

Adsorption of Toluene by Nickel Oxide Nanoparticles-Modified Diatomite (NONMD)

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Abstract: In the effort to find alternative low cost adsorbent for volatile organic liquids has prompted this research in assessing the effectiveness of nickel oxide nanoparticles-modified diatomite (NONMD) in removing toluene. This investigation discusses the effectiveness of a less expensive adsorbent in removing toluene from aqueous phase, due to the lack of information regarding the adsorption of these components in solutions. Effect of different operation parameters such as pH, contact time, initial toluene concentration and adsorption dosage on the adsorption process was evaluated and optimum experimental conditions were identified. The surface area and morphology of the nanoparticles were characterized by SEM, BET. The results of this work show that the maximum percentage removal of toluene from aqueous solution in the optimum conditions using 0.1 gr of NONMD at temperature $25\pm 1^\circ\text{C}$, agitation speed of 200 rpm, initial toluene concentration of 150 mg/L, and for a mixing time period of 90 min was 96.91% (145.36 mg/g). Furthermore, under same conditions, the maximum adsorption of raw diatomite was 71.45% (107.18 mg/g).

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1. Introduction

Volatile organic compounds (VOCs) vaporize easily at low temperatures and include most thinners, solvents, degreasers, cleaners, lubricants and liquid fuels. The most common VOCs include acetaldehyde, acetone, benzene, ethyl acetate, carbon tetrachloride, ethylene glycol, formaldehyde, heptane, hexane, isopropyl alcohol, methyl ethyl ketone, methyl chloride, mono-methyl ether, naphthalene, toluene and xylene. VOCs pollutants can come from indoor and outdoor sources. Indoor VOCs pollution often originates from household products such as office supplies, insulating materials, cleaning products and pressed woods, or may originate from tobacco smoke 1. On the other hand, outdoor VOCs pollution is mainly originated from emissions of industrial processes such as gas, petroleum or petrochemical industrials and automobile exhausts. From the environmental point of view, it is necessary to limit and control vapor emissions, which affect climate change, the growth and decay of plants, and the health of humans and animals 2F.I. Khan, A.Kr. Ghoshal, *J. Loss Prev. Process Ind.* 13 (2000) 527–

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Toluene is a typical indoor pollutant and its discharge may produce irritation of the eyes and the respiratory tract, nausea, headache, fatigue, dullness and thirst, even at very low concentrations4H. Ichiura, T. Kitaoka, H. Tanaka, *Chemosphere* 50 (2003) 79–83.;5. Toluene is well known for its neurotoxicity and exposure to it may decrease neuronal activities in vitro and cause mental depression and cognitive impairment in humans 6. Toluene inhalation also results in various symptoms such as fatigue, headache, vertigo and ataxia. It is rapidly absorbed through respiratory and gastrointestinal tracts and, to a lesser extent, through the skin. American Conference of Governmental Industrial Hygienists (ACGIH) has recommended an 8-h time-weighted average (TWA) of 50 ppm (189 mg/m³) for toluene to protect against effects on the central nervous system. Occupational Safety & Health Administration (OSHA) has promulgated an 8-h permissible exposure limit (PEL) of 200 ppm (754 mg/m³) 7. Research on VOC removal has focused on single components, mostly from the groups of ketones, aromatics and alkanes 8- J. Benkhedda, J.N.

Jaubert, D. Barth, L. Perrin. Experimental and modeled results describing the adsorption of toluene onto activated carbons. *J Chem Eng Data*; 45(4) (2000) 650–3.15. Previous studies 10M.A. Lillo-Ro´denas, J. Carratala´-Abril, D. Cazorla-Amoro´s, A. Linares Solano. Optimisation of the properties of activated carbons for the adsorption of VOC's at low concentrations. In: Extended abstracts, carbon'01. An international conference on carbon, University of Kentucky Center for Applied Energy Research Library,5 (2001) 1371–3.– M.A. Lillo-Ro´denas, D. Cazorla-Amoro´s, A. Linares-Solano. Behaviour of activated carbons with different pore size distributions and surface oxygen groups for benzene and toluene adsorption at low concentrations. *Carbon*; 43(8) (2005) 1758–67. et al., 2005) carried out to determine the adsorption characteristics of different activated carbons (ACs), reaching adsorption capacities of 34 g per 100 g of activated carbon for benzene and 64 g per 100 g of activated carbon for toluene. These studies 10M.A. Lillo-Ro´denas, J. Carratala´-Abril, D. Cazorla-Amoro´s, A. Linares Solano. Optimisation of the properties of activated carbons for the adsorption of VOC's at low concentrations. In: Extended abstracts, carbon'01. An international conference on carbon, University of Kentucky Center for Applied Energy Research Library,5 (2001) 1371–3.– M.A. Lillo-Ro´denas, D. Cazorla-Amoro´s, A. Linares-Solano. Behaviour of activated carbons with different pore size distributions and surface oxygen groups for benzene and toluene adsorption at low concentrations. *Carbon*; 43(8) (2005) 1758–67.12 also confirmed that porosity and surface oxygen group content have major influences on low-concentration-VOC adsorption.

Diatomite (SiO₂.nH₂O) is a pale-coloured, soft, lightweight siliceous sedimentary rock made up principally from the skeletons of aquatic plants called diatoms. Diatomite contains a wide variety of shape and sized diatoms, typically 10-200 µm, in a structure including up to 80-90 % pore spaces 15. Diatomite's extremely porous structure, low density and high surface area make it suitable as an adsorbent for organic and inorganic chemicals. Diatomite is found in abundance in Iran. Several studies have been carried out on the use of diatomite as an adsorbent for removing some contaminants such as heavy metals spaces 15, basic dye (Methylene blue) 16, basic and reactive dyes (Methylene blue, reactive black, reactive yellow) 17M. A. M. Khraisheh, M. A. Al-Ghouti, S. J. Allen, M. N. Ahmad, *Water Res.*, 39 (2005) 922-931.; M. Al-Ghouti, M. A. M. Khraisheh, M. N. M. Ahmad, S. Allen, *J. Colloid Interf. Sci.*, 287 (2005) 6-16.) and some textile dyes (SifBlau

BRF, Everzol Brill Red 3BS, Int Yellow 5GF) 19. Furthermore, the unique properties of diatomite caused its applications as filtration media in a number of industries 15Y. Al-Degs, M. A. M. Khraisheh M. F. Tutunji, *Water Res.*, 35 (2001) 3724-30.; E. Erdem, G. Çölgeçen, R. Donat, *J. Colloid Interf. Sci.*, 282 (2005) 314-320.). Diatomite is approximately 500 times cheaper than commercial activated carbon 19 and has the potential of being successfully used as a cost-effective alternative to activated carbon.

In general, the literature includes few experimental data for modified natural adsorbent for removal of VOCs pollutants. In the present investigation, the possibility of utilization of nickel oxide nanoparticles-modified diatomite (NONMD) has been studied as a less expensive adsorbent for removal of toluene from an aqueous medium.

2. Experimental Procedure

2.1 Preparation of adsorbent

Diatomite was washed several times with distilled water and HCl (1M) to remove fines and other adhered impurities and to achieve neutralization. The sample was finally filtered, dried at 60°C for 24 h, and stored in closed containers for further use.

The nanoparticles of NiO were synthesized by using following reaction (Equation1):



The nanoparticles of NiO were synthesized by adding NiSO₄ and NaOH (1M) to the solution. It means that 2.0 g of previously dried diatomite was added to 25 ml of Nickel hydroxide (1 M), Stirrer speed of 200 rpm, for 1 h. The new material, Ni-diatomite was sequentially separated by filtration. The calcination process was carried out by placing Modified diatomite sample in the furnace at 250°C for 4.5 h. The sample was then allowed to cool in a desiccator. The modified sample was used to examine the effect of nickel oxide nanoparticles, silanol groups and the role of pore size distribution on the adsorption process.

2.2 Reagents and solutions

Toluene (AR grade min. 99.6% Merck) was supplied by Quick Lab Sdn. Bhd., Ipoh, Perak. The chemical structure of this is shown in Fig. 1. Distilled water was throughout employed as solvent. For adsorption experiments, various concentrations of toluene solutions (100, 150, 200, 250 and 300 mg/L) were prepared. The pH measurements were made using Hach pH meter. These chemicals were purchased from Merck, Germany.

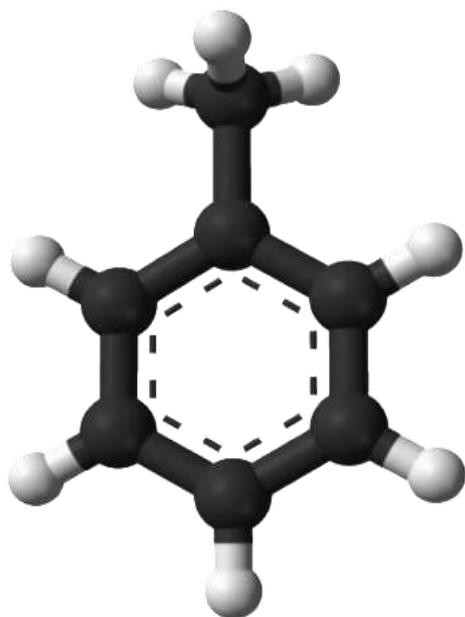


Figure 1. Chemical structure of toluene

3. Adsorption procedure

The adsorption experiments were performed by mixing various amounts of diatomite (0.03 – 0.12 g) in 100 mL of toluene solutions with varying concentrations (ranging from 100-300 mg/L) at natural pH (pH=6). The natural pH to determine the maximum toluene removal could be achieved with diatomite, because this pH was more suitable for industrial purposes. Adsorption experiments were conducted at optimum amount of diatomite (0.1 g) at pH 6, an agitation speed of 200 rpm and temperature $25 \pm 1^\circ\text{C}$ for 1 h to attain equilibrium conditions.

The changes of absorbance were determined at certain time intervals (5, 10, 30, 60 and 90 min) during the adsorption process. After adsorption experiments, the toluene solutions were centrifuged for 10 min in a Hettich EBA20 centrifuge at 4000 rpm in order to separate the sorbent from the solution and toluene concentration was then determined. The amount of toluene adsorbed by the adsorbent was determined from its concentration at initial condition (C_0) and equilibrium (C_e). The amount of adsorbed toluene on the adsorbents was calculated by using the following equation:

$$q_e = \frac{V (C_0 - C_e)}{W} \quad (2)$$

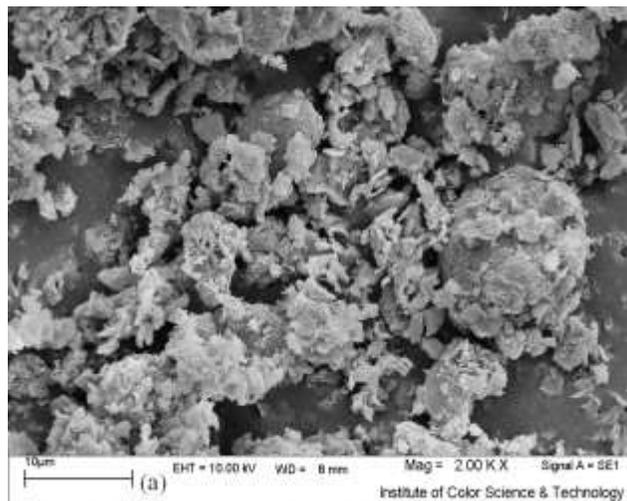
4. Analysis

The residual toluene concentrations in aqueous medium were determined using a Perkin-Elmer spectrophotometer corresponding to maximum wavelength (λ_{max}) of toluene. Scanning electron microscopic (SEM) of both raw and modified diatomite were carried out using LEO 1455VP scanning electron microscope before and after modification process. By using nitrogen adsorption method the BET specific surface area adsorbents was measured, using Autosorb-1MP apparatus from Qantachrome at 77 K.

5. Results and Discussion

5.1 Surface characterization

Scanning electron micrographs of raw and modified diatomite are shown in Figs. 2(a) and 2(b) respectively. As evident from Fig. 2(a), raw diatomite does not have considerable numbers of pore spaces where toluene can be adsorbed into these pores. An important change in the surface characteristics and the size of the pore spaces of the diatomite is seen after modification and calcination process at 250°C , as evident from Fig. 2(b), the modification treatment of the diatomite increased the volume of the pore spaces and improved the surface functional groups from the raw diatomite. In addition, the modified diatomite has considerable numbers of pore spaces where toluene can be adsorbed into these pores. As a result, the adsorption of toluene by modified diatomite is increased.



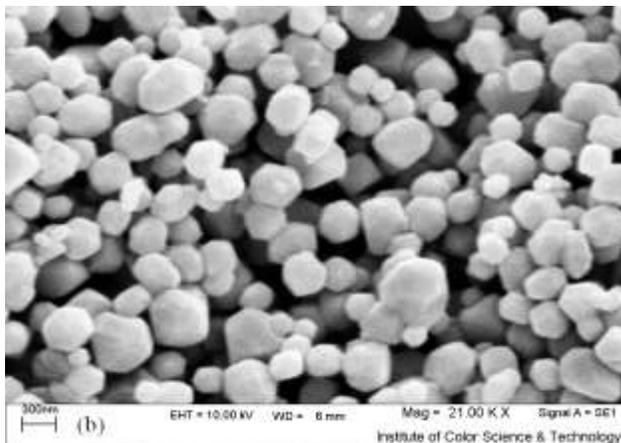


Figure 2. Scanning electron micrographs of (a) raw diatomite and (b) Modified diatomite

The surface area of the diatomite was determined by BET method. By using nitrogen adsorption method the BET specific surface area adsorbents was measured, using Autosorb-1MP apparatus from Qantachrome at 77 K. In this investigation, the values $7.5 \text{ m}^2/\text{g}$ for raw and $28.45 \text{ m}^2/\text{g}$ for modified diatomite were calculated. A particle size analysis was carried out to determine the distribution of particles of the adsorbent. The maximum distribution of particles is varied from 200 to 400nm.

5.2 Effect of adsorbent dosage

The effect of raw and modified diatomite dosage on the adsorption of toluene was investigated at $25 \pm 1^\circ\text{C}$ by varying the adsorbent amount from 0.03 to 0.12 g while keeping the volume of toluene solution constant equal to 100 mL, with an initial toluene concentration of 150 mg/L. Figure 3 shows the percentage removal of toluene versus adsorbent amount.

As it is clear from the figure, the removal percentage of toluene increased with an increase in the adsorbent amount. The main reason for this fact is due to the greater availability of the adsorption sites at higher concentrations of the adsorbent 1920. Based on the results shown in Fig. 3, 0.1 g of the raw and modified diatomite was used for further experiments. Similar behaviour was previously investigated by other researchers 21F. Doulati Ardejani, Kh. Badii, N. Yousefi Limaee, N. M. Mahmoodi, M. Arami, S. Z. Shafaei, A. R. Mirhabibi, *Dyes Pigments*, 73 (2007) 178-189.; Kh. Badii, F. Doulati Ardejani, M. Aziz Saberi, N. Yousefi Limaee, S. Z. Shafaei, *Indian Journal of Chemical Technology*, 17 (2010) 7-1.22.

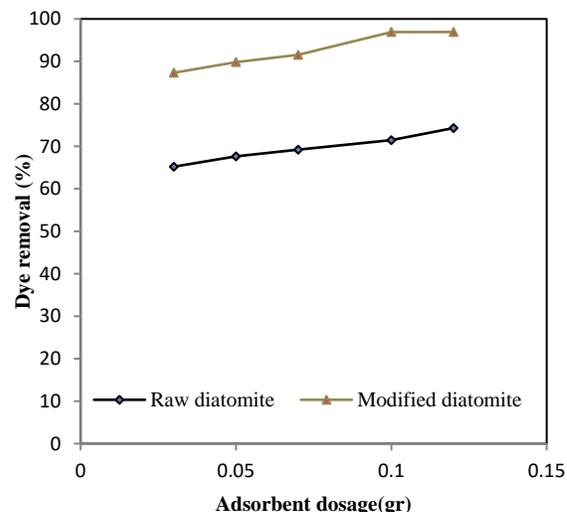


Figure 3. Effect of adsorbent dosage on the removal percentage of toluene by raw and modified diatomite, Temperature= $25 \pm 1^\circ\text{C}$, initial toluene concentration = 150 mg/L, pH = 6, agitation speed = 200 rpm.

5.3 Effect of initial toluene concentration

A change in the initial toluene concentration can considerably affect the adsorption process. Figure 4 depicts the effect of toluene concentration on the percentage removal of toluene by adsorbents. Evident from the figure, when the toluene concentration increased from 100 to 300 mg/L, the percentage removal of toluene decreased from 97.68 to 88.09 % for modified and from 74.3 to 65.21 for raw diatomite.

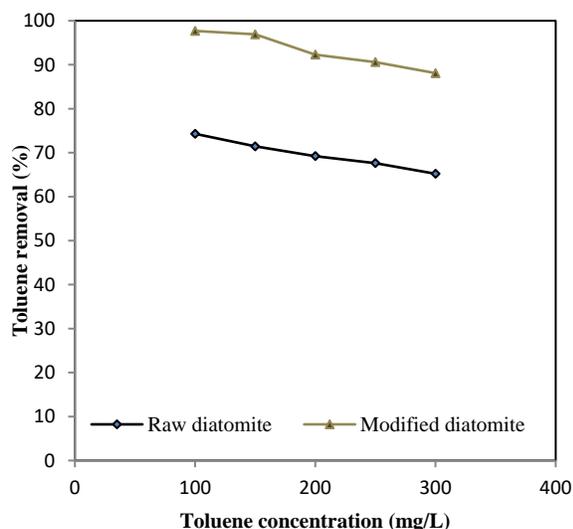


Figure 4. Effect of initial toluene concentration on adsorption of toluene by raw and modified diatomite. Contact time = 90 min, Temperature = $25 \pm 1^\circ\text{C}$, pH = 6, agitation speed = 200 rpm.

As expected, when the concentration of toluene is increased, the limited capacity of the adsorbent checks any further adsorption of toluene and hence the overall removal percentage decreased. Similar behaviour was previously investigated by other researchers 21F. Doulati Ardejani, Kh. Badii, N. Yousefi Limaee, N. M. Mahmoodi, M. Arami, S. Z. Shafaei, A. R. Mirhabibi, *Dyes Pigments*, 73 (2007) 178-189.; Kh. Badii, F. Doulati Ardejani, M. Aziz Saberi, N. Yousefi Limaee, S. Z. Shafaei, *Indian Journal of Chemical Technology*, 17 (2010) 7-1.22.

5.4 Effect of contact time

The adsorption of toluene onto diatomite was evaluated as a function of contact time. Figure 5 shows the effect of contact time on the percentage removal of toluene in the aqueous phase by raw (Fig. 5a) and modified diatomite (Fig. 5b). The initial toluene concentration was varied from 100 to 300 mg/L. At all initial toluene concentrations investigated, the adsorption occurs very fast initially. After 5 min of adsorption process, the amount of adsorption by raw diatomite reaches to 66.99 and 64.09% of the ultimate adsorption of toluene for initial toluene concentrations of 100 and 150 mg/L respectively.

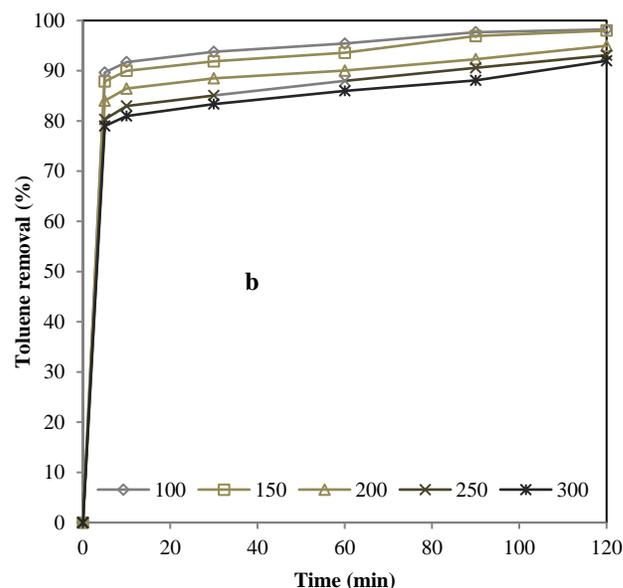
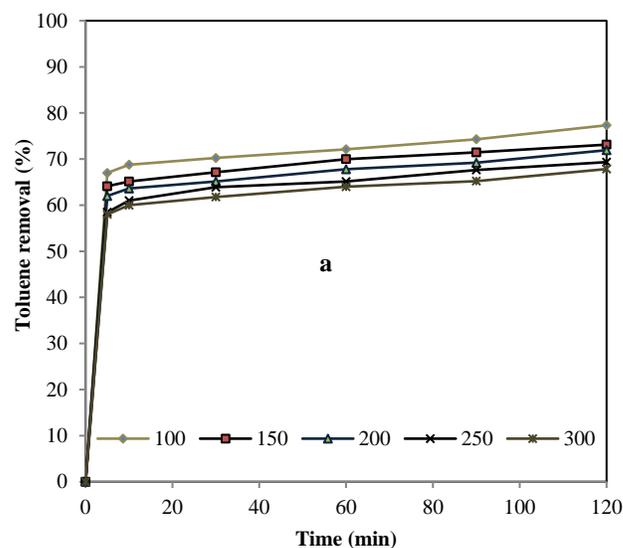


Figure 5. Effect of contact time on adsorption of toluene on (a) raw and (b) modified diatomite, Equilibrium time = 90 min, pH = 6, agitation speed = 200 rpm, adsorbent dosage = 0.1 g.

As illustrated in Fig. 5b, the adsorption is also fast at early stage of the adsorption process for modified diatomite. Typically about 87.87% of the ultimate adsorption of toluene with an initial concentration of 150 mg/L takes place within the first 5 min of contact and it almost remains constant thereafter. It means that the most of mass transfer resistance is in bulk of fluid and high rate agitation would decrease this resistant.

In addition, these results show that the most of the toluene molecules are adsorbed on the external

surface of the adsorbent, and transferred to the pores and internal surfaces layer. More experiments are necessary to be carried out to prove this investigation. As expected, when the concentration of toluene is increased, the limited capacity of the adsorbent checks any further adsorption of toluene and hence the overall removal percentage decreases. Similar behaviour was previously investigated by other researchers 22S. Venkata Mohan, P. Sailaja, M. Srimurali, J. Karthikeyan, *Environ Eng. Pol.*, 1 (1999) 149-157.- Y. S. Ho, G. McKay, *J. Chem. Eng.*, 70 (1998) 115-124.).

6 Conclusions

Diatomite has been studied for the removal of toluene from aqueous solution. Modification treatment of the adsorbent with nickel oxide nanoparticles was useful and its adsorption capacity increased. The adsorption process was not influenced by solution pH and used natural pH of the solutions. It was found that in order to obtain the highest possible removal of toluene, the experiments can be carried out at pH 6, temperature 25°C, an agitation speed of 200 rpm, an initial toluene concentration of 150 mg/L, a centrifugal rate of 4000 rpm, adsorbent dosage = 0.1 g and a process time of 90 min. The results of this work show that the maximum percentage removal of toluene from aqueous solution in the optimum conditions for NONMD was 96.91% (145.36 mg/g). Furthermore, under same conditions, the maximum adsorption of raw diatomite was 71.45% (107.18 mg/g).

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