Release Control of Nanomagnetic Particles in Water and Wastewater Treatment
Liberação Controlada de Partículas Nanomagnéticas no Tratamento de Águas e Águas Residuais

Hamidreza Pourzamani; Saeid Fadaei & Mohammad Mehdi Amin*

*Isfahan University of Medical Sciences, Environment Research Center,
Hezar Jerib Avenue Postal Code: 81746-73461. Isfahan, Iran
Emails: pourzamani@hlth.mui.ac.ir; saed_fadaei@hlth.mui.ac.ir; amin@hlth.mui.ac.ir
Corresponding author

Abstract

The present study was targeted to use of nanomagnetic column to remove toluene from water and wastewater and decrease release of nanomagnetic particles in environment. Based on the design of experiments (DOE), 16 experiments were arranged at 4 levels with 4 factors. The results showed that optimum condition for toluene concentration, NM dose, contact time and pH were100 mg.L^{-1}, 2000 mg.L^{-1}, 14 min, and 8, respectively. Although the toluene removal percent in batch system (greater than 98%) was higher in comparison to continuous system (greater than 95%), mass percent of nanomagnetic particles release in continuous system (7.6%) was less than batch system (28.3%).The equilibrium data was nicely fitted to the Brunauer-Emmett-Teller (BET) models. Our results indicated that these magnetic nanoparticles have high efficiency in toluene removal and nanomagnetic column has the capacity to reduce nano particles release into the environment by 20.7% in comparison to batch system.
Keywords: release control; nanomagnetic particles; water treatment; waste water treatment

Resumo

O presente estudo objetivou a utilização da coluna nanomagnética para remover tolueno a partir de água e esgoto e diminuição da liberação de partículas nanomagnéticas no ambiente. Com base no planejamento de experimentos (DOE), 16 experimentos foram organizados em 4 níveis com 4 fatores. Os resultados mostraram que a condição ótima para concentração de tolueno, a dose NM , o tempo de contacto e pH eram de 100 mg L- 1 , 2.000 mg L- 1, 14 minutos, e 8 minutos, respectivamente. Embora a percentagem de remoção de tolueno em sistema descontínuo (superior a 98 %) foi mais elevada em comparação com sistema contínuo (maior do que 95 %), a percentagem em massa de partículas nanomagnéticas liberadas no sistema contínuo (7,6 %) era menor do que o sistema do lote (28,3 %). Os dados de equilíbrio foram bem equiparados com os modelos de Brunauer-Emmett-Teller (BET). Os resultados indicaram que estas nanopartículas magnéticas têm alta eficiência na remoção de tolueno e a coluna nanomagnética tem a capacidade de reduzir as partículas nano liberadas no meio ambiente em 20,7 % comparada com o sistema de lotes.
Palavras-chave: liberação controlada; partículas nanomagnéticas; tratamento da água; água de esgoto

1 Introduction

Toluene (C_7H_8) is an aromatic hydrocarbon belonging to the BTEX group of hazardous volatile organic compounds (VOC), which includes benzene, ethylbenzene and xylene (Wei *et al*., 2010). Toluene is a volatile, monoaromatic compound, and is a common constituent in petroleum product, which is used as a raw material in numerous chemical productions and also often as a solvent in a wide variety of manufacturing processes (Pourzamani *et al*., 2012; Bina *et al*., 2012). This pollutant has been found to cause many serious health side effects to humans (*e.g*., skin and sensory irritation, central nervous system depression, respiratory problems, leukemia as well as disturbance of the kidney, liver, and blood systems) (Bina *et al*., 2011). For this reason researchers have paid increasingly more attention to toluene effluents in some industries, such as paints, paint thinners, fingernail polish, lacquers adhesives, rubber, some printing and leather tanning processes (Zhu *et al*., 2009).

Toluene concentration in industrial wastewaters varies between 7–753 mg.L^{-1} depending on the manufacturing type (Enright *et al*., 2007). Toluene is classified as a priority pollutant regulated by the U.S. Environmental Protection Agency (EPA) and is among the target compounds in EPA's 33-50 program (Shim *et al*., 2002). Toluene present in refinery and chemical industry effluents has a high polluting potential, due to its neurotoxin, carcinogenic and teratogenic properties, representing a high risk to the environment and human health (Mello *et al*., 2010).

Because of these health concerns, the U.S. Public Health Service (1989) has recommended that drinking water should contain no more than 2 mg.L^{-1} of toluene for lifetime exposure. Toluene is particularly important in this respect due to its relatively high solubility in water (Fornazzari *et al*., 2003). Since toluene is classified as a flammable, toxic, carcinogenic, and/or mutagenic agent, its presence in aqueous solutions, even at low concentrations, is of major environmental concern. Hence, the removal of these organic pollutants from water and wastewater is critical to ensure the safety of water supplies (Wibowo *et al*., 2007). Nanoparticles, often characterized by an extremely high surface to-volume ratio, have been attracting much interest because of their unique physical and chemical properties distinguishing them from their coarse sized counterparts. It has been well established that the magnetic nanoparticles are favorably chosen for water purification due to their larger surface area and high activity as well as the easy separation of absorbent from wastewater by means of an external magnetic field. Furthermore, with a proper control of crystallographic structures in the Fe_3O_4 nanoparticles, their functional performance can be greatly improved (Shen *et al*., 2009). Earlier studies (Amin *et al*., 2010) evaluated the efficiency of magnetic nanoparticles for removal of hexavalent chromium from simulated electroplating wastewater and concluded that 82% of Cr(VI) was removed. Earlier studies (Zhao *et al*., 2008) employed mixed silica-magnetite nanoparticle for extraction of several typical phenolic compounds from environmental water samples. They used nanoparticles for removal of bisphenol A (BPA), 4-tert-octylphenol (4-OP) and 4-n-nonylphenol (4-NP). The results of their experiment indicated that mixed Fe_3O_4/SiO_2 nanoparticles had good performance for removal of phenolic compounds from environmental water.

The present study aimed to decrease nanomagnetic particle release to environment by applying nanomagnetic column and determine the significance and optimum condition (pH, nano materials dose, initial toluene concentrations and contact time) for removing toluene from contaminated water and wastewater. Using magnetic column in the research not only helps reduce the space for the treatment of water and wastewater but also decrease the new pollutants to the environment.

2 Materials and Methods
2.1 Materials

A solution of 100 mg.L^{-1} of toluene was prepared by dissolving appropriate amounts of toluene (Merck, purity: 99.7%) in deionized H_2O. The mixture was solved thoroughly by using ultrasonic bath (Bandline Sonorex Digitex DT156, Sonorex Digiteccompany, Germany) for 60 min, and then, stirred continuously for 24 h at 25ºC. After shaking, the solution was put in ultrasonic bath again for 30 min (Bina *et al*., 2012) and was used to prepare initial solution of toluene with 10-100 mg.L^{-1} concentration. Standard series and samples were made using deionized H_2O to the desired concentrations.

2.2 Experimental Conditions

All of the batch experiments were conducted in 110 ml glass flask. In each experiment, a varied

amount of the adsorbents, 50 to 200 mg, was added to 100 ml of toluene solution, with the initial concentration (C_0) of 10-100 mg.L^{-1}. In addition, pH was changed from 2-11. These bathes were representatives of the low toluene level in gasoline-polluted water. The glass flasks were sealed with 20 mm stopper. Headspace within each flask was minimized to exclude any contaminant volatilization phenomena. After preparing all batches, the flasks were placed on a shaker (Orbital Shaker Model KS260B, IKA Company, Germany) and stirred at 240 rpm in room temperature for 2-20 minutes. The solution samples were then settled for 2 min. Magnetic field was used to separate suspended magnetic NM (nanomagnetic particle).

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 Tesla from the outside (Figure 1). The column was operated at the optimum condition that earns in batch experiments with retention times of 2, 8, 14, and 20 minutes.
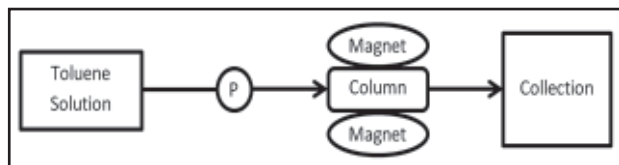

Figure 1 Up flow magnetic column used for continuous experiments.

Before and after each experiment, toluene was determined by using gas chromatograph-flame ionization detection (GC-FID). All of the experiments were repeated three times, and only were the mean values reported. Blank experiments, without the addition of adsorbents, were also conducted to ensure the decrease in toluene concentration that had actually been adsorbed on glass bottle wall or via volatilization.

The solution pH was measured at the beginning (pH$_{in}$) and at the end (pH$_{fin}$) of each experiment. The pH$_{in}$ was adjusted using 0.05 M HCl and 0.05 M NaOH. The amount of adsorbed toluene on adsorbent (q_e, mg.g^{-1}), distribution ratio (K_D, L.g^{-1}) and percent removals (%R) were calculated in equations 1 to 3.

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

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

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

Where C_0 and C_t (mg.L^{-1}) are the toluene concentrations at the beginning and end of each run, V is the initial solution volume (L), and m is the adsorbent weight (g).

2.3 Chemical Analysis

Initial samples were quantified via GC-FID at injection temperature of 210ºC, splitless mode of 80 ml.min^{-1} in 2 min, and detector temperature of 250ºC. The following temperature program was used: 36ºC for 1 min and 10ºC.min^{-1} to 90ºC, direct to 150ºC with 25ºC.min^{-1} rate and hold in 150ºC for 6 min. The hydrogen gas was used as the fuel (flow 30 ml.min^{-1}), air flow was 300 ml.min^{-1} and nitrogen was used as the makeup gas at a flow rate of 30 ml.min^{-1}. The column was a CP-sil 5 Cb 25m×320µm×1.2µm with helium (purity 99.995%) as carrier gas at the flow rate of 1.11 ml.min^{-1}.

The GC-MS was used for determining the toluene in low concentrations after treatment by Fe$_3$O$_4$. The Agilent technologies system consists of 5975C Inert MSD with Triple Axis Detector that is equipped with a 7890A GC with a split/splitless injector. A fused silica column, HP-5 ms (5%phenyl-95%dimethylpolysiloxane; 30 m 0.25 mm I.D, 0.25µm), was employed with helium (purity 99.995%) as carrier gas at a flow rate of 1 ml.min^{-1}. The column temperature was programmed as follows: 40°C for 10 min, increasing to 150°C at 10°C.min^{-1} 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 from 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 using 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 Amin and colleagues' article (Amin *et al.*, 2013). The headspace gas was injected to GC-FID or GC-MS injector from an automatic headspace sampler after 25 min shaking in 70ºC. No NaCl was added to the samples and the pH measurements were made on a pH meter (CyberscanpH1500, Thermo Fisher Scientific Inc, Netherland).

2.4 Adsorbents

During the experimental procedure, nanomagnetic particle was used as adsorbent. The NM (Nanostructured & Amorphous Materials Inc., United States) was characterized by the following specifications: Fe_3O_4, 20-30 nm, average particle size, 98+% purity, ≥ 40 $m^2.g^{-1}$ specific surface area, Stock #2650TR, CAS # 1317-61-9, Lot # 2650-031010. The X-Ray Diffraction (XRD) pattern was obtained for the iron oxide particles to determine its crystalline phase (X-Ray Diffractometer, Bruker, D8ADVANCE, Germany (X-Ray Tube Anode: Cu, Wavelength: 1.5406 Å (Cu Kα), Filter: Ni)). Figure 2 shows XRD pattern for the magnetic iron oxide (Fe_3O_4) particles. The particles are Fe_3O_4 and crystalline in nature. The particle size and shape of iron oxide was determined by transmission electron microscopy (TEM Philips CM10) at 100 kV (Figure 3). The particle had narrow distribution with a diameter of 20-30 nm.

2.5 Analysis of Data

DOE software (Design Expert 6) was used to ascertain the individual effects of pH, NM doses, initial concentrations of toluene, and contact time on removal of toluene. Also used for data analysis and to decrease the number of the experiments. The Taguchi OA plan was applied by four factors at four levels (Table 1). The matrix involved 16 runs and each run was triplicated. The corresponding factor values, in Table 1, were in compliance with the brain storming and literature (Lu *et al.,* 2008; Harja *et al.*, 2013; Koh & Dixon, 2001).

Factors	Level 1	Level 2	Level 3	Level 4
Toluene concentration (mg.L^{-1})	10	30	70	100
NM dose (mg.L^{-1})	500	1000	1500	2000
Contact time (min)	2	8	14	20
pH	2	5	8	14

Table 1 Controlling factors and their levels.

Isotherm study was evaluated for toluene adsorption by NM in optimum condition with initial concentration of 0-100 mg.L^{-1} (interval 10 mg.L^{-1}), NM dose 2 g.l^{-1}, contact time 14 min, and pH 8. Water solubility (S_w) of toluene was estimated to be 1790 mg.L^{-1} at pH 7. Isotherm Fitting Tool (ISOFIT) software was used to fit isotherm parameters to
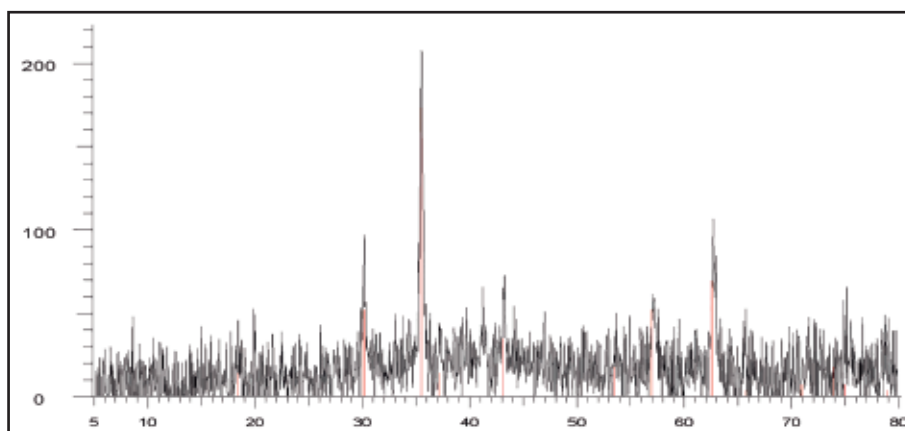

Figure 2 XRD pattern of Fe_3O_4

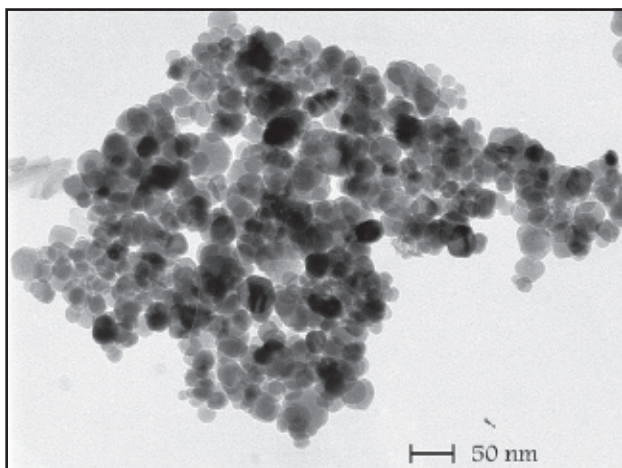

Figure 3 TEM monograph of Fe_3O_4

experimental data. ISOFIT is software that fits isotherm parameters to experimental data via the minimization of a weighted sum of squared error (WSSE) objective function (Koh & Dixon, 2001).

The ISOFIT supports 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 and Discussion

Table 2 shows that using Fe_3O_4 in batch experiments helped adsorb more than 98 % of toluene in run 10, which is consistent with previous studies (Amin *et al.,* 2013). Figure 4 shows the effect of parameters on toluene removal.

Response1: Toluene				Factors				
K_D (L.g^{-1})	qe (mg.g^{-1})	R %	Ct (mg.L^{-1})	pH	Time (min)	NM dose (mg. L^{-1})	Toluene concentration (mg.L^{-1})	Run
5.4	43.9	73.1	8.1±.6	8	8	500	30	1
21.8	14.7	97.8	0.7±0.1	5	14	2000	30	2
18.3	6.4	96.5	0.4±0.1	8	14	1500	10	3
11.6	119.4	85.3	10.3±.6	11	14	500	70	4
16.5	62.3	62.3	3.8±0.1	5	8	1000	10	5
2.2	20.7	69.1	9.3±.4	11	2	1000	30	6
22.3	95.7	95.7	4.3±.6	2	14	1000	100	7
6	4.6	92.4	0.8±0.1	11	20	2000	10	8
1.3	13.2	65.8	10.29±.1	2	2	1500	30	9
43	49.4	98.9	1.1±.2	8	20	2000	100	10
22.2	183.4	91.7	8.3±.8	5	20	500	100	11
6	90.1	90.1	9.9±.9	11	8	1500	100	12
1.7	27	77.3	15.9±2.1	2	8	2000	70	13
1.9	34.6	74.2	18±.2	5	2	1500	70	14
1.8	9.4	47.1	5.3±.1	2	2	500	10	15
14.7	65.5	93.6	4.5±.1	8	20	1000	70	16

Table 2 Design matrix and results of toluene removal by NM at different conditions.
Note: (qe) equilibrium amounts of the absorbed toluene on the NM /(mg . g^{-1}), (KD) the distribution ratio / (L .g^{-1})

% Contribution	Prob>F	F value	Mean squares	Sum of squares	Degree of freedom	Factor/ Interaction
26.2	0.0001<	714.6	931.1	2793.3	3	A: Toluene conc. /(mg.L^{-1})
17.3	0.0001<	437.2	616.6	1849.8	3	B: NM dose / (mg.L^{-1})
44.6	0.0001<	1217.3	1586.2	4758.6	3	C: Contact time /min
11.3	0.0001<	307.9	401.1	1203.4	3	D: pH
0.23	0.0019	6.3	8.3	24.8	3	AB interaction
0.4	-	-	1.3	39.1	30	lack of fit
0.000	-	-	-	0.000	0	Pure error
-	-	-	1.3	39.1	30	Residuals

Table 3 Effects of the factors and interactions obtained by fractional factorial design.

As presented in Figure 4 A, with raising the initial toluene concentration from 10 to 100 mg.L^{-1}, the toluene adsorption increased from 47.8% to 67.4%. Earlier studies (Iram *et al.*, 2010) obtained similar results and showed that the amount of neutral red dye adsorption increased from 30 mg.g^{-1} to 90 mg.g^{-1} as the dye concentration increased from 10 to 110 mg.L^{-1}. Figure 4 B indicates that, according to our expectation, an increase in NM dose directly affects the removal of toluene, while the optimum condition of NM dose was selected to be 2 g.L^{-1}. Figure 4 C shows that the highest rate of toluene adsorption occurs after 14 min. In toluene removal by NM, the amount of adsorbed toluene increased from 2 to 14 min and then remained constant.

Table 3 shows the effect of factors on toluene removal and their contribution percent. Based on the statistical analysis shown in Table 3, there was no significant difference (P value > 0.1) between toluene removal percentage in 14 and 20 min of contact time. The high removal of toluene by the NM in low contact time may be attributed to the external surface adsorption in addition to the micro-porous adsorption process. Figure 4 D shows that lowest toluene removal percent occurred at pH 2 as it increased by increasing the pH up to 8 and then was fixed. Besides, statistical analysis for toluene removal showed that there was no significant difference between pH 8 and 11 (P value > 0.1). On the contrary, the results of earlier studies (Khodabakhshi *et al.*, 2011) showed that maximum percentage of Cr removal was at pH 2, which decreased by increasing the pH. It is likely that the adsorption of toluene on NM sorbent was because of opposite charges between the sorbent and the toluene. However, these results cannot be satisfactorily 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 pH is greater than 6, some iron oxides may precipitate and produce $Fe(OH)_2$ as colloidal suspensions with high specific surface area. The solution pH would affect both aqueous chemistry and surface binding sites of the adsorbent. At low pH, the H ions would compete with toluene while the magnetic nanoparticles had higher negative charge at higher pH. That enhanced the positively charged toluene capturing through electrostatic force of attraction. Table 4 shows the toluene removal by nanomagnetic column as well as the acquired optimum condition used in nanomagnetic column, and maximum toluene uptake was 95.7 percent.
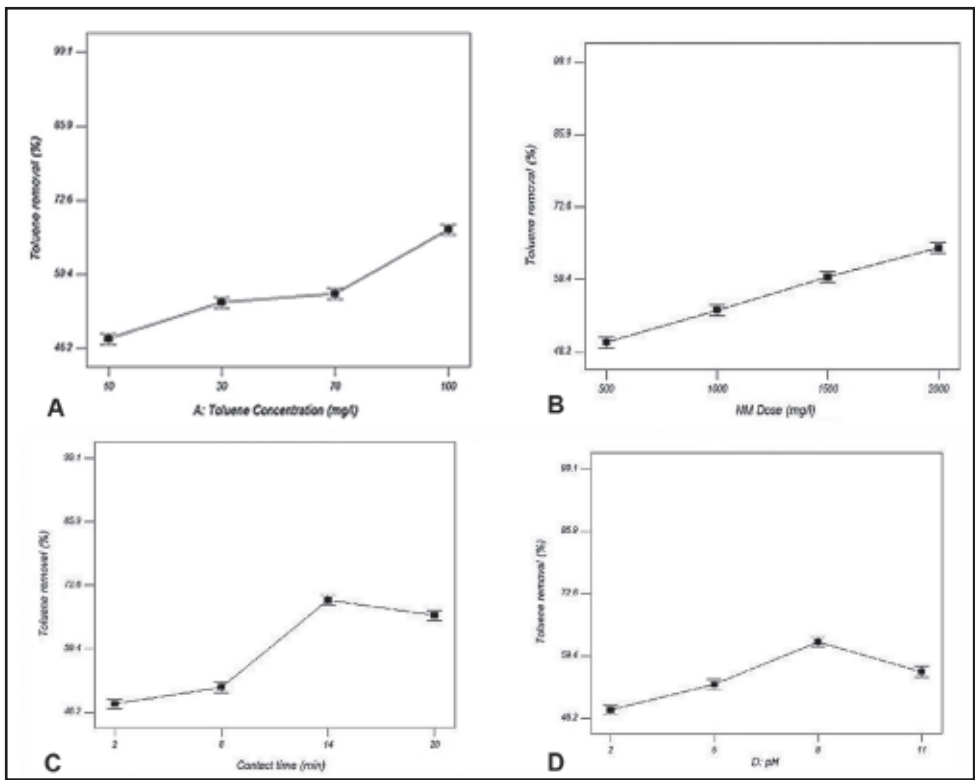
Figure 4 Expert plot of factors effect on toluene removal by NM in: (A) toluene concentration, (B) NM dose, (C) contact time, (D) pH.

Response1: Toluene				Factor				
KD (L.g^{-1})	qe (mg.g^{-1})	R (%)	Ct (mg.L^{-1})	pH	Time (min)	NM dose (mg. L^{-1})	Toluene concentration (mg.L^{-1})	Run
3.4	43.5	87.1	12.9±.43	8	2	2000	100.27	1
6.3	46.3	92.7	7.3± 0.44	8	8	2000	100.	2
11.1	47.8	95.7	4.3± 0.48	8	14	2000	100.	3
10.7	47.8	95.6	4.4± 0.37	8	20	2000	100.40	4

Table 4 Toluene removal by nanomagnetic column.

Thus, the optimum condition for toluene concentration, NM dose, contact time and pH are 100 mg.L^{-1}, 2000 mg.L^{-1}, 14 min, and 8 respectively. Whereby, in the optimum condition 98.9% of toluene was removed by NM. As shown in Figure 5, contribution of each parameter in toluene removal in batch experiments was obtained from DOE software. According to F value test, contact time plays the main role in toluene adsorption, and insignificant factors are interaction between toluene concentrations, NM doses, and pH. Thus, time is an effective factor for assessing adsorption capacity in liquid phase.

The toluene removal by the NM could be represented as equation 4:

Toluene removal (%) = 83.07-(11.02×toluene concentration)-(8.49×NM dose)-(-7.54×contact time)-(1.13×pH)   (4)
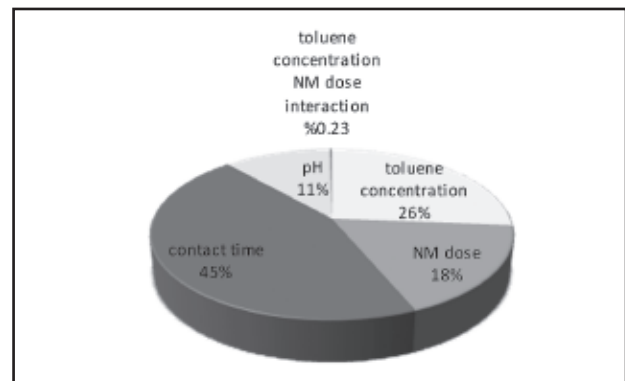

Figure 5 Contribution of each parameter in toluene removal in batch experiment.

Earlier studies (Lu *et al.,* 2008) used modified carbon nanotubes for enhancing BTEX adsorption at initial concentration of 200 mg.L^{-1}. They found modified carbon nanotubes had an adsorption capacity of 252.1 mg.g^{-1}. Earlier studies (Koh & Dixon, 2001) used montmorillonite (S/L: 0.1/40,C_0= 100), organominerals (S/L: 0.1/25,C_0= 100,Ct=18), and PAC (pH: 7,T: 25, S/L: 0.001/40,C_0= 200) for removal toluene, the qe (mg.g^{-1}) was obtained 27, 26, 40 respectively in this study. In our research according to Table 2 and run 11 the qe (mg.g^{-1}) was 183.3. (Note: T= temperature °C; S/L = solid/liquid (g.mL^{-1}); C_0= initial toluene concentration (mg.L^{-1}); Ct= contact time (h)).

The present study showed that under similar conditions for removal of toluene with various adsorbents, the NM had a better performance that, due to high efficiency and rapid adsorption, is able to be applied for toluene removal from water and wastewater.

ISOFIT (Isotherm Fitting Tool) is a software program that fits isotherm parameters to experimental data via the minimization of a weighted sum of squared error (WSSE) objective (Matott & Rabideau, 2008). As shown in Table 5, with ISOFIT reported in the output file, the corrected akaike information criterion (AICc) values indicate that the BET isotherm expression provides the best fit of toluene adsorption by NM. Earlier studies (Wibowo *et al.*, 2007) research the adsorption of toluene from aqueous solutions onto activated carbon. They reported that the Langmuir equation could describe the experimental data fairly better than Freundlich equation.

linearity assessment	M^2	R^2_N	R^2_y	AICc	Isotherms
Linear	2.3×10^{-3}	.906	.997	2.1	BET
Linear	2.3×10^{-9}	.889	.993	8.5	Langmuir
Linear	4.6×10^{-9}	.889	.993	8.5	Linear
Linear	2.2×10^9	.889	.993	8.5	F-P
Linear	4.2×10^{-9}	.889	.993	8.5	Toth
Linear	2.2×10^{-9}	.889	.993	8.5	L-P
Non-Linear	2×10^1	.891	.993	11.8	Freundlich
Non-Linear	4.5×10^{-1}	.906	.993	15.3	P-P
Non-Linear	8.1×10^1	.943	.994	12.5	GLF
uncertain	-	.977	0.000	58.62	Polanyi

Table 5 Summary of selected diagnostics for toluene adsorbed by NM.

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

Figure 6 contains plots of the fitted isotherms, organized into visually indistinguishable groups, along with the observed data points.
Figure 6 Plots of fitted isotherms and observed data: (a) P-P, Polanyi; (b) Langmuir, F-P, L-P, (c) GLF, (d) linear, Freundlich, (e) Toth, (f) BET.
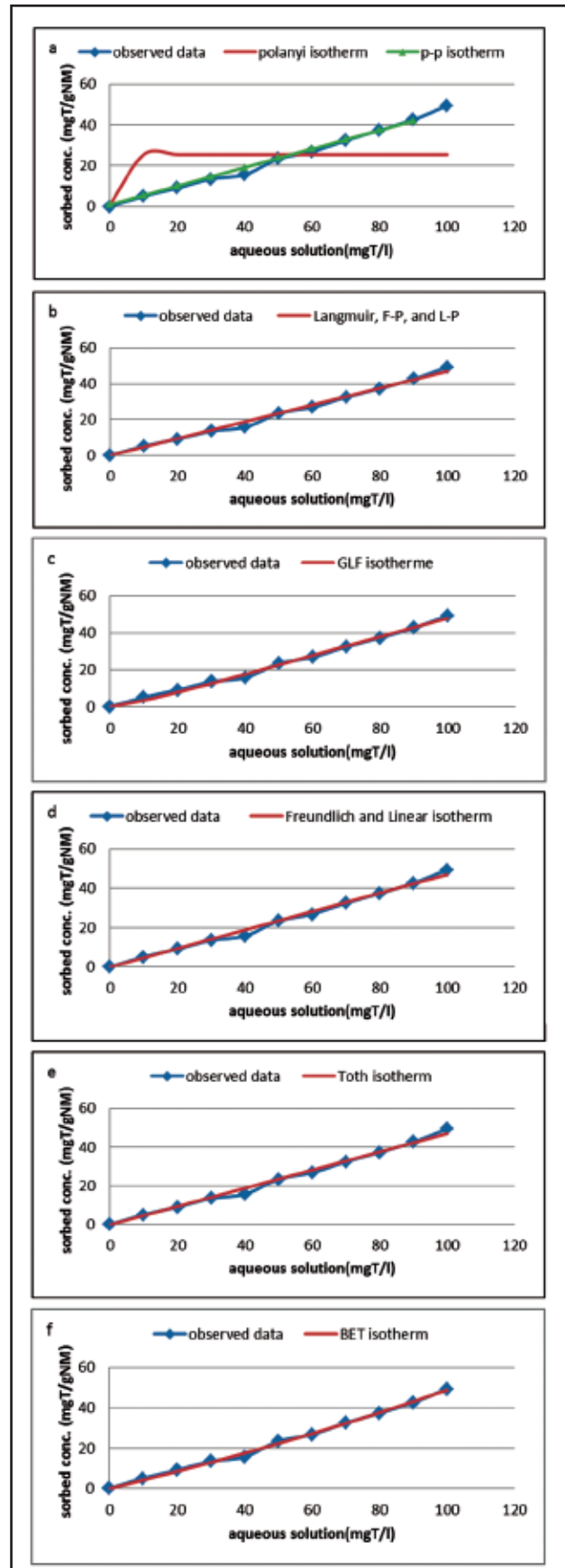
Table 6 shows the adsorption capacity of NM in different initial toluene concentrations that indicated, with rising the initial toluene concentration, the toluene adsorption capacity increased and the maximum adsorption capacity amounted to 49.4 mg.g^{-1}.

Initial toluene concentration (mg.L^{-1})	Adsorption capacity (qe) (mg.g^{-1})
0	0
10	5.1
20	9.1
30	13.5
40	15.7
50	23.4
60	26.8
70	32.5
80	37.4
90	42.6
100	49.4

Table 6 Adsorption capacity of toluene removal by NM in different initial toluene concentrations.

Table 7 shows the comparison between the means of NM release in batch and continuous system. As shown in Table 7 during a contact time of 20 min the average value of NM release in batch and continuous system was 28.3% and 7.6% respectively. It shows that use of NM column in toluene removal could prevent NM release to environment and saves it from new pollutant. In addition, it has a high efficiency in toluene removal.

Type of system	Toluene concentration (mg.L^{-1})	NM doses (mg.L^{-1})	pH	Contact time (min)	Means of NM recovery (mg.L^{-1})	Means of NM release %
Batch	100	2000	8	20	1434.3	28.3
Continuous	100	2000	8	20	1848.2	7.6

Table 7 Comparison of the mean value of NM release in batch and continuous system.

6 Conclusion

The effective parameters in toluene removal including contact time, initial toluene concentration, NM dose and pH were investigated and optimal conditions were determined in 16 experiments. The results showed that batch system had 3% more efficiency in toluene removal from aqueous solutions in comparison to nanomagnetic column, but the mass release of nano particles from nanomagnetic column reduced 20.7%. The maximum toluene uptake in the optimum situation was 49.4 mg.g^{-1}. The adsorption data was well fitted by the BET models. The advantages of using NM in removal of toluene are rapid adsorption, high efficiency, cost-effectiveness and simplicity. This suggests that the nanomagnetic column particles are efficient toluene adsorbents and are able to reduce nanoparticle release into the environment.

7 References

Amin, M.; Bina, B.; Majd, A. & Pourzamani, H. 2013. Benzene removal by nano magnetic particles under continuous condition from aqueous solutions. *Frontiers of Environmental Science & Engineering*, p. 1-12.

Amin , M.M.; Khodabakhshi, A.; Mozafari, M.; Bina, B. & Kheiri, S. 2010. Removal of Cr (VI) from simulated electroplating wastewater by magnetite nanoparticles. *Environmental Engineering and Management Journal, 9:* 921-927.

Bina, B.; Amin, M.M.; Rashidi, A. & Pourzamani, H. 2012. Benzene and toluene removal by carbon nanotubes from aqueous solution. *Archives of Environmental Protection, 38*(1):3-25.

Bina, B.; Pourzamani, H.; Rashidi, A. & Amin, M.M. 2011. Ethylbenzene Removal by Carbon Nanotubes from Aqueous Solution. *Journal of Environmental and Public Health,* 2012.

Enright, A.-M.; Collins, G. & O'Flaherty, V. 2007. Low-temperature anaerobic biological treatment of toluene-containing wastewater. *Water Research, 41*: 1465-1472.

Fornazzari, L.; Pollanen, M.S.; Myers, V. & Wolf, A. 2003. Solvent abuse-related toluene leukoencephalopathy. *Journal of Clinical Forensic Medicine, 10*: 93-95.

Harja, M.; Buema, G.; Sutiman, D. & Cretescu, I. 2013. Removal of heavy metal ions from aqueous solutions using low-cost sorbents obtained from ash. *Chemical Papers, 67*: 497-508.

Iram, M.; Guo, C.; Guan, Y.; Ishfaq, A. & Liu, H. 2010. Adsorption and magnetic removal of neutral red dye from aqueous solution using Fe3O4 hollow nanospheres. *Journal of Hazardous Materials, 181*: 1039-1050.

Koh, S.-M. & Dixon, J.B. 2001. Preparation and application of organo-minerals as sorbents of phenol, benzene and toluene. *Applied Clay Science, 18*: 111-122.

Lu, C.; Su, F. & Hu, S. 2008. Surface modification of carbon nanotubes for enhancing BTEX adsorption from aqueous solutions. *Applied Surface Science, 254*: 7035-7041.

Matott, L.S. & Rabideau, A.J. 2008. ISOFIT - A program for fitting sorption isotherms to experimental data. *Environmental Modelling & Software, 23*: 670-676.

Mello, J.M.M.D.; Lima Brandão, H.; Souza, A.A.U.; Silva, A. & Souza, S.M.D.A.G.U. 2010. Biodegradation of BTEX compounds in a biofilm reactor--Modeling and simulation. *Journal of Petroleum Science and Engineering, 70*: 131-139.

Pourzamani, H.; Bina, B.; Rashidi, A. & Amin, M. 2012. Performance of raw and regenerated multi-and single-walled carbon nanotubes in xylene removal from aqueous solutions. *International Journal of Environmental Health Engineering, 1*: 4.

Shen, Y.F.; Tang, J.; Nie, Z.H.; Wang, Y.D.; Ren, Y. & Zuo, L. 2009. Tailoring size and structural distortion of Fe3O4 nanoparticles for the purification of contaminated water. *Bioresource Technology, 100***:** 4139-4146.

Shim, H.; Shin, E. & Yang, S.-T. 2002. A continuous fibrous-bed bioreactor for BTEX biodegradation by a co-culture of *Pseudomonas putida* and *Pseudomonas fluorescens*. *Advances in Environmental Research, 7***:** 203-216.

Wei, Z.; Sun, J.; Xie, Z.; Liang, M. & Chen, S. 2010. Removal of gaseous toluene by the combination of photocatalytic oxidation under complex light irradiation of UV and visible light and biological process. *Journal of Hazardous Materials, 177***:** 814-821.

Wibowo, N.; Setyadhi, L.; Wibowo, D.; Setiawan, J. & Ismadji, S. 2007. Adsorption of benzene and toluene from aqueous solutions onto activated carbon and its acid and heat treated forms: Influence of surface chemistry on adsorption. *Journal of Hazardous Materials, 146***:** 237-242.

Zhao, X.; Shi, Y.; Wang, T.; Cai, Y. & Jiang, G. 2008. Preparation of silica-magnetite nanoparticle mixed hemimicelle sorbents for extraction of several typical phenolic compounds from environmental water samples. *Journal of Chromatography A, 1188***:** 140-147.

Zhu, T.; Li, J.; Liang, W. & Jin, Y. 2009. Synergistic effect of catalyst for oxidation removal of toluene. *Journal of Hazardous Materials, 165***:** 1258-1260.