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Ultrasound regeneration of multi wall carbon nanotubes saturated by humic acid

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ABSTRACT

The main purpose of this study was to evaluate the efficiency of ultrasound technique for regeneration of multi wall carbon nanotubes exhausted by humic acid. Carbon nanotubes (CNTs) were prepared by chemical vapor deposition method in the presence of Co–Mg/MgO as the catalyst. Results of ultrasound regeneration (in frequencies of 130 and 35 kHz) showed higher regeneration efficiency at 130 kHz after five cycles of regeneration. The slight decrease in adsorption capacity after each regeneration cycle may be due to the deposition of decomposed residues in CNT pores, which blocked carbon porosity and decreased specific surface area. In conclusion, ultrasonic regeneration showed the possibility as an alternative to chemical and thermal regeneration of CNTs.

Keywords: Multi wall carbon nanotubes; Regeneration; Ultrasound; Humic acid

1. Introduction

Carbon nanotubes (CNTs) are promising materials for many potential applications such as adsorption of organic pollutants, compared with activated carbon due to their unique structure and properties [1–3]. Previous studies have shown that CNTs may present good removal capacity for organic pollutants [4]. Lu et al. [5] reported that thermally treated CNTs are efficient adsorbents for natural organic matters and possess good potential to be used in applications to produce water of high quality. In another research, this author investigated the removal of trihalomethanes by CNTs and found that purified CNTs have higher adsorption capacities for $CHCl_3$ in comparison to activated carbon.

The economics of the adsorption process by application of CNTs for removal of pollutants from water greatly depends not only on the adsorption capacity but also on the regeneration of CNTs. Until now, regeneration of CNTs exhausted with organic pollutants has been less studied.

In recent years, new techniques for regeneration of activated carbon have been developed, such as thermal treatment [6], chemical extraction [6,7], bioregeneration [8], supercritical regeneration [9] and ultrasonic regeneration [10].

Though thermal regeneration techniques are widely used, they also have several disadvantages such as loss of 5–10% carbon due to oxidation and attrition, and high energy consumption to keep the temperature between 800–850˚C. On the other hand, chemical regeneration is not necessarily acceptable

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because of the necessity for additional separation or decomposition steps [6]. Although bio-regeneration may be the most economical process, it also requires a long reaction time for regeneration [8]. Supercritical regeneration of carbon through extraction of the adsorbate into a supercritical fluid such as CO_2, is considered to be very expensive.

Hence these techniques are presenting drawbacks; it is of interest to explore other methods of regeneration. Ultrasonic regeneration has attracted attention due to its advantages such as removal of unwanted contaminants, decomposition of toxic organic pollutants, and for saving energy [11,12]. Previous studies have employed ultrasonic waves for regeneration of activated carbon exhausted with organic pollutants and found that high regeneration efficiency (RE) can be achieved.

The objectives of this study were to evaluate the feasibility of ultrasonic regeneration of multi wall carbon nanotubes (MWCNTs) saturated with humic acid which is widely known as an important contaminant of soil and surface water and to suggest the likely mechanism of ultrasonic regeneration.

2. Materials and methods

2.1. Preparation and purification of CNTs

MWCNTs were prepared by a special chemical vapor deposition (CVD) technique in the Research Institute of Petroleum Industry, Tehran, Iran. For synthesis of CNTs, the catalytic reactions were accomplished in the presence of Co–Mo/MgO as the catalyst. The CVD method was carried out in a horizontal furnace consisting of a quartz tube. The catalyst was set in a quartz boat that was placed into the quartz tube followed by purging in hydrogen stream in order to reduce the catalyst. The reaction was carried out using methane as the carbon source and hydrogen as the carrier gas at 900–1,000°C. The furnace was then cooled to room temperature under nitrogen atmosphere.

The black product was not pure and contained many impurities including various types of carbon (graphitic nanoparticles, amorphous carbon, fullerenes poly aromatic hydrocarbons, etc.) and catalyst material (particles containing metals and catalyst support). In order to purify and remove the metal nanocatalysts from CNTs, the product was dissolved in 37% hydrochloric acid solution for about 16 h at ambient temperature and then washed several times with distilled water until the solution's pH was adjusted to approximately neutral.The treated MWCNTs were dried in vacuum at 40°C overnight. For eliminating the amorphous carbons, the purified MWCNTs were placed in the furnace at 400°C for 30 min.

2.2. Adsorption-regeneration experiments

Humic acid stock solution (500 mg/L) was prepared by mixing a known amount of humic acid (Acros Organics Company, New Jersey, USA) with deionized water. Batch adsorption experiments were carried out in 250 mL glass bottles with MWCNTs at 25 ± 1°C at the Department of Environmental Health Engineering, Tehran University of Medical Sciences. At equilibrium, humic acid concentration remaining in the solution was determined at a UV absorbance wavelength of 254 nm by a Lambda UV/VIS-spectrophotometer (Perkin–Elmer) with cuvettes of 1 cm length. The amount of the adsorbed humic acid on to CNTs was calculated from:

$$q = \frac{(C_0 - C_e)V}{m} \tag{1}$$

where q is the amount of humic acid adsorbed by MWCNTs (mg/g); C_0 is the initial humic acid concentration (mg/L); C_e is the equilibrium concentration of humic acid (mg/L); V is the initial solution volume (L) and m is the MWCNTs dosage (g).

One gram of MWCNTs as the adsorbent was placed in the bottles and 1 L of a solution containing 100 mg/L of humic acid was added to the adsorbent. Then, the bottles were sealed with aluminum foil and placed on a rotary shaker IKA® RCT basic model and shaken at 180 rpm for 2 h to ensure that the adsorption process reached equilibrium. Our previous study has shown that under such conditions, MWCNTs were saturated. MWCNTs were separated from water by filtration, dried at 60°C for 2 h and milled (particle size < 0.15 mm).

One gram of saturated MWCNTs was loaded in a new bottle with 100 mL of ultra pure water and then placed at the ultrasonic bath and regenerated in frequencies of 35 and 130 kHz and with a power of 500 W. The temperature was controlled at 25 ± 1°C by a temperature-controlled circulation water bath. Additionally, 100 mL of 100 mg/L solution of humic acid was treated in the same experimental apparatus to examine the effect of sonochemical degradation of humic acid in aqueous solution.

To assess the effect of re-adsorption of desorbed humic acid onto MWCNTs, ultrasonically treated water was replaced with new ultra pure water every 10 min. For the replacement of water, treated MWCNTs were separated from the solution and then reloaded with new ultra pure water.

After each ultrasonic regeneration cycle, the MWCNTs were separated and dried. The saturation–regeneration process was carried out in five cycles and after each cycle the adsorption capacity of the regenerated MWCNTs was evaluated by measuring the adsorption isotherm at 25℃ and pH = 3.

RE of humic acid was calculated using Eq. (2)

$$\mathrm{RE}(\%) = (\mathrm{HA}_{\mathrm{total}}) - (\mathrm{HA}_{\mathrm{residual}})/\mathrm{HA}_{\mathrm{total}} \times 100 \qquad (2)$$

where $\mathrm{HA}_{\mathrm{total}}$ is the total amount of humic acid adsorbed on MWCNTs before ultrasonic regeneration (mg) and $\mathrm{HA}_{\mathrm{residual}}$ is the residual amount of humic acid within MWCNTs after ultrasonic regeneration (mg).

2.3. Characterizations of MWCNTs

In order to verify the desired structure of the synthesized nanotubes, the specific surface area (S_{BET}) and the mesopore volume (V_{meso}) were determined according to the N_2 adsorption isotherms. The X-ray diffraction (XRD) spectra was recorded in a diffractometer with (Model Xpert PRO-Philips) graphite monochromatized Cu Kα radiation wavelength (λ = 1.54056 Å). The samples were scanned at a scanning rate of 0.05℃/s in the 2θ range of 5–75˚.

3. Results and discussion

To evaluate the feasibility of desorption of humic acid, 1 g MWCNTs which had adsorbed 59.14 mg humic acid was regenerated in 100 mL ultrapure water by 35 and 130 kHz ultrasound of 500 W power. During ultrasonic irradiation, MWCNTs were completely dispersed in the solution due to acoustic streaming. As shown in Fig. 1, the RE of humic acid increased with increasing ultrasonic irradiation time in both frequencies. In 130 kHz, about 98% of humic acid adsorbed on MWCNTs was desorbed for 30 min, but in 35 kHz only 50% of humic acid desorbed for 80 min and after that no desorption occurred. Therefore ultrasound regeneration with 130 kHz required less exposure time and provided higher efficiency.

Figs. 2 and 3 show the isotherms of original and regenerated MWCNTs in frequencies of 35 and 130 kHz, respectively. As shown in these figures, the RE in frequency of 130 kHz was higher than in 35 kHz. These findings are in accordance with Breitbach et al. [13] who reported that with increasing frequency, ultrasound RE increased. As can be seen in Fig. 3, after each cycle of regeneration, the removal of humic acid by MWCNTs decreased slightly.

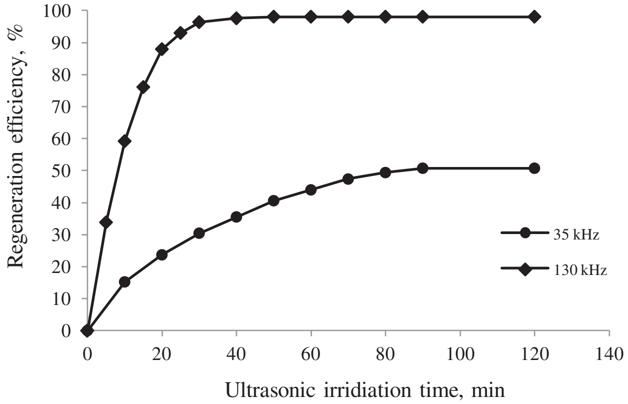

Fig. 1. Desorption of humic acid from MWCNTs by ultrasound (frequencies of 35 and 130 kHz).

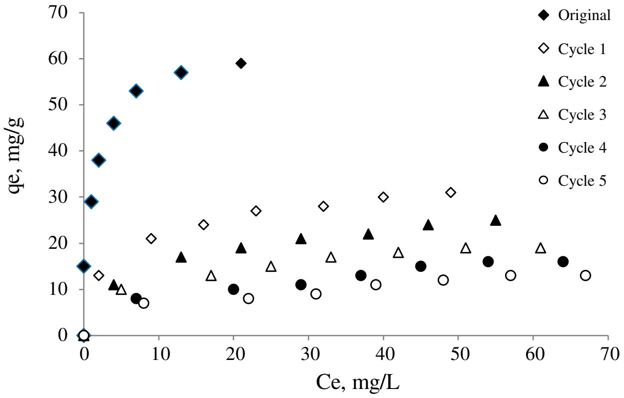

Fig. 2. Adsorption isotherms of original MWCNTs and regenerated MWCNTs (in 35 kHz).

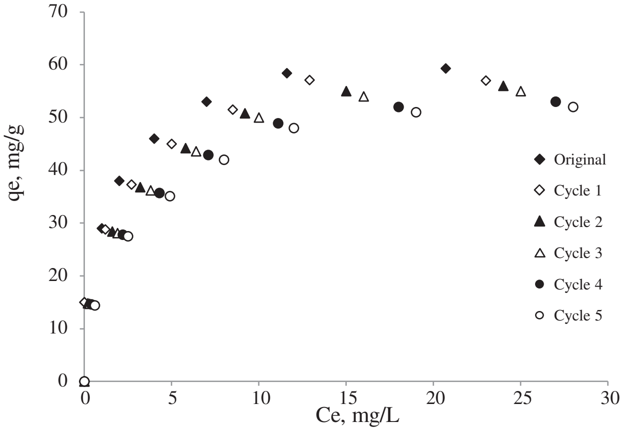

Fig. 3. Adsorption isotherms of original and regenerated MWCNTs (in 130 kHz).

Therefore, it was found that with increasing ultrasound intensities, the amount of humic acid desorbed

Table 1
Adsorption capacity of original and regenerated MWCNTs (mg/g)

Frequency	Original CNTs	Cycle 1	Cycle 2	Cycle 3	Cycle 4	Cycle 5
35 kHz	59.14	31.12	24.78	19.22	16.95	13.56
130 kHz	59.14	57.55	56.04	54.76	53.91	53.08

Table 2
Surface area and mesopore volume of original and regenerated MWCNTs

Frequency	Parameters	Original CNTs	Cycle 1	Cycle 2	Cycle 3	Cycle 4	Cycle 5
35 kHz	S_{BET} (m^2/g)	130.52	67.65	46.34	35.92	31.07	25.83
	V_{meso} (cm^3/g)	0.56	0.31	0.23	0.17	0.14	0.12
130 kHz	S_{BET} (m^2/g)	130.52	125.30	121.87	119.49	116.71	115.25
	V_{meso} (cm^3/g)	0.56	0.53	0.51	0.50	0.48	0.47

S_{BET}: surface area calculated by BET method; V_{meso}: mesopore volume calculated by BJH method.

increased, because with high intensities more cavitation events occurred and more molecules were desorbed. Desorption, which is an endothermic process, is promoted if such a bubble collapse occurs in the vicinity of the adsorbent surface, wherefore adsorbed molecules at these sites re-enter into the solution. Thus, it was concluded that high intensity of ultrasound leads to breaking of bonds formed between humic acid and the MWCNTs' surface [14].

The adsorption isotherms were fitted to Freundlich isotherm model and the adsorption capacity of original and regenerated MWCNTs were obtained and shown in Table 1.

Adsorption capacity of original MWCNTs was 59.14 mg/g and after five cycles of ultrasound regeneration with frequency of 130 kHz, the capacity decreased to 53.08 mg/g. But after five cycles of regeneration with frequency of 35 kHz, the adsorption capacity was reached to 13.56 mg/g. Adsorption capacity of MWCNTs after five cycles of regeneration with frequency of 130 kHz was 89.7% compared to 21.9% in frequency of 35 kHz, which indicates that frequency of 130 kHz of ultrasound irradiation is rather effective for the regeneration of MWCNTs exhausted with humic acid. Otherwise, the measurement of MWCNTs mass variation during ultrasound regeneration showed no significant change in sample weight.

S_{BET} and V_{meso} characterization results are shown in Table 2. It can be clearly seen that at 35 kHz, a rapid fall in S_{BET} and porosity occurred after successive cycles of regeneration. But in 130 kHz, a slight decrease in these parameters was occurred after regeneration cycles.

Hence, the ultrasound irradiation process with frequency of 35 kHz created more residual deposits in the pores of MWCNTs, which blocked the porosity and reduced S_{BET} and V_{meso}, compared to the frequency of 130 kHz.

Fig. 4 shows the XRD patterns of original and regenerated MWCNTs at a frequency of 130 kHz. A sharp peak (at 25.9) and a small diffraction peak (at 43) corresponded to the graphene structure of CNTs. Therefore, it was found that after each cycle of regeneration, MWCNTs had a good graphite structure as the original MWCNTs, with no obvious graphite-to-amorphous transformation of outer walls during ultrasound irradiation regeneration; this indicated that the regeneration process did not damage MWCNTs' graphite structure.

The regeneration process by ultrasound is possible due to the physical and chemical phenomena within the aqueous solution. In fact, the propagation of an ultrasound wave in the aqueous solution causes high

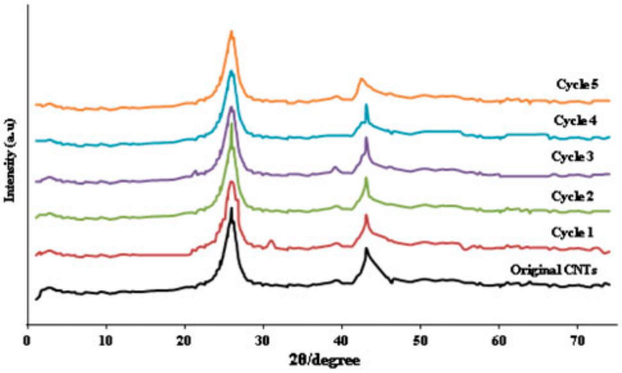

Fig. 4. XRD spectra of original and exhausted MWCNTs regenerated under ultrasound irradiation in frequency of 130 kHz.

energy acoustic cavitations; the formation, growth and implosive collapse of bubbles in liquid. As the bubble collapsed, localized areas with high temperature and pressure are generated in the fluid. The former would make the temperature of the system increase slightly and the latter would have microjets of the solvent to be formed. This phenomenon leads to the dissociation of H_2O, the production of radical species such as OH radical, and the production of high speed microjets and high pressure shock waves causing high velocity inter particle collisions [15]. Consequently, these microjets and high pressure shock waves during bubble collapse in the nearby adsorbent surface enhances the breaking of bonds between humic acid and adsorption surface of MWCNTs, hence increases the desorption of humic acid. Likewise, acoustic vortex microstreaming produced within the pores as well as at solid–liquid interface in ultrasonic field could increase the desorption rates through enhancement in diffusional transport.

4. Conclusion

The feasibility of ultrasonic regeneration of MWCNTs loaded with humic acid was studied. The frequency of 130 kHz showed to be effective for regeneration of MWCNTs exhausted with humic acid. The RE reached 89.7% after five cycles of regeneration. The slight decrease in adsorption capacity maybe due to the deposition of decomposed residues in MWCNTs' pores which blocked the carbon porosity and decreased the S_{BET}.

References

[1] R.H. Baughman, A.A. Zakhidov, W.A.D. Heer, Carbon nanotubes—The route toward applications, Science 297 (2002) 787–792.

[2] C. Yuan, U.-D. Dai, C.-H. Hung, Regeneration of spent carbon nanotube by electrokinetic process with binary metallic oxide electrodes of MnO2/Ti RuO2/Ti, and PbO2/Ti, Separ. Purif. Technol. 79 (2011) 238–245.

[3] A. Naghizadeh, A.R. Yari, H.R. Tashauoei, M. Mahdavi, E. Derakhshani, R. Rahimi, P. Bahmani, Carbon nanotubes technology on removal of arsenic from water, Arch. Hyg. Sci. 1 (2012) 6–11.

[4] K.L. Salipira, B.B. Mamba, R.W. Krause, T.J. Malefetse, S.H. Durbach, Carbon nanotubes and cyclodextrin polymers for removing organic pollutants from water, Environ. Chem. Lett. 34 (2007) 13–17.

[5] C. Lu, F. Su, Adsorption of natural organic matter by carbon nanotubes, Separ. Purif. Technol. 58 (2007) 113–121.

[6] P.C. Chiang, E.E. Chang, J.S. Wu, Comparison of chemical and thermal regeneration of aromatic compounds on exhausted activated carbon, Water Sci. Technol. 35 (1997) 279–285.

[7] W. Tanthapanichakoon, P. Ariyadejwanich, P. Japthong, K. Nakagawa, S.R. Mukai, H. Amon, Adsorption–desorption characteristics of phenol and reactive dyes from aqueous solution on mesoporous activated carbon prepared from waste tires, Water Res. 39 (2005) 1347–1353.

[8] Y. Nakano, L.Q. Hua, W. Nishijima, M. Okada, Biodegradation of trichloroethylene (TCE) adsorbed on granular activated carbon (GAC), Water Res. 34 (2000) 4139–4142.

[9] F. Salvador, C.S. Jimenez, A new method for regenerating activated carbon by thermal desorption with liquid water under subcritical conditions, Carbon 34 (1996) 511–516.

[10] S.U. Rege, R.T. Yang, Desorption by ultrasound: Phenol on activated carbon and polymeric resin, AIChE J. 44 (1998) 1519–1528.

[11] A.D. Farmer, A.F. Collings, G.I. Jameson, Effect of ultrasound on surface cleaning of silica particles, J. Miner. Process 60 (2000) 101–113.

[12] B. Niemczewski, Estimation of the suitability of selected organic solvents for ultrasonic cleaning, Ultrason. Sonochem. 6 (1999) 149–156.

[13] M. Breitbach, D. Bathen, Influence of ultrasound on adsorption processes, Ultrason. sonochem. 8 (2001) 277–283.

[14] O. Hamdaoui, E. Naffrechoux, L. Tifouti, C. Pétrier, Effects of ultrasound on adsorption–desorption of p-chlorophenol on granular activated carbon, Ultrason. Sonochem. 10 (2003) 109–114.

[15] N.H. Ince, G. Tezcanli, R.K. Belen, I.G. Apikyan, Ultrasound as a catalyzer of aqueous reaction systems: The state of the art and environmental applications, Appl. Catal. B: Environ. 29 (2001) 167–176.