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Benzene removal by hybrid of nanotubes and magnetic nanoparticle from aqueous solution

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ABSTRACT

A single-wall carbon nanotube devised by magnetic nanoparticles (SWCNT-MN) on their internal surface was synthesized via the modified sol–gel method and implemented in a batch and continuous reactor for benzene removal from aqueous solutions. The presence of MN in SWCNT changed its surface properties and increased its adsorption efficiency displaying the good ferromagnetic property. The results obtained from the design of the experiment demonstrated that optimum pH and adsorbent dose for benzene removal by SWCNT-MN was 8 and 2,000 mg/L, respectively, and resulted in the best performance of the adsorption, 98.6% benzene removal, in a 100 mg/L solution in only 20 min. A comparative study on benzene adsorption capacity shows that the SWCNT-MN showed better performance than the single-wall carbon nanotube and magnetic nanoparticles. This suggests that the SWCNT-MN was efficient for benzene adsorption from aqueous solutions and it possessed a good potential for benzene removal from polluted water and wastewater.

Keywords: Benzene; Carbon nanotubes; Magnetic nanoparticle; Aqueous solution

1. Introduction

Benzene is one of the volatile organic compounds that have carcinogenic effects on human health. Every year, a large amount of wastewater polluted by benzene is discharged into the environment from manufacturing, transportation, and disposal landfills [1]. Since the benzene is toxic, flammable, and carcinogenic, the presence of excessive amounts of benzene in the environment has adverse effects on human health and welfare [2]. The removal of toxic components from wastewater prior to its disposal is crucial due to its general safety concerns and environmental consequences [3]. The conventional adsorption process via activated carbon diatomite was used widely for benzene removal from aqueous solutions [1,4]. Carbon nanotubes (CNT) have been proved to pose a good potential for adsorbing many kinds of organic substances. Recently, CNT has attracted both academic and industrial interests because it has unique electronic properties associated with its spatial one-dimension structure that facilitates the charge transfer [5]. The comparison of SWCNT with MWCNT made by foregoing research suggested that the SWCNT was a promising adsorbent for benzene [2].

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But, use of SWCNTs in aqueous solution was limited because of their release and inability to restrain them. So, change in physical and chemical properties of CNT by modification is necessary for preventing its release. Also, surface modification of implants with CNTs is one of the most effective methods for improving the pollutants removal property [6]. Leghrib et al. used oxygen plasma-treated multi-wall carbon nanotubes decorated with metal nanoparticles (Rh, Pd, Au, and Ni) for recognition of benzene vapors at trace levels [7]. The carbon-coated TiO_2 was used for benzene removal in the Zhang et al. study. They found that the carbon residue has an inhibition effect on benzene removal by TiO_2 [8]. Fan and Li [9] used ultrasonic for synthesis of Fe_3O_4/MWCNT. Their results showed that the Fe_3O_4 contents in the composites were 26.6 and 29.3% for particle sizes of 6 and 10 nm. In this regard, one major focus of research has been surface modification of SWCNT using metallic materials. This is because, organic benzene in aqueous solution initially contacts the surface of SWCNT which then influences their initial response. Accordingly, surface modification with MN will be one of the most effective methods to create important surface properties such as oxidative potential.

In this study, SWCNT was devised by magnetic nanoparticles to improve the adsorption capacity and enhancing the separation of SWCNT from an aqueous solution.

2. Materials and methods

2.1. Materials

A solution of 100 mg/L benzene was prepared by dissolving appropriate amounts of benzene (Merck, purity: 99.7%) in deionized H_2O. The solution was dissolved thoroughly using ultrasonic bath (Bandline Sonorex Digitex DT156) for 60 min, and then, stirred continuously for 24 h at 25˚C. After shaking, it was put in ultrasonic bath again for 30 min [10] and was used to prepare initial solution of benzene with 10, 30, 70, and 100 mg/L concentrations. Standard series and samples were made using deionized H_2O to the desired concentrations.

2.2. Experimental conditions

Several experiments were conducted to evaluate the effective parameters. This investigation applied the design of experiments (DOE) approach to optimize parameters of benzene removal by SWCNT-MN. Planning of the experiment was based on the Taguchi orthogonal table. All experiments were conducted in 110-ml glass flasks. In each experiment, a varied amount of the adsorbents, 500–2,000 mg/L, was added to 100 ml of benzene solution, at the initial concentration (C_0) of 10–100 mg/L. Also, the pH value was changed from 2 to11. These baths were representatives of the low benzene level in water polluted by gasoline. The glass flasks were sealed with a 20-mm stopper. The headspace of each flask was minimized to exclude any contaminant volatilization phenomena. After preparing each batch, the flasks were placed on a shaker (Orbital Shaker Model OS625) and stirred at 240 rpm at the room temperature for 2–20 min. The solution samples were then settled for 2 min. A magnetic field was used to separate the suspended magnetic CNT-MN. Continuous experiments were performed using an up-flow magnetic column with 5-cm diameter and 20-cm length. The column was filled with stainless steel wool and surrounded by two magnets with 0.15 T from the outside (Fig. 1). The column was operated under the optimum condition achieved in batch experiments with retention times of 2, 8, 14, and 20 min.

Before and after each experiment, benzene was determined using gas chromatography–mass spectrometry (GC–MS) (Agilent GC, 7890A). All of the experiments were repeated three times and only the mean values were reported. Blank experiments without adding adsorbents were also conducted to ensure no benzene has been attached to the glass bottle wall or via volatilization loss. The pH of the solution was measured at the beginning (pH_{in}) and at the end (pH_{fin}) of each experiment by a pH meter (EUTECH, 1500). The pH_{in} was adjusted using 0.05 M HCl and 0.05 M NaOH. The amount of adsorbed benzene onto adsorbent (q_e, mg/g), distribution ratio (K_D, L/g), and percent removals R (%) were calculated as follows:

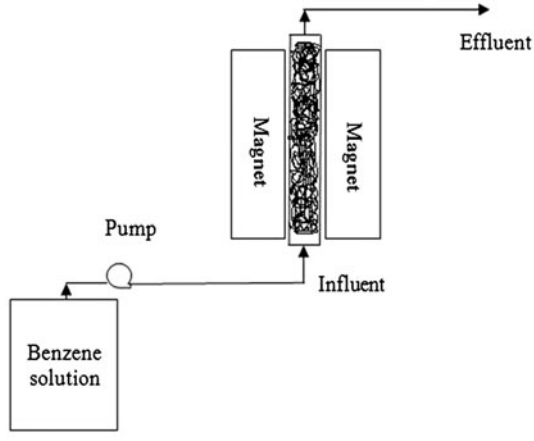

Fig. 1. Up-flow magnetic column used for continuous experiments.

$$q_e = (C_0 - C_t)\left(\frac{V}{m}\right) \quad (1)$$

$$R\ (\%) = \left(\frac{C_0 - C_t}{C_0}\right) \times 100 \quad (2)$$

$$K_D = \left(\frac{C_0 - C_t}{C_t}\right)\left(\frac{V}{m}\right) \quad (3)$$

where C_0 and C_t (mg/L) are the benzene concentrations at the beginning and after each run, V is the initial solution volume (L), and m is the adsorbent weight (g).

2.3. Chemical analysis

The GC–MS was used for determination of benzene. The Agilent Technologies system consisted of 5975C Inert MSD with Triple Axis Detector and equipped with a 7890A GC and split/splitless injector. This system was used for determination of benzene after treating by CNT-MN. A fused silica column, HP-5 ms (5% phenyl-95% dimethyl polysiloxane; 30 m × 0.25 mm I.D, 0.25 μm), was implemented with helium (purity 99.995%) as a carrier gas at a flow rate of 1 mL/min. The column temperature was programed as follows: 40˚C for 10 min, increasing to 150˚C at 10˚C/min, and holding for 2 min. The injector port was maintained at 250˚C and 1-mL volume of headspace was injected in splitless mode (2 min). The effluent of the column was transferred via a transfer line held at 280˚C and fed into a 70 eV electron impact ionization source held at 280˚C. The analysis was performed in the scan mode. The data were acquired and processed by the data analysis software.

Static headspace analysis was performed using a CTC PAL-Combi PAL headspace sampler. Experimental optimum parameters of the headspace sampler were based on what was reported in Table 1.

2.4. Adsorbents

During the experimental procedure, single-wall carbon nanotube combined with magnetic nanoparticle was used as adsorbent. SWCNT was purchased from Iranian Research Institute of Petroleum Industry. To synthesize SWCNT-MN 20% (where weight ratio of MN to SWCNT was 20/100), nitrogen was initially injected to 30.6 mL of deionized water for 10 min at 85˚C. Then, 2.6 g of $FeCl_2{\cdot}4H_2O$ and 1 g of $FeCl_3{\cdot}6H_2O$ were added and stirred for 5 min. Thereafter, 15 g of SWCNT was introduced to the solution and mixed manually. 1.5 mL of NH_3 (25%) was added to the mixed solution and the mixture was loosely covered and stirred until a homogenous gel was formed. The gel was left in the lab air for 3 d and then crushed into a fine powder. The fine powder was dried in an oven with 105˚C for 2 h which was calcined at 350˚C in a flow of nitrogen for 1.5 h to obtain SWCNT-MN.

Table 1
Experimental optimum parameters of headspace sampler

Parameter	Value
Incubation time	25 min
Incubation temperature	70˚C
Sample loop volume	250 μL
Syringe/transfer line temperature	110˚C
Flash time	2 min with N_2
Loop fill time	0.03 min
Injection time	1 min
Sample volume	2 mL in 10 mL vials

TEM images of SWCNTs (1–2 nm), are shown in Fig. 2. The surface area, pore volume, and pore size distribution (PSD) were measured by nitrogen adsorption at 77 K using an ASAP-2010 porosimeter from the Micrometrics Corporation GA. The samples were degassed at 350˚C and 1.33–0.67 kPa overnight, prior to adsorption experiments. The PSD was evaluated from the adsorption isotherms using the Barrett, Joyner, and Halenda (BJH) algorithm (ASAP-2010) available as a built-in software from Micromeritics. The surface area, average pore size diameter, and pore volume of the adsorbents are presented in Table 2.

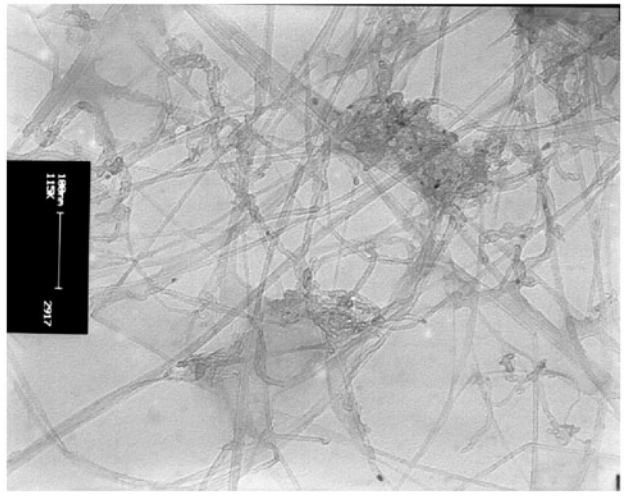

Fig. 2. TEM image of SWCNT.

Table 2
N_2 adsorption data of SWCNT

Adsorbents	BET surface area (m^2/g)	Average pore diameter by BET (nm)	BJH adsorption cumulative surface area of pores (m^2/g)	BJH adsorption average pore diameter (MN)	BJH adsorption cumulative pore volume of pores (cm^3/g)
SWCNTs	273.64	11.87	248.35	13.06	0.73

2.5. Recycling method

The reversibility of sorbents used for benzene removal from aqueous solution was evaluated via two successive adsorptions followed by two successive desorptions. Recycling was also conducted at 105 ± 2°C in an electric oven (Memmert D-91126, Schwabach FRG) for 24 h. Then, it was placed in a desiccator for cooling. All samples were performed at least in triplicate.

2.6. Kinetics of benzene removal

To ascertain the individual effects of pH, MN doses, initial concentrations of benzene, and contact time on removal of benzene, DOE software (Design Expert 6) was used. DOE was also used in order to decrease the number of the experiments and also data analysis. The analysis of variance (ANOVA) was adapted to identify the most influential factors on benzene removal efficiency by SWCNT-MN. The Taguchi OA plan was applied by four factors at four levels and is reported in Table 3 close to the literature reports [11–13]. The matrix involved 16 runs and each run was triplicate.

Isotherm study was evaluated for benzene adsorption by MN under optimum condition with an initial concentration of 0–100 mg/L (interval 10 mg/L), MN dose 2 g/L, contact time 14 min, and pH 8. Water solubility (S_w) of benzene was estimated to be 1,790 mg/L at pH 7. Isotherm Fitting Tool (ISOFIT) software was used to fit isotherm parameters to experimental data. ISOFIT is a software program that fits isotherm parameters to experimental data by minimizing the weighted sum of squared error (WSSE) of the objective function [14]. ISOFIT supported a number of isotherms including (1) Brunauer–Emmett–Teller (BET), (2) Freundlich, (3) Freundlich with linear partitioning (F-P), (4) generalized Langmuir–Freundlich (GLF), (5) Langmuir, (6) Langmuir with linear partitioning (L-P), (7) Linear, (8) Polanyi, (9) Polanyi with linear partitioning (P-P), and (10) Toth.

3. Results

3.1. SWCNT-MN structure

Based on previous study, the SWCNT was selected as a base for synthesizing of nanocomposite showing a better efficiency for benzene removal than MWCNT [2]. Fig. 3(a) and (b) presents the TEM image of SWCNT-MN.

Fig. 3(a) displays the SWCNT-MN wrapped together. When CNTs aggregate together, they can form bundles or pores, which create lots of adsorption sites, such as interstitial channel, the external groove, and partial coating of the external surface with a nanometer-thick layered carbon [15]. All of these sites contributed to the overall adsorption. As shown in Fig. 3(b), some magnetic nanoparticles are attached along the sidewall of SWCNT. This figure shows that the magnetic nanoparticles have an almost spherical shape and a well-controlled size. Table 4 shows the N_2 adsorption data for the SWCNT-MN and important changes occurring on SWCNT surface area and volume of pores by introducing MN.

3.2. Batch experiments performance

SWCNT and MN were chosen based on their ability to actively absorb benzene. In order to optimize this ability, the adsorption conditions including pH solution, sorbent amount, contact time, and benzene concentration were investigated in the DOE approach

Table 3
Controlling factors and their levels

Factors	Level 1	Level 2	Level 3	Level 4
Benzene concentration (mg/L)	10	30	70	100
MN dose (mg/L)	500	1,000	1,500	2,000
Contact time (min)	2	8	14	20
pH	2	5	8	14

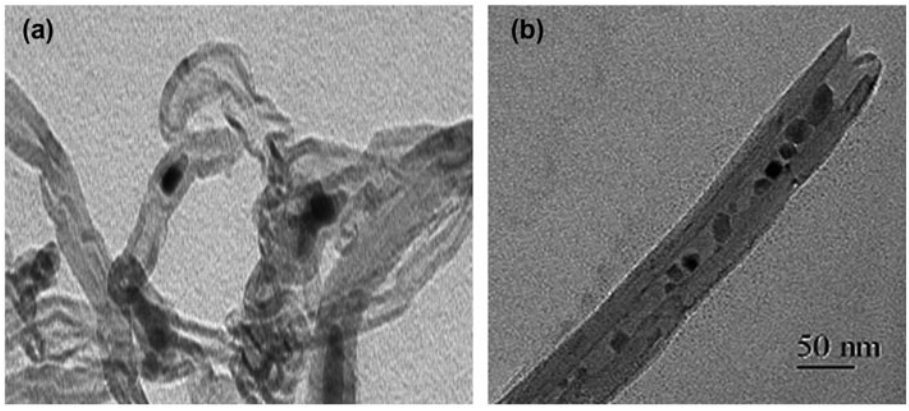

Fig. 3. Transmission electron microscopy image of SWCNT-MN: (a) general view and (b) SWCNT-MN in details.

Table 4
N_2 adsorption data of SWCNT-MN

Adsorbents	BET surface area (m^2/g)	Average pore diameter by BET (nm)	BJH adsorption cumulative surface area of pores (m^2/g)	BJH adsorption average pore diameter (nm)	BJH adsorption cumulative pore volume of pores (cm^3/g)
SWCNT-MN	303.2	11.87	284.21	14.1	0.85

[16]. Table 5 shows the benzene removal percentage (R) by SWCNT-MN, equilibrium amounts of benzene adsorbed (q_e), distribution ratio (K_D) with different initial benzene concentrations, adsorbent dose of SWCNT-MN, contact time, pH, and shaking at 240 rpm.

Based on Table 5, more than 98% benzene was adsorbed using SWCNT-MN in run 10. The comparison of benzene removal with SWCNT, MN, and SWCNT-MN demonstrated that SWCNT-MN shows better performance than SWCNT (85%) and MN (67.2%) under the condition.

The estimated effects of the factors and their interactions can be seen in Table 6. These results are obtained from ANOVA test after removing the insignificant terms of model. F-value of model and any individual factor was calculated by dividing mean square with residual mean square in order to compare variances to residual variances. If the variances and residual variances were closed, the ratio of these two would approach to one and mean the term was less likely significant. Furthermore, if p-value of the term was less than 0.05, the term had a significant effect on the response.

In Table 6, model F-value of 25.98 with model p-value of <0.0001 implies that the selected model was significant and there was less than 0.01% chance that the model F-value could occur due to noise. The statistical significance of each effect was tested by comparing the mean square with an estimate of the experimental error. In this case, five effects have F-value less than 0.05 indicating that they are significantly different from zero at the 95% confidence level. The F-value test showed that the contact time acted significantly in affecting the adsorption performance. Besides, the influences of interaction between benzene concentrations with SWCNT-MN dose and pH seemed to be less significant because of the F-values, 216.7 and 20, for interaction and pH, respectively. As expected, the contact time contributed to the major part in affecting the adsorption capability, i.e. 33.5%. This result is very reasonable because the contact time is one of the most important factors in determining adsorption capacity in liquid phase. The effective parameters in benzene removal were following the order of: contact time > benzene concentration > SWCNT-MN dose > benzene concentration and SWCNT-MN dose interaction > pH. In this way, the benzene removal by SWCNT-MN could be expressed as the following equation:

$$\text{Benzene removal } (\%) = 88.7 - (2.76 \times A) - (2.56 \times B) - (5.6 \times C) - (0.03 \times D) \quad (4)$$

where A is initial benzene concentration, B is SWCNT-MN dose, C is contact time, and D is pH.

Table 5
Design matrix and results of benzene removal by SWCNT-MN under different conditions

Run	Factors				Response 1: benzene			
	Benzene concentration (mg/L)	SWCNT-MN dose (mg/L)	Time (min)	pH	C_t (mg/L)	R (%)	q_e (mg/g)	K_D (L/g)
1	30	500	8	8	4.3 ± 0.1	85.8	51.2	12.1
2	30	2,000	14	8	2.6 ± 0.2	91.4	13.7	5.3
3	10	1,500	14	8	0.6 ± 0.05	94.2	6.3	10.8
4	70	500	14	11	9.6 ± 0.4	86.2	120.7	12.5
5	10	1,000	8	5	1.7 ± 0.04	82.5	8.3	4.7
6	30	1,000	2	11	5.1 ± 0.1	82.9	24.9	4.8
7	100	1,000	14	2	7.7 ± 1.2	92.3	92.3	12
8	10	2,000	20	11	0.7 ± 0.1	93.5	4.7	7.2
9	30	1,500	2	2	6.6 ± 0.1	78.1	15.6	2.4
10	100	2,000	20	8	1.4 ± 0.2	98.6	49.3	34.1
11	100	500	20	5	3.4 ± 0.7	96.6	193.1	56.4
12	100	1,500	8	11	7.7 ± 0.4	92.3	61.6	8
13	70	2,000	8	2	3.2 ± 0.4	95.5	33.4	10.5
14	70	1,500	2	5	10.5 ± 0.3	85.1	39.7	3.8
15	10	500	2	2	3.1 ± 0.1	69.2	13.8	4.5
16	70	1,000	20	8	3.3 ± 0.3	95.3	66.7	20.1

Table 6
Contribution of the factors and interactions for benzene removal by SWCNT-MN

Source	DF	Sum of squares	Mean squares	F-value	p-value	% Contribution
Model	12	2,523	210.3	25.98	<0.0001	100
A: benzene concentration (mg/L)	3	890	296.7	755.5	<0.0001	31.9
B: SWCNT-MN dose (mg/L)	3	647.6	224.9	572.6	<0.0001	24.2
C: contact time (min)	3	934.8	311.6	793.5	<0.0001	33.5
D: pH	3	23.5	7.9	20	<0.0001	0.8
AB interaction	3	255.3	85.1	216.7	<0.0001	9.2
Lack of fit	30	11.8	0.4	–	–	0.4
Pure error	0	0.000	–	–	–	0.000
Residuals	30	11.8	0.4	–	–	–
Total	47	2,790.3				

The proportion of total variability in the benzene removal efficiency can be explained by Eq. (5):

$$R^2 = \frac{\text{Sum of squares}_{\text{Model}}}{\text{Sum of squares}_{\text{Total}}} = \frac{2523}{2790.3} = 0.9 \quad (5)$$

The study also showed that there were significant interactions between initial benzene concentrations and SWCNT-MN dose factors.

Fig. 4 shows the plots of factors effecting benzene removal by SWCNT-MN to determine the optimum condition.

The experimental results of DOE were first analyzed using the direct observation analysis, because the responses vs. the levels of different factors were observed directly from a broken line plot. The mean value of the degradation efficiencies for the corresponding factors at each level was calculated according to the assignment of the experiment. Fig. 4(a) indicates that the benzene adsorption increased from 70.9 to 77.5% with rising of the initial benzene concentration from 10 to 100 mg/L. Wang et al. [11] showed that the adsorption of metals onto Fe_3O_4 decreased sharply when the initial metal concentration was higher than 35 mg/L due to the decrease in fraction of free ions in aqueous solution. Fig. 4(b) shows that the optimum benzene removal happens at 2 g/L SWCNT-MN dose. So, it was selected as optimum condition at SWCNT-MN dose. The results showed that the higher initial concentration of adsorbent enhanced the

sorption process up to 98.6% even though the dose exceeded 2 g/L. Fig. 4(c) shows that most of the benzene was adsorbed to achieve the equilibrium in about 20 min. Benzene adsorption from 2 to 14 min was increased at higher rate than the adsorption from 14 to 20 min. Also based on statistical analysis, there was a significant difference between contact times in benzene removal percentages (values of "*p*-value" less than 0.05). Comparing to the other literature, benzene adsorption was not long [4]. Although pH was reported to be effective [15], the benzene removal by SWCNT-MN was not affected greatly by pH of the solution. Fig. 4(d) shows that the removal efficiency was at minimum level, at pH 2, and increased by increasing pH up to 8 and then reached plateau at pH 8 or higher. So that, there were no significant differences between pH 8 and 11 in benzene removal percentages (values of "*p*-value" greater than 0.1). Most likely, the adsorption of benzene onto SWCNT-MN sorbent was due to opposite charges between the sorbent and the benzene. However, these results were not explained by the nature of the electrical charges on adsorbent surfaces since the zero points of charge for iron oxides are generally between 7 and 8. When the pH is greater than 6, some iron oxides may precipitate and produce $Fe(OH)_2$ as colloidal suspensions with the high specific surface area. The solution pH would affect both aqueous chemistries and surface binding sites of the adsorbent. At low pH, the H ions would compete with benzene while the magnetic nanoparticles had a higher negative charge at higher pH. That enhanced the positively charged benzene capturing through electrostatic force of attraction. In Wang et al. study, it was found that the adsorption

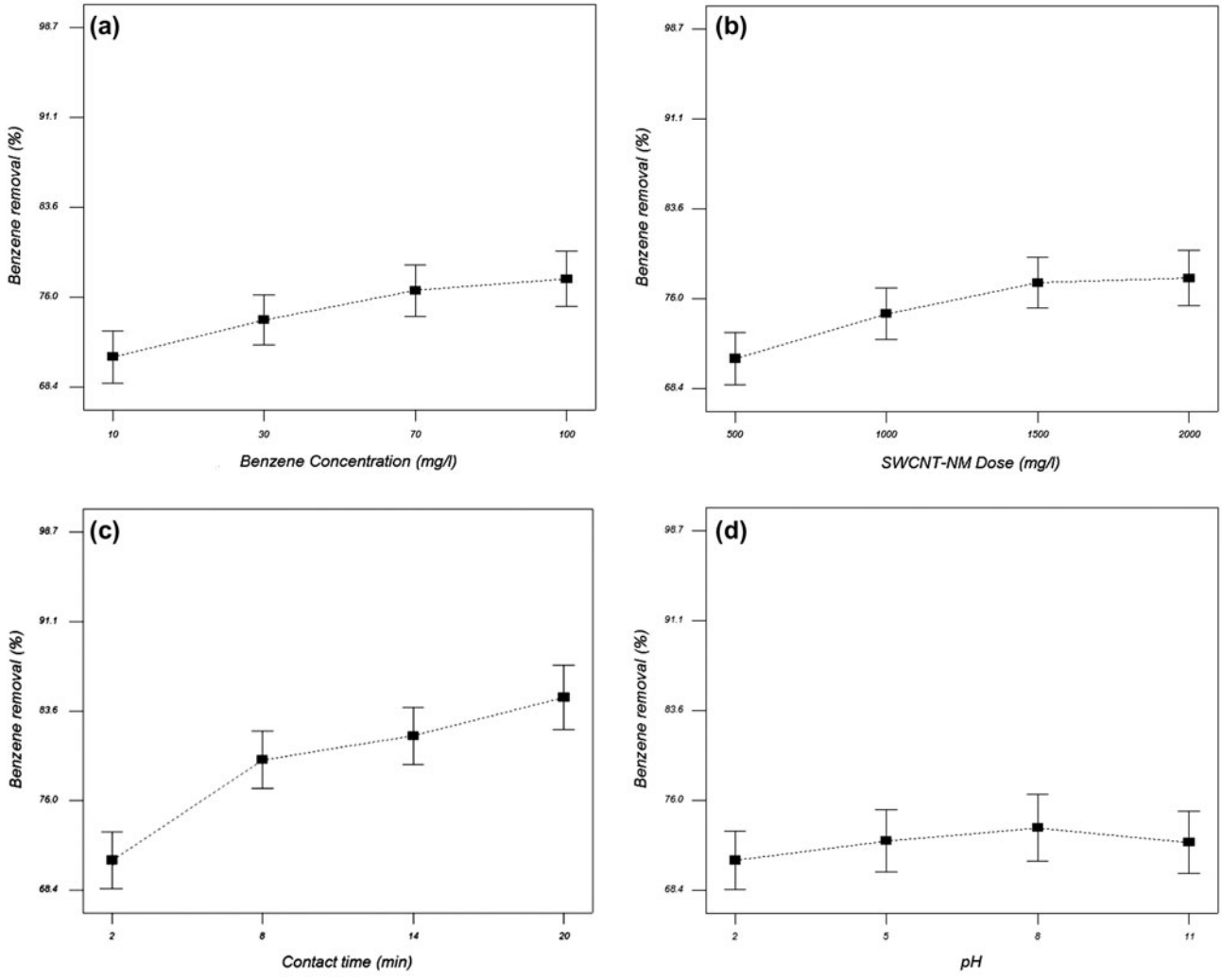

Fig. 4. Design expert plot of factors' effect on benzene removal by SWCNT-MN in: (a) benzene concentration, (b) SWCNT-MN dose, (c) contact time, and (d) pH.

performance of Fe_3O_4 strongly depended on solution pH. The adsorption efficiency increased sharply when the solution pH exceeded a threshold value of 6.2 [11]. The pH primarily affected the degree of ionization of the benzene sorbents and the surface charge of SWCNT-MN. Thus, the optimum conditions for benzene removal by SWCNT-MN were benzene concentration of 100 mg/L, MN dose of 2,000 mg/L, contact time of 20 min, and pH 8. These most effective parameters were in run 10 and so the results of this run were considered as verification run. The comparison of benzene removal with SWCNT, MN, and SWCNT-MN illustrated that SWCNT showed better performance than SWCNT (85%) and MN (67.2%) under the same condition. The comparisons between q_e and K_D of this study with various adsorbents such as carbon nanotubes (CNT), powdered activated carbon (PAC), and granular activated carbon (GAC) reported in the literature are given in Table 7. Under analogous conditions, the present study showed better performance of benzene adsorption than other adsorbents. This suggested that the SWCNT-MN is an efficient benzene adsorbent, and it is possible to utilize these novel nanoreactors for benzene removal in water and wastewater treatment in the near future. The functionalization of SWCNT sidewalls is an option to improve its performance for environmental pollutant removal. In particular, fictionalization of magnetic nanoparticle can lead to high adsorption and magnetic properties of SWCNT. This effect is caused by the catalytic activity of MN.

Two possible mechanisms can be expected for combined nanomaterials in benzene removal: (1) benzene molecule is directly adsorbed onto SWCNT sidewall and MN; and (2) molecules that are adsorbed onto MN and sidewall oxide by MN.

3.3. Continuous experiments performance

An up-flow SWCNT-MN column was evaluated under optimum condition obtained in batch experiment at different contact times. Table 8 and Fig. 5 show the benzene removal in SWCNT-MN column. Benzene removal efficiency in batch and continuous experiments are compared in Fig. 6.

Results show that benzene removal efficiency under batch condition is higher than continuous experiments. Because of SWCNT-MN was compacted in pill form and stabilized on stainless steel wool in a vertical column magnetic field. This may be due to decreased level of absorption area. Bystrzejewskiet et al. [19] used carbon-encapsulated magnetic nanoparticles as mobile sorbents for removing heavy metal ions from aqueous solutions. The ion uptakes achieved 95% for cadmium and copper. The sorbents also had adsorption capacities between 1.23 and 3.21 mg/g.

Table 7
Comparisons of q_e for benzene adsorption via various adsorbents

Adsorbents	q_e (mg/g)	K_D (L/g)	Condition	Refs.
SWCNT-MN	193.1	56.4	pH 5, S/L: 0.05/100, C_0 = 100, C_t = 0.3	This study
CNT	18.1		pH 7, S/L: 0.06/100, C_0 = 200	[17]
Diatomite	0.2		pH 8.5, S/L: 33/100, C_0 = 50, C_t = 240	[4]
GAC	183.3		pH 7, S/L: 0.15/100, C_0 = 35–442	[16]
Organominerals	28.8		S/L: 0.1/25, C_0 = 100, C_t = 18	[12]
PAC	4.76		pH 6.5, S/L: 0.5/100, C_0 = 10, C_t = 72	[18]
Peach stones (PS)	–	0.43	S/L: 0.1/100, C_0 = 10	[18]

Notes: S/L = solid/liquid (g/mL); C_0 = initial benzene concentration (mg/L); C_t = contact time (h).

Table 8
Benzene removal by SWCNT-MN column

	Factors				Response1: benzene			
Run	Benzene conc. (mg/L)	SWCNT-MN dose (mg/L)	Time (min)	pH	C_t (mg/L)	R (%)	q_e (mg/g)	K_D (L/g)
1	100.3 ± 1.9	2,000	2	8	15.1 ± 0.2	84.9	42.5	2.8
2	100 ± 2.1	2,000	8	8	6.8 ± 0.7	93.2	46.6	6.8
3	100 ± 2.4	2,000	14	8	5.2 ± 0.4	94.8	47.4	9.1
4	100 ± 2	2,000	20	8	3.6 ± 0.2	96.4	48.2	13.4

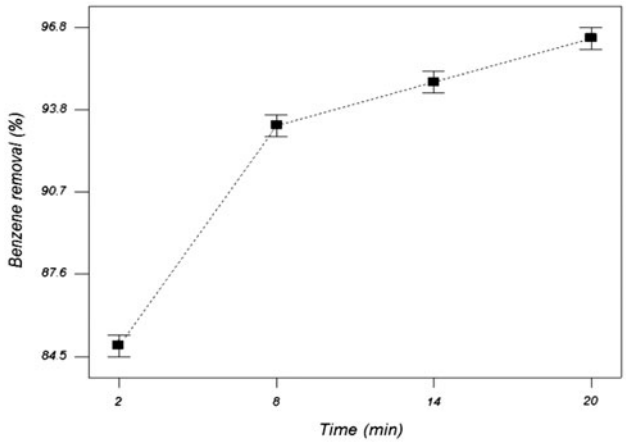

Fig. 5. Benzene removal efficiency by SWCNT-MN column at different retention times.

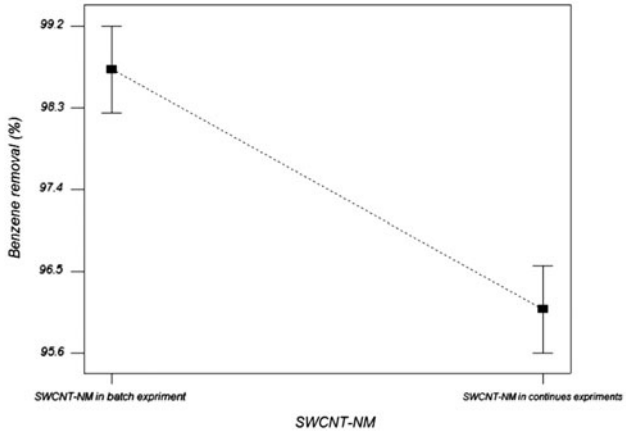

Fig. 6. Comparison of benzene removal efficiency by SWCNT-MN in batch and continuous experiments.

3.4. Isotherm study

In this study, ISOFIT was applied to involve the benzene adsorption by SWCNT-MN under batch condition. Water solubility (S_w) of benzene was estimated to be 1,790 mg/L at pH 8. Table 9 shows the q_e for optimum condition of benzene removal by SWCNT-MN at different initial benzene concentrations.

Table 10 summarizes some of the diagnostic statistics computed by ISOFIT and reports in the output file.

Table 10 shows the corrected akaike information criterion (AICc) values of isotherm study. The results indicate the GLF isotherm expression provided the best fit of the sorption data based on its relatively low value of multi model ranking (AICc). Non-linear regression techniques overcame many of the deficiencies associated with trial-and-error and linearization approaches to isotherm fitting. However, the performance of non-linear regression techniques could be impeded by the presence of local minima or excessive parameter correlation.

In Table 11, the Linssen measure indicates significant WSSE nonlinearity near the optimal parameter values. The statistical measures such as R_N^2 and Durbine Watson test (D) implied normally distributed weighted residuals with no serial autocorrelation.

Fig. 7 presents the plot of the fitted isotherm (GLF), organized into visually indistinguishable groups, along with the observed data points.

Table 11 contains selected ISOFIT output for the GLF isotherm. ISOFIT provides two "standard" measures for evaluating isotherm goodness of fit, namely the root mean squared error (RMSE, Eq. (6)) and the correlation between measured and fitted observations (R_y, Eq. (7)).

$$\mathrm{RMSE} = \sqrt{\frac{\mathrm{WSSE}}{(m-p)}} \tag{6}$$

$$R_y = \frac{\sum_{i=1}^{m}\left(w_i S_{i,\mathrm{obs}} - S_{\mathrm{obs}}^{\mathrm{avg}}\right)\left(w_i S_i - S^{\mathrm{avg}}\right)}{\sqrt{\sum_{i=1}^{m}\left(w_i S_{i,\mathrm{obs}} - S_{\mathrm{obs}}^{\mathrm{avg}}\right)^2 \sum_{i=1}^{m}\left(w_i S_{i,\mathrm{obs}} - S^{\mathrm{avg}}\right)^2}} \tag{7}$$

where WSSE is weighted sum of squared error, m is the total number of experimental observations, p is the number of isotherm parameters, w_i is the weight given to observation i, $S_{i,obs}$ is the i-th experimentally measured sorbed concentration, and S_i is the i-th simulated sorbed concentration computed via an isotherm expression, S_{obs}^{avg}, and S^{avg} are the averages of the weighted measured and weighted isotherm simulated adsorbed concentrations, respectively.

Table 9
Adsorption capacity of benzene removal by SWCNT-MN at different initial benzene concentrations

Initial benzene concentration (mg/L)	Adsorption capacity (q_e) (mg/g)
0	0.0
10	2.1
20	5.2
30	10.1
40	15.8
50	23.4
60	27.6
70	32.1
80	35.4
90	45.5
100	49.3

Table 10
Summary of selected diagnostics for benzene adsorbed by SWCNT-MN

Isotherms	AICc	R_y^2	R_N^2	M^2	Linearity assessment
GLF	15.5	0.993	0.987	5.9×10^{1}	Non-linear
Linear	22	0.992	0.941	4×10^{-9}	Linear
Langmuir	22.1	0.991	0.932	3.6×10^{-9}	Linear
BET	21.2	0.993	0.952	1.9×10^{1}	Non-linear
L-P	22.8	0.982	0.938	2.9×10^{-9}	Linear
F-P	23.2	0.972	0.915	4.2×10^{-9}	Linear
Toth	24.1	0.952	0.921	3.6×10^{-9}	Linear
Freundlich	25.2	0.962	0.921	1.4×10^{1}	Non-linear
P-P	28.1	0.892	0.913	4.7×10^{-1}	Non-linear
Polanyi	60.5	0.000	0.972	–	Uncertain

Notes: AICc: multi model ranking, R_y^2: correlation between measured and simulated observation, R_N^2: correlation between residual and normality, M^2: Linssen measure of non-linearity.

Table 11
Selected ISOFIT post regression output (GLF isotherm)

Parameter or statistic		ISOFIT result
Overall quality of fit	WSSE	1.7×10^{1}
	RMSE	1.5
	R_y	0.996
Parameter statistics	Q_0	1.8×10^{2}
	B	5.2
	$1/n$	1.5
Parameter std. error	Q_0	1.5×10^{2}
	B	4.4×10^{-3}
	$1/n$	2.5×10^{-1}
Test of assumptions	M^2	5.9×10^{1}
Linssen (M^2)	Threshold	0.2
	Assessment	Non-linear
Normality (R_N^2)	R_N^2	0.987
	Critical value	0.861
	Assessment	Normal residuals
Runs test	Number of runs	4
	p-value	0.952
	Assessment	No correlation
Durbine Watson test (D)	D	2.2
	p-value	0.550
	Assessment	No correlation

[a](CI_{low}, CI_{high}): lower and upper 95% confidence bounds.

3.5. Adsorbent recycling

Repeated availability is an important factor for an advanced adsorbent. The adsorbent not only possesses higher adsorption capability but also should show better desorption property, which will significantly reduce the overall cost for the adsorbent. Although SWCNT-MN showed high benzene sorption capacities from aqueous solution, very high unit cost currently restricts their potential use in water and wastewater treatment. Thus, testing the reversibility of the sorbents used for benzene removal is required in order to reduce their replacement cost. For this purpose, as a part of the study, probability of SWCNT-MN recycling was investigated. It should be highlighted that the major advantage of magnetic separation was the ability to recover the SWCNT-MN and reuse them for further benzene removal.

Table 12 shows the benzene removal percentage; SWCNT-MN was recycled in the first cycle (SWCNT-MNrec1) and was recycled in the second cycle (SWCNT-MNrec2) under optimum condition. Fig. 8 compares raw SWCNT-MN with their recycling in cycles of 1 and 2.

It is apparent from Fig. 8 that SWCNT-MN can be reused for the removal of benzene through a large number of water and wastewater treatment and regeneration cycles. But with increasing SWCNT-MN regeneration cycles, the benzene removal efficiency decreased. There were statistics differences between raw MN, MNrec1, and MN rec2 in benzene removal percentage (prob. > t less than 0.05). The results could hint that no strong bonds were created between the surface of SWCNT-MN and the benzene. Thus, the benzene adsorbed by the SWCNT-MN could be easily desorbed by temperature and thereby could be employed repeatedly in water and wastewater management. Zhang et al. [15] used ethanol/sodium hydrate solution (3:7, v/v) for bisphenol F desorption from MWCNT. They found that this solution had recovered MWCNT. Shen et al. [20] used 0.1 M NaOH to regenerate Fe_3O_4 for metal removal. They found that most of the adsorbed ions were desorbed in the

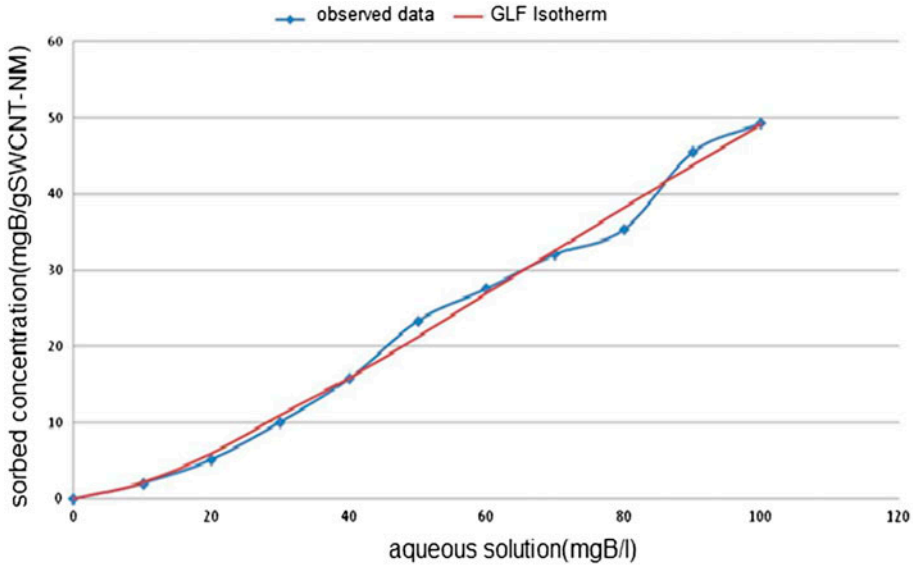

Fig. 7. Plot of fitted isotherm (GLF) and observed data for benzene removal by SWCNT-MN nonreactor.

Table 12
Benzene removal by raw and recycled SWCNT-MN under optimum condition

	Benzene		
Adsorbent	C_0 (mg/L)	C_t (mg/L)	Removal percentage (%)
Raw SWCNT-MN	100	1.4	98.6
SWCNT-MNrec1	100	4.3	95.7
SWCNT-MNrec2	100	5.6	94.4

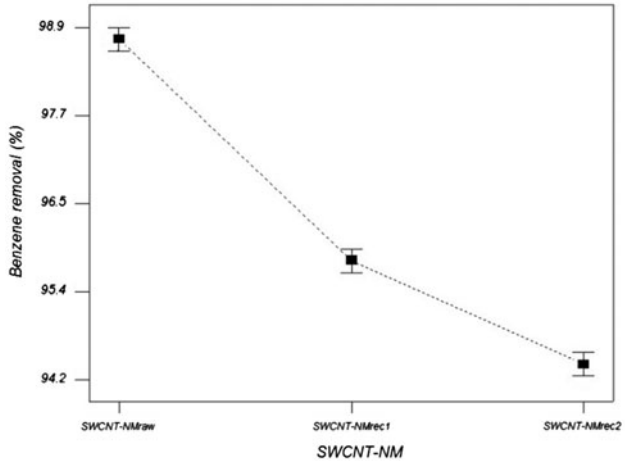

Fig. 8. Design expert plot for raw and recycled SWCNT-MN in benzene removal under optimum condition.

first cycle. This is the key factor whether a novel sorbent can be implemented in practice. It is expected that the unit cost of SWCNT-MN can be further reduced in the future by heat recycling processes. So, SWCNT-MN can be attractive as a cost-effective sorbent in removing benzene from the water and wastewater. The sorbent weight loss was neglected in the recycling processes.

4. Conclusion

The optimum condition was investigated to identify the highest capability of SWCNT-MN for benzene adsorption. Four effective parameters including benzene concentration, SWCNT-MN dose, contact time, and pH at four different levels were applied. It was concluded that SWCNT-MN had high capacity for benzene adsorption from the aqueous solution under the batch and continuous conditions. This effect was dependent on initial benzene concentration, adsorbent dose, and contact time but independent of pH over the entire studied range. The contact time was the most important factor to attain a better benzene removal and improved the SWCNT-MN efficiency. Under the optimum condition, SWCNT-MN had high benzene removal in batch experiment (98.6%). The GLF isotherm described the equilibrium adsorption data better than other alternative isotherms . SWCNT-MN was recycled and showed that the particles can be regenerated and reused in water and wastewater treatments. But, heating may reduce adsorption capacity of recycled SWCNT-MN. The application of SWCNT-MN for benzene removal and recovery of

them provides a simple and unique tool for benzene removal from water and wastewater. Benzene adsorption by new types of nanosorbent showed the adsorbents to be reusable, cost-effective, and simple to use. It is expected that the nanomaterials with will be used as one of the effective, convenient and low-costing methods for removal and recovery of benzene from water and wastewater.

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