

Batch adsorption of methyl tert-butyl ether (MTBE) from aqueous solution by combined CNT and zeolite

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ABSTRACT

Combined zeolite and carbon nanotube (CNT), as an economic solution, were utilized in different experimental conditions for methyl tert-butyl ether (MTBE) removal from aqueous solution. The work deals with the influence of several parameters including contact time (30–600 min), pH (3–10), temperature (10°C–40°C), adsorbent concentration (0.5–10 mg/L), and adsorbate concentration (10–120 mg/L) through using a batch technique in an aqueous system. The results of the experimental data revealed that the adsorption efficiency of MTBE on combined CNT and zeolite decreased by increasing the contact time, temperature, and adsorbent concentration above 60 min, 20°C and 1.5 g/L, respectively. Therefore, the above measurements were chosen as the optimum for the removal of MTBE from the contaminated solutions. Also, any changes in the pH showed no significant effect on the adsorption capacity.

Keywords: Adsorption; Methyl tert-butyl ether (MTBE); Carbon nanotubes (CNTs); Zeolite; Removal efficiency

1. Introduction

A commonly detected volatile organic compound (VOC) is methyl tert-butyl ether (MTBE) which has been generally employed as an octane enhancer in gasoline so as to replace the lead compounds for environmental considerations. The MTBE industrial production process involves the reaction of methanol with isobutylene, in which an excessive amount of methanol is added to increase the conversion rate of isobutylene [1]. MTBE, which is frequently detected in surface and groundwater, became a major concern because of its high solubility, mobility, weak sorption to soil particles, and resistance to biodegradation in groundwater [2,3].

The U.S. Environmental Protection Agency has set a drinking water advisory level of 20 to 40 µg/L for MTBE based on taste and odor issues [4]. In order to remove the emission of VOC, different methods such as adsorptive recovery, liquid absorption, catalysis combustion, and bio-filtration have attracted considerable attention in recent years [5–7].

Carbon-based materials including activated carbon [5], graphene oxide [8], and carbon nanotubes (CNTs) are of the great adsorbents. CNTs are more favorite not only for their wonderful mechanical, thermal, and electrical properties but also for convenience in their production [9–11]. They are rolled up from one or more graphene sheets concentrically. Regarding the number of graphene layers, CNTs

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are classified as single-wall CNTs (SW-CNTs), double-wall CNTs (DW-CNTs), or multi-wall CNTs (MW-CNTs) [12]. It has been found that CNTs are more effective for the natural organic matter (NOM) removal compared to activated carbon [13].

Zeolites are a group of microporous aluminosilicate minerals with biporous structure [14], which occur naturally in the environment or can also be synthesized in a laboratory [15]. Natural zeolites are available and inexpensive resources. They are known as good adsorbents, because of their high cation exchange capacity (CEC), high surface area and cage-like structure [16,17]. There is a permanent negative charge on the crystal structures of zeolites. This is the reason that raw natural zeolites often show little or no tendency for anions and have low performance in the adsorption of organic materials in aqueous solution [18]. Therefore, to enhance the ability of zeolites to remove anions and organic water contaminants, it is necessary to modify their surfaces [19]. Conventional modifications of zeolites to improve their adsorption capacity are an incorporation of amine groups into their structure [20,21] and using different metal ions [22,23].

A few studies were reported about the synthesis of the carbon/zeolite composite materials. Thus, the main goal of this study is to survey the combination of CNTs and zeolite on the removal efficiency of MTBE in contaminated water. To this end, the effects of two different synthesized methods, pH, initial MTBE concentration, contact time, temperature, and adsorbent dosage on the adsorption performance were investigated through batch adsorption tests.

2. Material and method

2.1. Material characterization

2.1.1. Carbon nanotube

NANOCYL™ NC7000 carbon nanotubes used in this study were obtained from NANOCYL (Sambreville, Belgium) manufactured by catalytic carbon vapor deposition process. According to the suppliers' technical data sheets details are summarized in Table 1.

2.1.2. Zeolite

The Clinoptilolite zeolite provided from the Semnan province in Iran was purchased from Afrazand Mining Corporation. The chemical and physical compositions are presented in Table 2. The specific surface area (SSA) was calculated by the Brunauer–Emmett–Teller method.

Table 1
CNT properties supplied by the manufacturer

Product name	Nanocyl™ NC7000
C purity (%)	90
Diameter (nm)	9.5
Length (μm)	1.5
SSA (m ² /g)	250–300
Density (g/m ³)	1.3

2.1.3. Methyl tert-butyl ether

The MTBE used in this study was acquired from Merck Company. Their physicochemical properties are shown in Table 3.

2.2. Adsorbent preparation

2.2.1. Zeolite preparation

In order to find out the best efficiency for adsorption, the zeolite preparation was done by using two following methods. First, zeolite was washed with distilled water three times to ensure that all traces of pollutants were eliminated, then it was dried completely at 120°C (autoclave). In the second method, a certain weight of zeolite has been placed in a 0.1 M NaOH solution for 24 h, then it was thoroughly washed with distilled water to remove its alkali until neutralization (pH = 7) and completely dried in an oven at 120°C.

2.2.2. CNT functionalization

The hydrophobic nature and bundling arrangement of pristine CNT cause low dispersibility in a solution and

Table 2
Clinoptilolite physical and chemical properties

Product type	Clinoptilolite elemental compositions (%)
Fe ₂ O ₃	1.45
CaO	5.1
MgO	0.58
MnO	0.031
K ₂ O	3.68
SO ₃	1.44
SiO ₂	63.82
BaO	2.85
TiO ₂	0.844
Al ₂ O ₃	8.28
Cl	0.31
SrO	0.24
P ₂ O ₅	0.026
Na ₂ O	3.1
LOI	11.35
CEC (meq/g)	1.76
SSA (m ² /g)	39.26
Density (g/cm ³)	2.2

Table 3
MTBE and Toluene physical and chemical properties

Product name	MTBE
Chemical formula	(CH ₃) ₃ COCH ₃
C purity (%)	99.9
Kinematic viscosity (mm ² /s)	0.409 at 40°C
Molar mass (g/mol)	88.15
Density (g/m ³)	0.74 at 20°C

Table 4
EDX for CNT and zeolite washed with distilled water and NaOH solution

Element	Element (%)		Element (%)	
	RH-W	RH-A	RH-W	RH-A
C	9.24	14	28.25	40.62
O	56.53	64.29	37.06	39.99
Na	1.65	1.31	1.08	0.81
Mg	0.68	0.51	0.42	0.3
Al	4.79	3.23	3.66	2.34
Si	21.49	13.92	16.42	10.09
S	1.36	0.77	1.6	0.86
K	2.64	1.23	2.57	1.13
Ca	1.63	0.74	8.93	3.85
Total	100	100	100	100

make its application restricted. In order to resolve these two problems, chemical treatment is essential to get a hydrophilic group on the surface of CNT [24,25]. This method will allow CNT to disperse in solution and lose the agglomeration of nanotubes [26]. Therefore, in this study each 0.1 g of CNT was dispersed in 10 mL of sulfuric acid 98%–95% at 40°C using ultrasonic apparatus (YAXUN YX-2050) for 1 h. Then CNTs were rinsed with distilled water to neutralize their acidity, and finally they were dried completely.

2.2.3. Combination of CNT and zeolite adsorbents

0.5 g CNT plus 10 g zeolite (1:20) were mixed with 6 mL distilled water in a beaker glass, covered with paraffin to prevent contamination, heater stirred for 24 h, and then dried at room temperature (20°C). This trend was the same for both zeolites prepared from two methods (part 2.2.1). It should be noted that zeolites are able to hold water up to 60% of their weight due to their high porosity crystalline structure [27]. This is the reason for using 6 mL of deionized water in the mixture.

2.3. Batch adsorption experiments

The impact of different operating parameters such as time, adsorbent dosage, temperature, pH, and initial contaminant concentration on the adsorption efficiency of CNT and zeolite for MTBE removal was studied using batch adsorption experiments. Certain adsorbent quantities (0.5–10 g/L) were added to an aqueous solution containing distilled water accompanied by different concentrations of MTBE (10–120 mg/L). The solutions were stirred at room temperature (20°C) by a shaker at 110 rpm to reach equilibrium, then stored in Agilent sterile vials at 4°C in the refrigerator. At the end of the adsorption process, the adsorbents were filtered out and the concentration of MTBE in the residual solution was analyzed by Gas Chromatography (Agilent 19091J-413). Since MTBE is highly volatile, all the samples were analyzed on the same day. The percent of MTBE removal is calculated by Eq. (1):

$$\% \text{ Removal} = \left[\frac{(C_0 - C_f)}{C_0} \right] \times 100 \quad (1)$$

where C_0 and C_f (mg/L) are the MTBE initial concentration and the concentration at the time of sampling, respectively.

2.3.1. Effect of two synthesized adsorbents methods on MTBE removal efficiency

As it was mentioned in part 2.2.1, two methods were followed to synthesize the adsorbents. Once the zeolite was washed with distilled water and once with 0.1 M NaOH solution. In order to determine the best method, two synthesized adsorbents with different concentrations from 0.5 to 10 g/L were mixed with 20 ppm MTBE, shaking for 1 h at room temperature (20°C) and filtered for further analyses.

2.3.2. Effect of time and adsorbent dosage on MTBE adsorption

All the experiments were carried out in different shaking times from 30 min to 300 min and various adsorbent concentrations from 0.5 to 10 g/L in order to find out the optimal time and dosage to complete the adsorption process. During these tests the MTBE concentration (20 ppm), temperature, and pH were constant.

2.3.3. Effect of initial solution pH on MTBE removal

The nature of the water source and wastewater streams from different industries cause the pH to vary and affect the adsorption process. In this regard, the effect of hydrogen ion concentration on adsorption efficiency was examined over a pH range of 3.0 to 10 with the aid 0.1 M of H_2SO_4 and 0.1 M of NaOH solutions. Other parameters such as optimal time, optimal adsorbent dosage, MTBE concentration (20 ppm), and temperature were kept without any variations. The pH values were measured by using a WTW (340i) pH meter model.

2.3.4. Effect of temperature on MTBE adsorption

In this part, all of the adsorption experiments were performed at different temperatures from 10°C to 40°C. Other parameters such as pH, optimal time, optimal adsorbent dosage, pH, and MTBE concentration (20 ppm) were fixed.

2.3.5. Effect of MTBE concentration on adsorption

At this stage, the adsorbent mass and the solution volume were fixed, however, the MTBE concentration was gradually increased to the extent that the adsorbent adsorption capacity reached its maximum level. MTBE uptake (q) by adsorbent was determined using Eq. (2):

$$q = \left[\frac{(C_0 - C_f)}{m} \right] \times V \quad (2)$$

where V is the volume of MTBE solution and m is the adsorbent mass.

3. Results and discussion

3.1. Scanning electron microscopy/energy-dispersive X-ray analyzes of combined CNT and zeolite synthesized with two methods

In order to find out the best method of synthesizing zeolite, SEM images were taken by an AIS 2100 scanning electron microscope with a magnification of 15,000. As shown in Fig. 1b CNT was better combined and blended with zeolite washed with distilled water compared to zeolite washed with 0.1 M NaOH solution. The larger inner diameter of zeolite pores makes it as a host material for CNT; therefore, in and out of zeolite pores, the hydrogen on $-COOH$ groups of carbon nanotubes established a hydrogen bond with oxygen in MTBE. Furthermore, the EDX spectra of zeolite washed with distilled water (Fig. 2b) indicated a higher percent ratio of RH-W and RH-A for carbon compared to the zeolite washed with NaOH solution (Table 4).

3.2. MTBE adsorption with combined CNT and zeolite

The modeled structure for MTBE adsorption by CNT and zeolite is shown in Fig. 3. In zeolite Si and Al have empty d orbitals which create a dative like bond with lone pairs of oxygen. In other words, these metals act like a Lewis acid while the MTBE contaminant acts like a Lewis base. Moreover, Fig. 4 presents the effect of two synthesized adsorbent methods on the MTBE removal from an aqueous solution. First, it was deduced that MTBE adsorption efficiency in the CNT and zeolite washed with distilled water is more than CNT and zeolite washed with NaOH solution. Second, the higher MTBE removal was achieved when an intermediate concentration of adsorbents (1.5 g/L) was used. By increasing the amount of adsorbent content, a lower percentage of MTBE removal was observed. The reason could be attributed to the fact that the adsorbent preferentially absorbs water and later the MTBE contaminant [28]. To be more clarified, higher adsorbent concentration can adsorb a larger amount of water leading to an MTBE-rich environment. However, in solution with the lower adsorbent (1.5 g/L), the MTBE removal was around

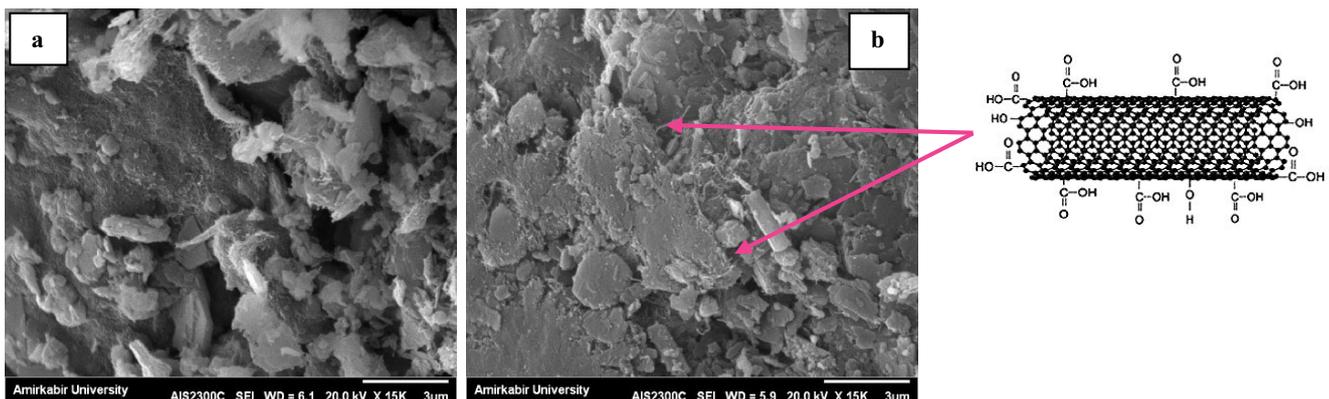


Fig. 1. SEM image of CNT and zeolite (a) washed with NaOH solution and (b) washed with distilled water.

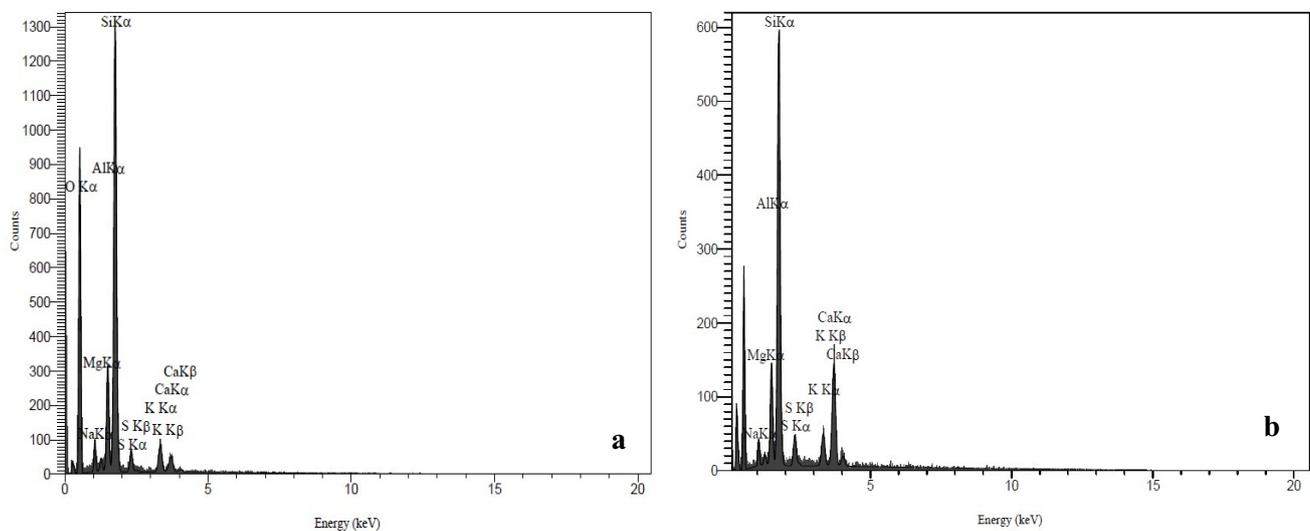


Fig. 2. EDX spectra for CNT and zeolite washed with (a) NaOH solution and (b) distilled water.

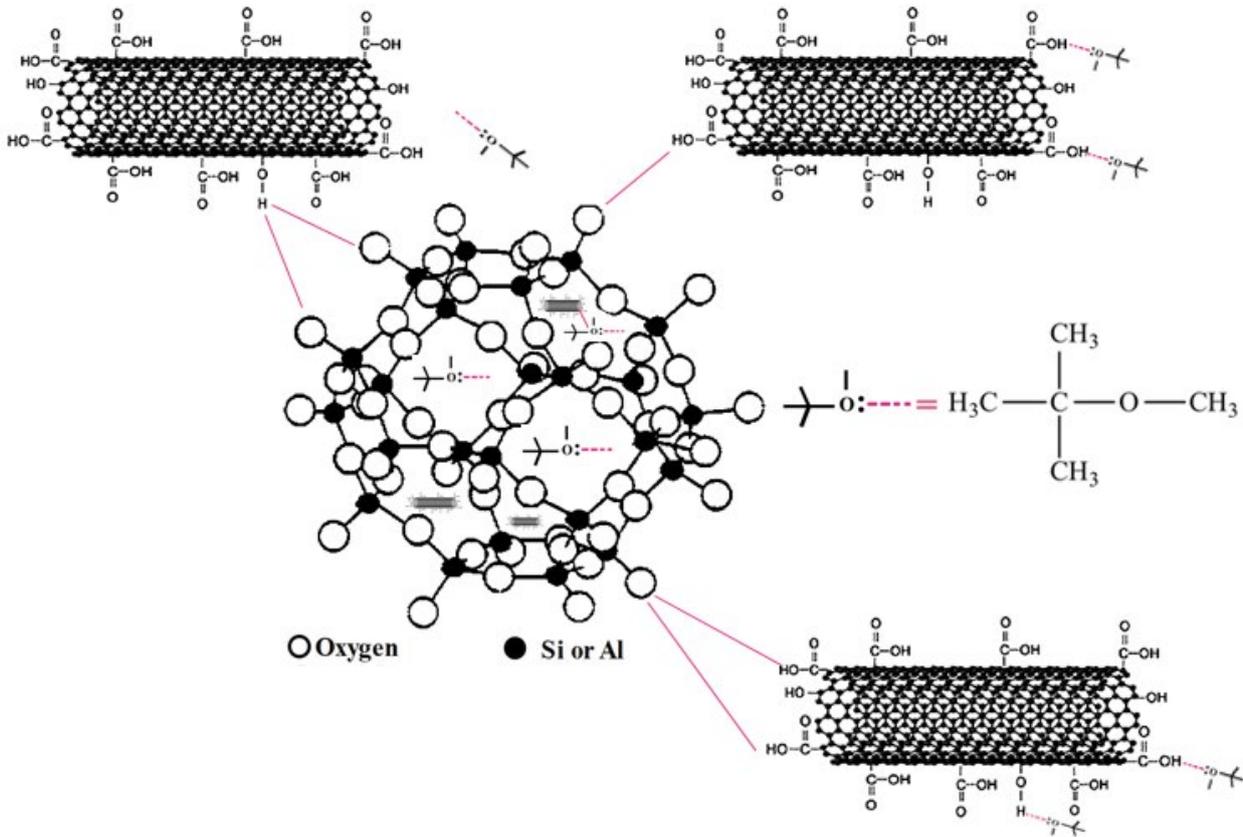


Fig. 3. Model for MTBE reaction with CNT and zeolite adsorbent.

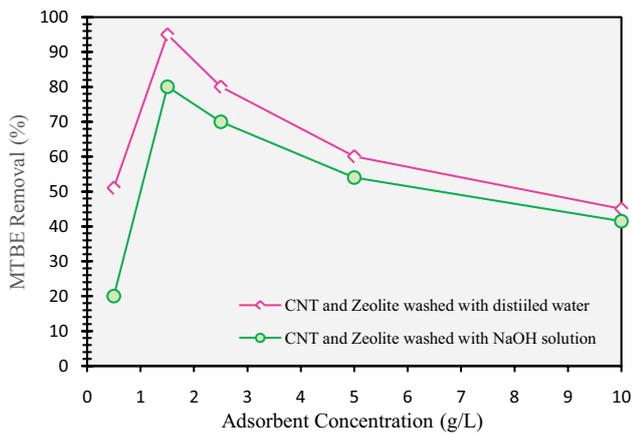


Fig. 4. Influence of CNT and zeolite adsorbent concentration on MTBE removal efficiency.

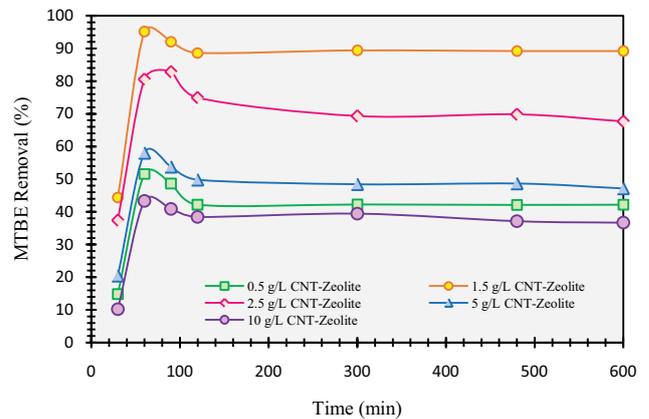


Fig. 5. Effect of time and adsorbent concentration on MTBE removal efficiency (at $T = 20^{\circ}\text{C}$, $\text{pH} = 7$, and initial MTBE concentration = 20 ppm).

95%. As a result, the optimum concentration for the desired adsorbent was considered as 1.5 g/L.

3.3. Time variation

As shown in Fig. 5, at the initial period of the experiments the rate of MTBE removal was increased in all specimens with different adsorbent dosage (0.5–10 g/L).

The optimum MTBE adsorption onto CNT and zeolite was achieved at 60 min, beyond that no remarkable improvement in MTBE removal was evident. The little drop in the removal efficiency after 60 min is may be due to the saturation of active sites on the adsorbents and a point in which the adsorption rate was slightly below the desorption rate [29,30]. Furthermore, as it was mentioned previously, the

adsorbent dosage of 1.5 g/L is the optimal content to reach the pinnacle of MTBE removal efficiency (95%).

3.4. pH variation

The solution pH determines the adsorbent surface charge and the protonation or dissociation of organic weak electrolytes [31]. In adsorption condition of 20 ppm MTBE, 1.5 g/L adsorbent, and 60 min contact time, the MTBE removal percentage at different pH from 3 to 10 was about 95% (Fig. 6). Therefore, any changes in the initial solution pH had no significant effect on the removal percentage. The reason can be explained by the fact that zeolite used in this study has a low CEC value (1.76), consequently, it has little potential for ion exchange. Moreover, MTBE is a non-polar molecule, and the protonation of the functional group is not high enough to relieve much competitive sorption of water molecules owing to the still strong H-bonding abilities of these groups in comparison with their deprotonated counterparts [32], therefore, electrostatic interactions between the adsorbent and adsorbate are weak. These results have good consistency with previous researchers [33].

3.5. Temperature variation

The temperature at which a sorption process is performed will affect not only on the sorption rate but also on the degree to which sorption takes place [34]. The relationship between the temperature variation and the MTBE removal efficiency is depicted in Fig. 7. It was observed that the MTBE removal percentage enhanced from 82% to 95% with a rise in temperature from 10°C to 20°C, indicating an endothermic reaction [35,36]. This could be due to the fact that increasing temperature leads to a rise in the diffusion rate of MTBE molecules across the external boundary layer and within the pores of CNT and zeolite. Furthermore, in super-absorbents, the increasing temperature may cause swelling of their internal structure, penetrating the MTBE molecule further [37]. However, regarding the MTBE boiling

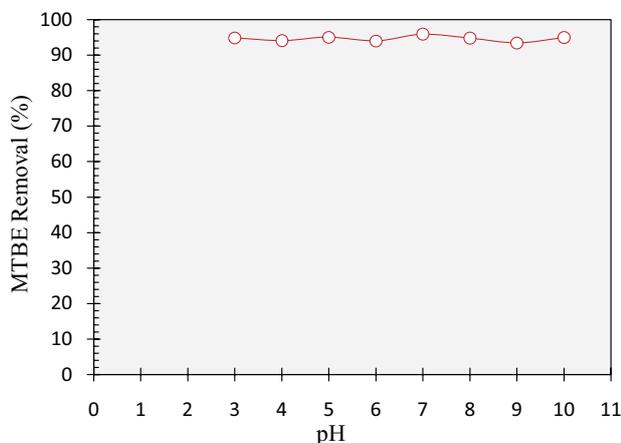


Fig. 6. Effect of pH on MTBE removal efficiency by CNT and zeolite (at $T = 20^{\circ}\text{C}$, adsorbent concentration = 1.5 g/L, and initial MTBE concentration = 20 ppm).

point ($\sim 53^{\circ}\text{C}$), in temperatures above 20°C the mobility of the MTBE molecules increased and lead to the reduction of adsorption efficiency.

3.6. MTBE concentration variation

The concentration studies were carried out with 1.5 g/L adsorbent over a wide range of initial MTBE concentrations from 10 to 120 ppm. The results from Fig. 8 showed that by increasing the MTBE concentration from 10 to 120 ppm, the removal percentage was declined gradually from 98.32% to 75.53%. Based on the number of available active adsorption sites, adsorbate dosage influences on removal efficiency [38]. The reduction in the MTBE adsorption may be attributed to overlapping or aggregation of adsorption sites resulting in surface area reduction [39].

4. Conclusion

In this study the mixture of zeolite and CNT were used as an effective adsorbent for MTBE removal from an aqueous solution. The highest MTBE uptake was measured through a series of batch adsorption experiments. The results

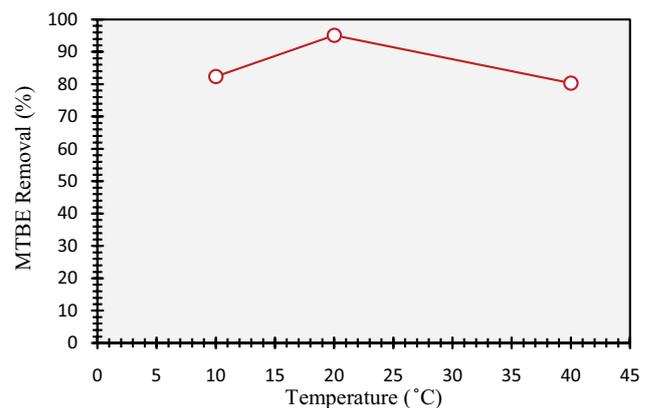


Fig. 7. Effect of temperature on MTBE adsorption by CNT and zeolite (at adsorbent concentration = 1.5 g/L and initial MTBE concentration = 20 ppm).

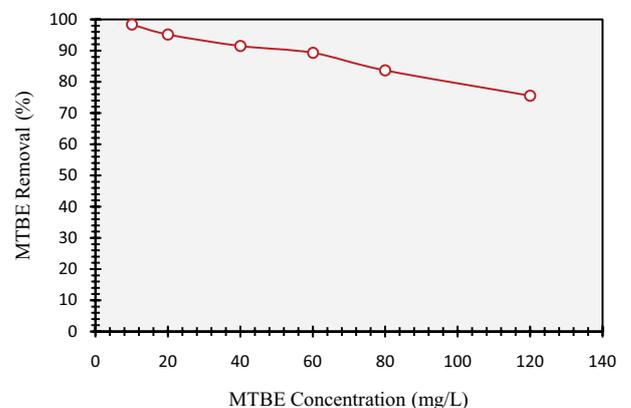


Fig. 8. Effect of initial MTBE concentration on the CNT and zeolite adsorption rate.

revealed that zeolite washed with distilled water was more successful in MTBE removal efficiency compared to zeolite washed with 0.1 M NaOH solution. The experimental parameters such as time, temperature, pH, adsorbent dosage, and adsorbate concentration were investigated in detail and showed that MTBE adsorption efficiency decreased by increasing contact time, temperature, and adsorbate concentration. However, the solution pH had no significant effect on the adsorption capacity.

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