

Ethylbenzene Removal from Aqueous Solutions by Nano Magnetic Particles

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A-R-T-I-C-L-E-I-N-F-O

Article Notes:

Received: Oct 10, 2015

Received in revised form:

Nov 24, 2015

Accepted: Dec 10, 2015

Available Online: Dec 24, 2015

Keywords:

Adsorption, Ethylbenzene, Nano magnetic particles, Iran.

A-B-S-T-R-A-C-T

Background & Aims of the Study: Ethylbenzene (EB) is a dangerously organic compound, which the presence of this pollutant in water solutions can be considered as an environmental and public health hazard. In this study, nano magnetic particles (Fe_3O_4) were used as an adsorbent to remove ethylbenzene from aqueous solutions.

Materials & Methods: The specification of the adsorbent was investigated by transmission electronic microscope (TEM) and X-ray diffraction (XRD) pattern. A 4×4 factorial design including initial concentration of ethylbenzene, nano magnetic particles dose, contact time and pH were studied.

Results: The results showed that the maximum ethylbenzene removal by nano magnetic particles was achieved in the following conditions; 100 mg.L⁻¹, 2000 mg.L⁻¹, 20 minutes and 8, in initial concentration, nano magnetic concentration, contact time and pH respectively. The most amounts of ethylbenzene adsorption and distribution ratio in optimum condition was 49.9 mg.g⁻¹ and 261.9 l.g⁻¹ respectively. The results demonstrated that the removal rate of ethylbenzene was higher in batch (99.8 %) rather than continuous (97.4%) condition.

Conclusions: The removal rate of ethylbenzene was higher in batch rather than continuous condition. The study of isotherm showed that adsorption data follow up linear isotherm. Comparing adsorption rate of NM particles and other adsorbents proved that Fe_3O_4 , as a material with high capacity of adsorption can apply for removing ethylbenzene as an efficient and also cheap adsorbent.

Please cite this article as: Hadei M, Aalipour MR, Mengli Zadeh N, Pourzamani H. Ethylbenzene Removal from aqueous solutions by nano magnetic particles. Arch Hyg Sci 2016;5(1):22-32.

Background

US Environmental Protection Agency has estimated that 35 percent of underground reservoir of diesel and gasoline fuels leak. 40 percent of these leaks are the main cause of underground water and soil pollution (1). Ethylbenzene (EB) is a dangerously organic compound, which can be usually found in most petroleum and gasoline materials leaked into aqueous solutions (2). This compound has currently the most amounts of benzene derivatives that over its 90 percent are used in styrene production. Ethylbenzene is also utilized massively as raw material and solvent for synthesizing of organic materials and

cleaning the instruments in industries (3,4). The presence of this pollutant in water solutions can be considered as an environmental and public health hazard (such as skin irritation, central nervous system suppression, respiratory problems, cancer, renal failure and circulation system) (1,2). Therefore, ethylbenzene removal from water solutions is necessary to minimize its health and environmental threats.

This has been studied tremendously and varied processes such as bioremediation, volatilization and chemical oxidation in addition to adsorption have led to remove ethylbenzene successfully. However, using these processes, practically and in large scale, has some benefits and also threatening effects including their

questionable effectiveness, dependency to site, production of secondary unwanted materials and high operational costs (2,5,6). Adsorption process is one of the commonest alternatives for removing this pollutant that is effective and economical, and it is efficient for recycling the adsorbent and adsorbate materials. In recent years, most of new and common adsorbents have been applied and studied (7,8), but application of nano magnetic particles (NM) to remove ethylbenzene from water solutions has been reported rarely. However, this adsorbent with great and controllable specifications can be applied in bioseparation processes and pollutant removal (6). NM have practical applications in medical, biotechnology, biological and chemical treatment of wastewater due to have some characteristics including chemical inertness, low level of toxicity, high specific surface area and bio compatibility (9). They also have the capability of simple separation by use of a strong magnetic field that is remarkably probable to being recycled and reused (10). Lin et al found that modified magnetic particles with amino groups had the most adsorption capacity of 10.41 mg.g^{-1} for copper metal (7). Bystrzejewski et al reported 95% effectiveness for Carbon-encapsulated magnetic nanoparticles for cadmium and copper removal (11). Nano magnetic had 98.7 and 94.5% effectiveness for benzene in batch and continuous condition, respectively (12). In present study, experimentally and continuous condition were used to remove ethylbenzene from aqueous solutions. In addition, the influence of some parameters such as initial pH, adsorbent dose, initial concentration of ethylbenzene and contact time over ethylbenzene removal were studied in this investigation. Different isotherms were assessed to adjust absorption data balance by use of ISOFIT program. This actually was done for predicting the specifications of adsorption process.

Aims of the study:

The influence of some parameters such as initial pH, adsorbent dose, and initial concentration of ethylbenzene and contact time over ethylbenzene removal was studied in this investigation.

Ethylbenzene removal from aqueous solutions in continuous condition base on optimum condition of bath experimental is novelty of this study.

Materials & Methods

Materials:

A 100 mg.L^{-1} ethylbenzene was provided by dissolving appropriate amount of ethylbenzene (Merck, purity: 99.7 percent) in deionized water. The solution was kept 60 minutes in ultrasonic shaking bath and then stirred in 24°C during 24 hours continuously. Then, the solution was put in ultrasonic bath for 30 minutes and used to make initial solutions of ethylbenzene with $10\text{-}100 \text{ mg.L}^{-1}$ concentrations.

Experiments:

Adsorption batch experiments were done in different initial pH levels (from 2 to 11) to study the effect of varied factors and effectiveness for ethylbenzene removal. In a 110 ml glass flask, 100 mg of adsorbent, 100 ml of ethylbenzene solution and 10 mg.L^{-1} initial NM concentrations were used. This amount represents the low-level polluted water by gasoline. The flask was sealed thoroughly by use of a 20 mm stopper. Then, it was rotated within 2, 8, 14 and 20 minutes with pH 2 to 11 ranges, in room temperature and with 240 rounds per minute. After that, the sediment was formed during two minutes. Finally, the concentration of ethylbenzene was measured in liquid phase by a gas chromatography-mass spectrometry (GC/MS). All the tests in this study were done three times and only mean value is reported.

Furthermore, a blank sample was provided with no adsorbent to ensure that ethylbenzene concentration decrease was due to adsorption

on NM but not because of being adsorbed by glass bottle or through volatilization.

NM performed the continuous experiments to study the effectiveness of ethylbenzene removal. The glass column, with 5 cm diameter and 20 cm height, was filled by stainless steel wool and covered externally by two magnets with 15 Tesla. Then raw water including ethylbenzene (100 mg.L⁻¹) was passed by use of a pump through the column with different rates of flow. Finally, the output of this filter was measured to determine the amount of removed ethylbenzene.

The pH of solution was measured by a pH meter (EUTECH, model 1500) in two forms including pH in and pH out. This was done before and after the contact of solution with NM in all conducted tests. The adjusting of pH was performed by 0.05 mol.L⁻¹ HCL and 0.05 mol.L⁻¹ NaOH. The amount of ethylbenzene adsorbed on NM (q_e , mg.g⁻¹), removal percentage (%R) and distribution ratio (K_D , l.g⁻¹) was measured through following equations:

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

$$\%R = \frac{C_0 - C_t}{C_0} \times 100 \quad \text{Equation 2}$$

$$K_D = \frac{C_0 - C_t}{C_0} \times \frac{V}{m} \quad \text{Equation 3}$$

In these equations C_0 , C_T (mg.L⁻¹), V (L) and m (g) represent initial and final concentration of EB, initial volume of solution and adsorbent weight, respectively.

Measurements:

A GC device having MSD, manufactured by Agilent Corporation, specified by 5975C model and regulated in split/splitless injection mode was used to measure the concentration of samples and determine the characteristics of compounds. For doing this measurement, a silica column (HP.5ms) helium gas (with 99.95 percent of Purity) and flow rate of 1 ml/min as carrier gas was used. The program of MSD column temperature was regulated as followed: temperature was adjusted 36 °C for one minute

and increased up to 140 °C with 10 °C/min rate and kept for two minutes. The temperature of injection site was regulated around 210 °C and 1 ml of head space gas volume was injected into MS device when it was in split less mode. The output of gas chromatography column was transferred to detector through transfer line with 280 °C. The analysis was done in scan mode by MS. The achieved data was studied by MS Data Analysis software.

Gas chromatograph-flame ionization detection (GC-FID), (model 7890A, Agilent Company, United Stat) was applied to measure the concentration of the samples before treatment. In this condition, the temperature of samples injection site and detector temperature were, in turn, 210 and 250 °C in splitless mode. The flow was 80 ml.min⁻¹ for 1 minute.

The program of column temperature was adjusted as followed; the temperature was regulated 30 °C for one minute and increased up to 90 °C with 10 °C/min rate. The temperature was raised to 150 °C with 25 °C/min rate and it was kept for 6 minutes. Hydrogen with 30 ml/min and air with 300 ml/min flow rates were used to induce flame as fuel. Nitrogen was also applied as the makeup gas with 30 ml/min flow rate. The column used in GC/FID included 320 μm×1.2 μm×CP-sil 5 Cb 25. The injection of sample was done by a head space (HS) which was called CTC PAL-Combi PAL and was planned according to Amin et al (2014) (12).

A transmission electronic microscope (TEM, Philips CM10) was used to determine NM's monograph and particle size. The crystal structure of these NM was analyzed by an X-ray diffraction (XRD) device.

Data Analysis:

The data analysis was done to find the impact of pH, NM dose, ethylbenzene initial concentration and contact time on ethylbenzene removal. This process was conducted through Taguchi orthogonal method and experiment designed by design expert software. Taguchi method was studied by four factors and in four

levels in present study, as done before in Amin et al (2014) (12). The isotherm results of ethylbenzene removal was calculated in NM's optimal condition (2 g/l), 14 minutes of contact

Results

Adsorbent characteristics:

time, PH 8 and 0-100 mg.L⁻¹ of initial concentration by use of ISOFIT software. calculated values.

Figure 1 shows XRD analysis and TEM image of Fe₃O₄ particles. According to this figure, the most percentage of Fe₃O₄ particles are those that their sizes are between 20 to 30 nm.

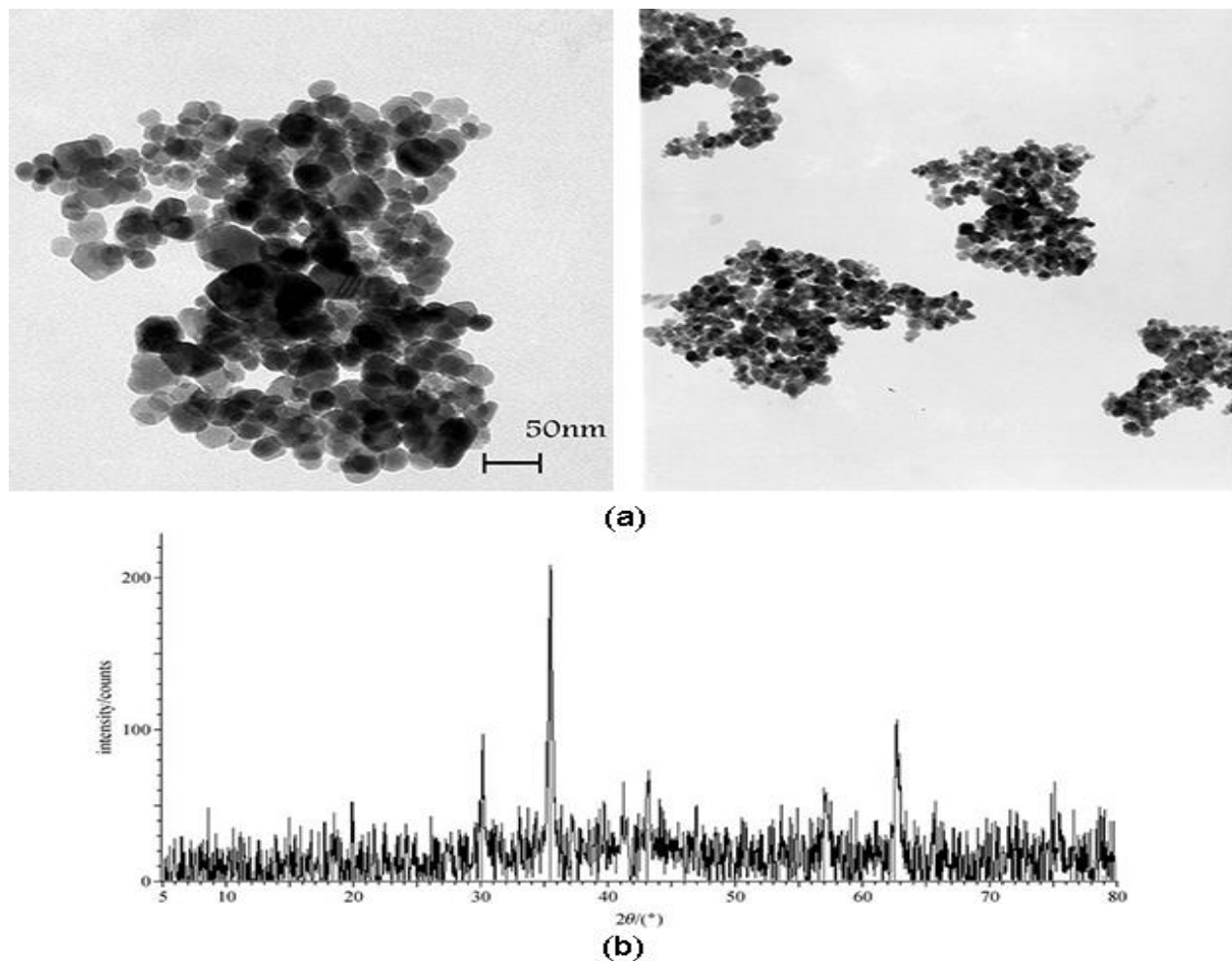


Figure 1) (a) TEM image related to NM, (b) XRD pattern related to NM

Table 1) ethylbenzene removal by NM in different conditions

	factors				results			
	EB concentration (mg.L ⁻¹)	NM concentration (mg.L ⁻¹)	time (min)	pH	efficiency (%)	q _e (mg.g ⁻¹)	K _D (L.g ⁻¹)	
stages	1	30	500	8	8	96.8±0.10	58.1±0.06	60.6±0.002
	2	30	2000	14	5	99.3±0.09	14.8±0.01	67.4±0.000
	3	10	1500	14	8	96.0±0.26	6.4±0.02	16.3±0.002
	4	70	500	14	11	94.2±0.00	131.8±0.00	32.3±0.000
	5	10	100	8	5	86.3±0.22	86.3±0.22	63.1±0.022
	6	30	1000	2	11	92.5±0.28	27.8±0.08	12.4±0.003
	7	100	1000	14	2	99.8±0.03	99.8±0.03	423.5±0.000
	8	10	2000	20	11	98.0±0.39	4.9±0.02	25.7±0.002
	9	30	1500	2	2	87.9±0.12	17.6±0.02	4.8±0.001
	10	100	2000	20	8	99.8±0.05	49.9±0.03	277.4±0.000
	11	100	500	20	5	99.7±0.03	199.4±0.06	639.8±0.001
	12	100	1500	8	11	96.2±1.77	64.1±1.18	19.1±0.012
	13	70	2000	8	2	99.1±0.04	34.7±0.01	54.5±0.000
	14	70	1500	2	5	99.1±0.06	46.2±0.03	73.9±0.000
	15	10	500	2	2	83.5±0.33	16.7±0.07	10.1±0.007
	16	70	1000	20	8	97.6±0.97	68.3±0.68	45.3±0.010

Table 2) Effects of the factors and interrelated interactions

factor-interaction	DF ^{a)}	sum of squares	mean squares	F value	prob>F	contribution %
A:initial concentration of ethylbenzene (mg.L ⁻¹)	3	449.3	149.8	527.1	<0.0001	36.8
B: NM dose (mg.L ⁻¹)	3	227.9	75.9	267.4	<0.0001	18.7
C: contact time	3	231.7	77.2	271.8	<0.0001	19
D: pH	3	72.9	24.3	85.6	<0.0001	5.9
AB interaction	4	229.6	57.4	201.9	<0.0001	18.8
lack of fit	29	8.2	0.3	-	-	0.7
pure error	0	0.000	-	-	-	0.000
residuals	29	8.2	0.3	-	-	-

Note: a) Degree of freedom

Table 3) ethylbenzene removal by NM column

	factors				results			
	EB concentration (mg.L ⁻¹)	NM concentration (mg.L ⁻¹)	time (min)	pH	efficiency (%)	q _e (mg.g ⁻¹)	K _D (L.g ⁻¹)	
stages	1	100	2000	2	8	90.4±0.72	45.2±0.36	4.7±0.39
	2	100	2000	8	8	93.7±0.55	46.8±0.27	7.4±0.71
	3	100	2000	14	8	98.4±0.90	49.2±0.45	37.4±16.27
	4	100	2000	20	8	97.8±0.41	48.9±0.21	22.6±3.93

Table 4) The summary of assessment parameters selected for adsorbing ethylbenzene by Fe₃O₄

isotherm	(AICc) _a	(R ² _N) _b	(M ²) ^c	the assessment of being linear
Linear	14.8	0.939	5.4×10 ⁻⁹	linear
Langmuir	14.9	0.939	5×10 ⁻⁹	linear
F-P	14.9	0.939	2.2×10 ⁻⁹	linear
L-P	14.9	0.939	2.7×10 ⁻⁹	linear
BET	17.2	0.964	10×10 ⁻²	uncertain
Freundlich	18.1	0.938	20	non-linear
P-P	19.6	0.947	4.7×10 ⁻¹	non-linear
GLF	20.5	0.934	38	non-linear
Toth	22.7	0.935	2.7×10 ⁻¹	linear
Polanyi	55.6	0.963	2.9×10 ⁻¹⁵	linear

Notes: a) multi model ranking, b) correlation between residual and normality, c) Linssen measure of nonlinearity.

Performing batch experiments:

Table 1 shows removal and adsorption rates of ethylbenzene and distribution NM particles. Table 2 demonstrates the impacts of every one of influencing factors and reactions in removing EB.

performing continuous experiments:

Batch experiments proved that NM has high capability to removing ethylbenzene from aqueous solutions. However, removing ethylbenzene from batch systems is not possible in real situations. Therefore, by performing continuous tests for removing ethylbenzene by

NM, the optimum condition achieved and compared with the batch results one.

Table 3 show removal rate of ethylbenzene in NM column.

Isotherm study:

ISOFIT statistical program assessed ethylbenzene removal rate by Fe₃O₄ in batch experimental condition. Error! Reference source not found. demonstrates the results of statistical calculations conducted by this program for determining the most appropriate isotherm in optimal conditions and different input concentrations

Discussion

XRD analysis of NM shows that the most percentage of these compounds included Fe₃O₄ nanoparticles. However, very few impurities (less than 1.5 %) are found in them, which are mostly consisted of Fe₃O₄. The comparison of XRD pattern of nanoparticles with standard diffraction of X-ray proved that produced material included mainly crystalized Fe₃O₄ and less amounts of Fe₂O₃ or Fe(OH)₂. The sharp peaks of this figure demonstrate vividly that Fe₃O₄ nanoparticles have high crystalized

specification. So, the unique structure of Fe_3O_4 nanoparticles crystals can assemble a large number of ions in four and eight-dimension sites. This makes especial magnetic interactions among these crystals. TEM image of nanoparticles showed that their size were between 20 to 30 nm. They also could be detected individually and identically.

Table 1 shows that the most amount of ethylbenzene removal (99.8%) by NM was seen in batch experiments which is compatible to other studied results (13,14). The influence of pH on chemical properties of water solution and absorption was an important factor when ethylbenzene adsorption was studied. The results of experiments proved that the most level of ethylbenzene removal efficiency by NM was happened in pH 8 (Table 1). Ion H^+ competes with EB's compound in adsorption process when pH is low. In pH higher than 7 surface charge of NM is mostly negative due to adsorption of OH^- ions. Therefore, this leads to more adsorbing of ethylbenzene by positive charge because of making electrostatic forces (14). Pang et al found in their study that the efficiency of copper removal by Fe_3O_4 was very low in acidic condition. In contrast, when pH raised, the efficiency increased sharply. However, it decreased again when pH was higher than 7 (15). Zhang et al reported that neutral condition was very appropriate to remove Aniline by NM (16).

Figure 2-b shows that the ethylbenzene adsorption increased and then reduced when contact time reached from 2 to 14 minutes. This can be related to functional groups of NM. However, these results are not compatible to previous studies. Seifi et al studied BTEX absorption on nanoparticles of natural zeolites modified by surfactant. They reported that the maximum adsorption of BTEX happened in a very long period of time (17). Yu et al investigated BTEX adsorption on multi wall nanotubes and found that the maximum adsorption of toluene, ethylbenzene and xylene happened during 50 minutes (18). The reason of

this difference in maximum adsorption by NM and other adsorbents may be due to have individual specifications of each adsorbent including its structure, functional groups and surface area.

The study of adsorbent amount impact on ethylbenzene adsorption rate shows that adsorption increase when the amount of adsorbent increase. This is caused by increasing surface area and the accessible sites to adsorb ions (19). This is compatible to Aisien et al study's results which was conducted to find the amount of ethylbenzene adsorption by use of recycled tyre (20). When EB's initial concentration increases, ethylbenzene adsorption rate develops, but removal efficiency decreases. This may be because of reducing the active sites of adsorbent in high concentrations of ethylbenzene (21). Ha et al study indicated that the efficiency of Cr (VI) removal decreased by NM (Fe_3O_4) when its initial concentration increased. They came to this conclusion that it was related to this fact that the numbers of adsorption sites are limited and fixed in a definite dose of nanoparticles (22).

Kakavandi et al found in their investigation that when Aniline's concentration increases, the adsorption rate of Fe_3O_4 by activated carbon nanoparticles increases (23). It was reported in Qadri et al study that the efficiency of Fe_3O_4 nanoparticles removal increased when initial concentration of acridine increased. They found that when its initial concentration reached from 3.7 mg.L^{-1} to 185 mg.L^{-1} , adsorption capacity reached from 3.6 mg.L^{-1} to 35 mg.L^{-1} respectively (13). So, the highest ethylbenzene removal rate by NM was achieved in 100 mg.L^{-1} of initial concentration, 2000 mg.L^{-1} adsorbent concentration, 20 minutes of contact time and pH 8. The removal rate of ethylbenzene by NM was 99.8 percent if these conditions were provided. The same results for Cr maximum adsorption on multi wall nanotubes were reported when pH, initial concentration, adsorbent dose and contact time

were 3.5 mg.L⁻¹, 60 mg and 150 minutes respectively. The highest rate of Cr removal was over 95 percent (19).

In addition, Table 2 shows that four factors were effective in removing ethylbenzene considerably among which initial concentration of ethylbenzene with 36.8 percent (F=527.1) of effectiveness portion is the most significant one. The impact of ethylbenzene initial concentration and NM concentration and their inter-related reactions had high efficiency (18.8%) over removing EB. Their influence was more than pH according to achieved results. The sequence of effective agents in removing ethylbenzene by NM is as followed respectively:

EB initial concentration > contact time > inter-related reactions between NM and EB initial concentration > NM concentration > PH

Amin et al (2013) investigated benzene removal by NM and indicated that contact time and pH were the most and least impact on benzene removal with 35.9 (F=1374) and 8.6 percent (F=239) portion, respectively. Furthermore, they reported that there was an interaction between benzene concentration and adsorbent dose which their changes are important in efficiency of benzene removal by NM (12). Özbay et al (2013) in their study to find the effective factors and their interaction in Dye adsorption came to this result that the impact of adsorbent dose and pH are more than Dye initial concentration and the interaction between pH and adsorbent dose (24).

Sun et al applied the DOE to find an optimum condition for the factors affecting preparation, morphology and catalytic activity of nano crystalline TiO₂ thin film. In this project, one-hour photo degradation efficiency of methyl orange in an aqueous solution and toluene in gaseous phase was obtained 98.9 and 100 percent respectively (25).

The DOE results of current study analyzed, firstly, by using direct observation analysis, because the responses versus the levels of different factors can be observed directly from

a broken line plot. The mean value of the degradation efficiencies for the corresponding factors at each level was measured according to the assignment of the experiment. This research showed that the experimental design methods applied in this project would have high significance in designing and improving high efficiency of performance for environmental and cost saving matters.

The study results of ethylbenzene removal by NM column showed that the removal increased when contact time developed from 2 to 14 minutes and then left constantly. The comparison which was made among different times designed in experiments demonstrated that there was a significant difference of in efficiency of ethylbenzene removal in 2, 8, 14 and 20 minute durations (Prob>|t| less than 0.05). There was not any significant difference between 14 and 20 minutes contact times (probe>|t| greater than 0.05). It proves that NM causes the highest level of ethylbenzene adsorption in the first 14 minutes. Furthermore, the study of removal efficiency indicated that the efficiency of ethylbenzene removal by NM was less than batch experiment. This may be related to being crystalized of NM on stainless steel wool. Vijayaraghavan et al (2005) used brown marine algae *Turbinaria Ornata* as adsorbent for removing zinc metal in column and batch conditions. The maximum levels of copper adsorption were 147.06 and 68 mg.g⁻¹ in batch and column experiments, respectively (26).

Table 4 which shows the corrected akaike information criterion (AICc) achieved from ISOFIT software demonstrate that the linear isotherm, with the least amount of AICc, is compatible with ethylbenzene adsorption data. Teixeira et al (2009) to analyze pyrene adsorption isotherm in Brazilian soils also applied this software. Their achieved results proved that ISOFIT was very useful to determine the isotherm being compatible with adsorption data (27). The study of benzene adsorption process on NM by Amin et al

showed that nonlinear adsorption isotherm was compatible with BET one (12). Aivalioti *et al* investigated the adsorption of BTEX, MTBE and TAME on thermally treated and raw lignite. They found that Freundlich equation could justify ethylbenzene adsorption data better than Langmuir (2). Nourmoradi *et al* research proved that the data of ethylbenzene adsorption on montmorillonite modified with nonionic surfactant followed Freundlich isotherm ($R^2=0.995$) (8).

One of the important factors that should be taken into consideration about the adsorbents using for removing contaminants from water and wastewater is the comparison of their efficiency with each other to determine their cost and compatibility to environment. In Table 5 ethylbenzene adsorption, in batch and column conditions by use of NM, was compared with

other studied adsorbents. Although the data in Table 5 do not show the optimum condition and mechanisms of ethylbenzene removal, it can draw a comparison among different kinds of adsorbents, which is very useful for engineers to make their decision to choose the most appropriate adsorbent. This table demonstrates 88 and 95 percent of ethylbenzene removal for natural materials (*Moringa oleifera*) and crumb rubber respectively (28,29). In addition, it shows that chitin and chitosan are efficient in ethylbenzene removal and also varied types of activated carbon have different adsorption levels between 4.8 up to 9.25 mg.g⁻¹(30,31). Regarding to the results of present study, ethylbenzene absorption by NM was very higher than other adsorbents even rather than natural materials such as chitosan and chitin.

Table 5) The comparison of NM efficiency with other EB's adsorbents.

adsorbents	q_e (mg.g ⁻¹)	K_D (L.g ⁻¹)	efficiency (%)	optimum condition	reference
moringa oleifera	-	-	86	pH=7, t=20 min, ^{a)} $C_{ad}=10$ g.L ⁻¹ ^{b)}	(28)
crumb rubber	48	-	95	pH=6, $C_{ad}=10$ g.L ⁻¹	(29)
activated carbon	4.8 – 9.25	0.923 – 6.69	-	-	(31)
chitin and chitosan	-	-	65	-	(30)
surfactant-modified Natural zeolite	-	-	41.33 – 77.19	pH=3, t=48 h	(32)
PAC	-	-	99.5	pH=7, t=20 min	(32)
nano magnetic particles	49.9	261.9	99.8	pH=8, t=20 min, $C_{ad}=2$ g.L ⁻¹	Present study

Notes: a) Contact time, b) Adsorbent concentration.

Conclusion

In current investigation, the optimum condition to recognize the high efficiency of NM for ethylbenzene adsorption was studied. The results proved that NM had high adsorption capacity for ethylbenzene from aqueous solutions in continuous and experimental conditions. It was also found that pH of solution and ethylbenzene initial concentration affect removal efficiency remarkably.

Ethylbenzene removal increased when NM amount raised because ethylbenzene molecules had more accessibility to them. The linear

isotherm models, in comparison to other models studied by ISOFIT program, were more related to data which demonstrated uniformity of NM surface. XRD investigation showed the production of crystallized Fe₃O₄.

Additionally, TEM image of nanoparticles indicated that the mean diameter of particles were 20-30 nm. The NM results compared with other adsorbents and proved high efficiency of NM. So, this can be used as an efficient adsorbent to remove ethylbenzene from aqueous solutions because of its high specific surface area, low cost, non-poisonous and adsorption capacity specifications.

Footnotes

Acknowledgments:

The authors wish to acknowledge to Vice Chancellor of Research at Isfahan University of Medical Sciences for the financial support.

Conflict of Interest:

The authors declared no conflict of interest.

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