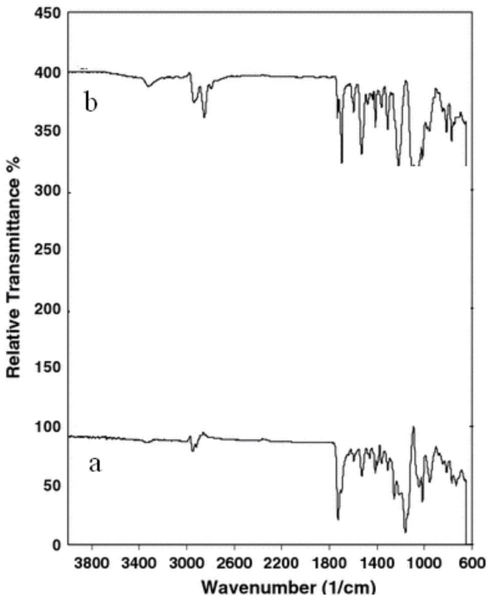

Figure 1: FTIR spectra of activated carbon and carbon nanotubes. a – activated carbon, b- carbon nanotubes.

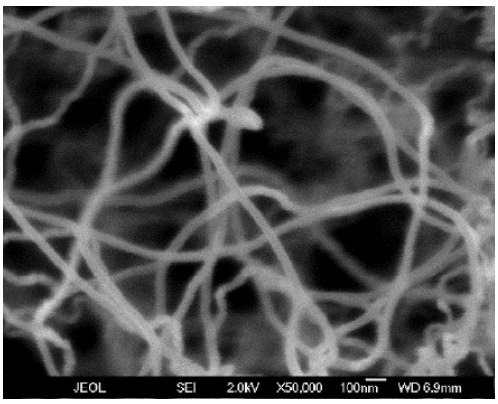

Figure 2: TEM image of carbon nanotube.

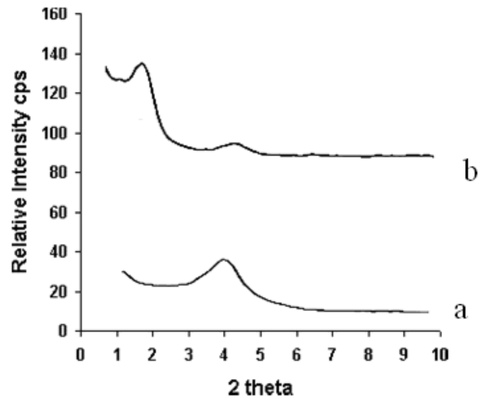

Figure 3: XRD gram of activated carbon and carbon nanotubes. a – activated carbon, b- carbon nanotube.

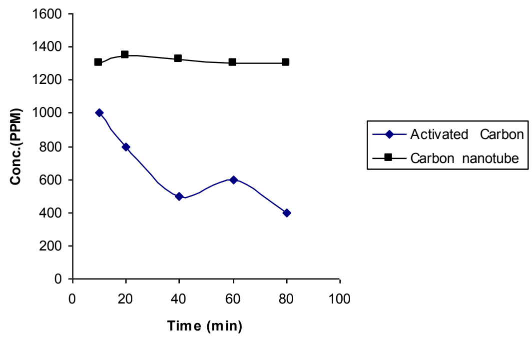

Figure 4: Time Vs carbon phase concentration curves for carbon adsorbents (Co = 2000ppm, 0.5 g adsorbents).

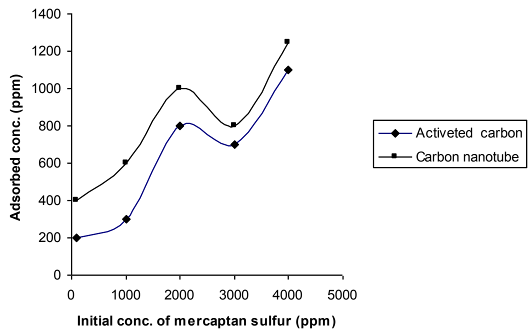

Figure 5: Effect of initial concentration on different adsorbents (adsorbents quantity -0.5g).

Figure 6 shows the effect of adsorbents onto the adsorption capacity of activated carbon and carbon nanotubes at 2000 ppm concentration of hexyl mercaptan. At 0.1 and 0.3 mg of adsorbent activated carbon shows less adsorption in comparison to carbon nanotubes at 2000 ppm concentration of hexyl mercaptan.

Isotherm models

The Langmuir isotherm model for carbon-based adsorbents sono-sorption (Figure 7) is shown by the linear plot of Ce/qe versus Ce. The parameters Qo and b were determined from the slope and intercept of the plot and were presented in table 2.The sono-sorption follows Freundlich isotherm model for activated carbon and carbon nanotubes is shown by the linear plot of log qe versus log Ce. From the intercept and slope k and 1/n were calculated for carbon nanotubes (Figure 8) the constants are 1.012 and 0.0053 (slope and intercept) [8]. It is generally stated that values of n (1/n=0.0053; n=188) less than 1 poor adsorption [9]. From R^2 values it is found that these two adsorbents favour both Langmuir and Freundlich adsorption isotherm.

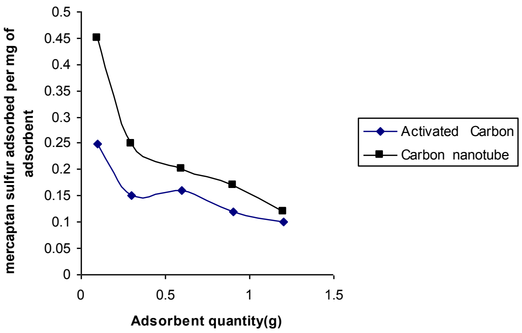

Figure 6: Hexyl mercaptan adsorbed on adsorbents (Initial hexyl mercaptan concentration 2000ppm).

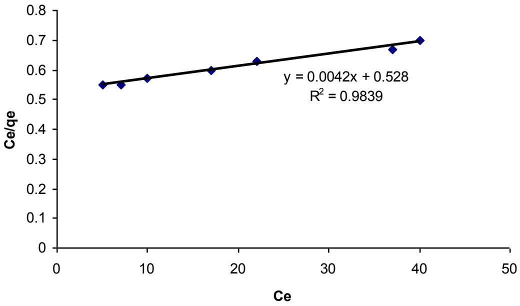

Figure 7: Langmuir adsorption isotherm for carbon nanotubes.

Langmuir parameters	Langmuir isotherm activated carbon	carbon nanotubes
Q_0(mg/mg)	0.0078	0.528
B(l/mg)	5.6363	0.0042
Correlation coefficient (R^2)	0.9795	0.9839
Freundlich parameters	**Freundlich isotherm activated carbon**	**carbon nanotubes**
Slope(1/n)	5.3023	0.0053
Intercept log k	0.0198	0.1913
Correlation coefficient (R^2)	0.9755	0.9813

Table 2: The Freundlich and Langmuir parameters of adsorption isotherm models.

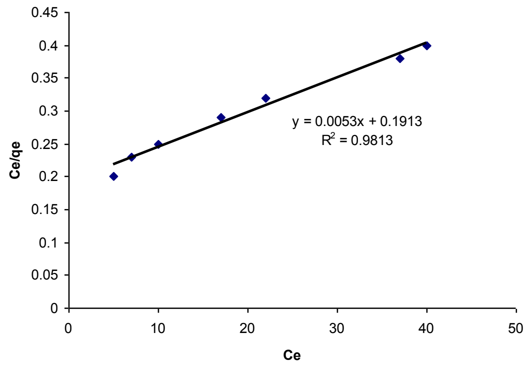

Figure 8: Freundlich adsorption isotherm for carbon nanotubes.

Intercalating agent	ΔH (kJ/mol)	ΔS (J/mol K)	-ΔG (kJ/mol) at temperature			
			308K	319K	329K	338K
activated carbon	7.48	16.41	20.00	13.39	15.00	15.32
carbonnanotubes	22.00	22.72	30.18	26.08	26.17	28.03

Table 3: Thermodynamic parameters for adsorption of hexl mercaptan (2000ppm) onto carbon adsorbent (5g/L).

Evaluation of thermodynamic parameters

Considering the equilibrium constant Thermodynamic data such as adsorption free energy change Ko can be obtained from the following equation:

$\Delta G^0 = RT\ln K^0$ (2)

Where ΔG^0 is the free energy change (kJ/mol), R the universal gas constant (8.314 J/mol K), K^0 the thermodynamic equilibrium constant and T the absolute temperature (K). The corresponding values of ΔG^0 are presented in table 3. The values of ΔG^0 obtained were ranged from -13 to -30 kJ/mol which indicates feasibility of adsorption. The Gibbs free energy shows the favourable adsorption in the following order activated carbon < carbon nanotube.

Conclusion

The hexyl mercaptan adsorbed per mg of carbon nanotubes is higher (0.40 mg) at higher hexyl mercaptan concentration (4000 ppm). The sono-sorption data of hexyl mercaptan on carbon-based adsorbents studied in this work fits well in Langmuir and and Freundlich model as can be seen from the regression coefficient values R^2 which is in the range of 0.97 to 0.98.

References

1. Ambal J, Gokhan OA, Margarita D, Mathew S, John M, et al. (2008) Desulfurization of liquid fuels by adsorption. TDA research Inc, USA.
2. Toida Y, Nankamura K, Matsumoto K (2010) Adsorptive Desulfurization of Commercial Kerosene with Sulfated Alumina Producing Heavier Organic Sulfur Compounds. J Japan petroleum Institute 53.
3. Manteghian M, Nouri Asl P, Pahlavanzadeh H, Soroush Samaneh (2008) Sulfur components removal from gasoline by carbon nanotubes. Iran.
4. Song, Chunshan, et al. (2006) EPA project. Pennsylvania State University.
5. Guy Francoise Tom varadi, Merichem Company (1993) Hydrocarbon Technology International.
6. Nelson WL (1958) Petroleum Refinery Engineering.
7. Misra A, Tyagi PK, Singh MK, Misra DS (2006) FTIR studies of nitrogen doped carbon nanotubes. Proceedings of the Applied Diamond Conference/ NanoCarbon 2005-ADC/NanoCarbon 2005.

8. Sonawane S, Chaudhari P, Ghodke S, Ambade S, Guliga S, et al. (2008) Combined effect of ultrasound and nanoclay on adsorption of phenol. Ultrasonics Sonochemistry 15: 1033-1037.
9. Robert E. Treybal (1981) Mass-Transfer Operations. (3rd edn), Mac- Graw Hill Publication, Singapore.