

Adsorption study of Chloroform onto Zero Valent Iron Supported on Mesoporous Silica

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ABSTRACT

In series of batch experiments, the performance of NZVI/MSN as adsorbent for the removal of chloroform (CHCl₃) from aqueous solution was determined. The prepared adsorbent as zero valent iron supported on mesoporous silica (NZVI/MSN) was characterized by the field emission scanning electron microscopy (FESEM), Fourier transform infrared spectroscopy (FTIR), Brunner –Emmett –Teller (BET) and X-ray powder diffraction (XRD). The BET surface areas of the adsorbents were 126, 41 and 72 m²/g for MSN, NZVI, and NZVI/MSNs, respectively. Adsorption reached equilibrium within 60 min at optimum pH value of 8. The capacity of NZVI/MSN in adsorption of CHCl₃ from aqueous solution was found to be 12.08 mg/g. The adsorption isotherm studies were conducted by series of batch adsorption at various initial concentrations of CHCl₃. Langmuir and Freundlich adsorption isotherm models were employed to fit the adsorption characteristic of the adsorbent. Maximum adsorption capacity of CHCl₃ onto NZVI/MSN was found to be 38.314 mg/g, which conducted from the Langmuir slope. It was found that Freundlich isotherm characterized the adsorption process better than that of Langmuir for NZVI/MSN as indicated by higher correlation coefficient value. Hence, the adsorption of CHCl₃ onto NZVI/MSN can consider as a multilayer adsorption rather than a monolayer adsorption.

Keywords: Chloroform, Nano scale zero-valent iron, Adsorption, Mesoporous silica, Isotherm studies

INTRODUCTION

Chloroform is the most commonly exist compound of the trihalomethane (THM); THMs are Halogen-substituted single-carbon compounds with the general formula CHX₃ [1]. Chloroform is volatile compound and the trace amount of it in water was harmful and caused many problems to the human being health [2]. Chloroform, is not flammable and is soluble in most organic solvents [3]. However, its solubility in water is limited.

Contaminate water with chloroform caused by the reaction between organic compounds and residual chlorine [3]. Furthermore, chloroform has been widely used to produce industrial products and in industrial processes, for example cleaning solvents, lubricants, paper bleaching and intermediates for herbicides, fungicides and pharmaceuticals [3]. Regrettably, these compounds are toxic or carcinogenic and thus appear direct health risk such as kidney cancer, hepatic damage and nervous system affect in addition to the venereal effects [4,5].

It is important to find a way to turn it into a less harmful substance. Various methods have been applied for the removal of THMs. Removal can be performed with adsorption on activated carbon, oxidation, stripping and biological treatment [6]. Previously the adsorption of chloroform onto activated carbons made from lignite's, anthracite and apricot stones were

studied [7]. Also, adsorption of chloroform and trichloroethylene onto charcoals was investigated [8]. One effective removal method is adsorption using different adsorbents with high surface area capacity such as Nano materials. The zero valent iron (NZVI) is the most Nano adsorbent which used in the adsorption process. The use of NZVI was the promising method for the remediation of organic pollutants since because of its harmless, eco-friendly and inexpensive.

Chloroform was selected as model compound among chlorinated organic pollutants in water. Regrettably, the emissions of this compound are hurtful to the environment, and in particular it is an important contributor to the devastation of the ozone layer [9]. In this study, the fumed silica was activated for the preparation of MSN, followed by impregnation of the ferric chloride hex hydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$) on MSN. This NVZI/MSN Nano composite then used as highly efficient adsorbent with excellent separation properties. Batch adsorption studies were carried out to evaluate the optimum adsorption condition included contact time, initial pH solution, temperature and initial concentration effect.

METHODOLOGY

Materials

Sodium borohydride (NaBH_4) 98.5%, iron (III) chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$) 99% were obtained from Merck. Chloroform was supplied by the Aldrich Co. with a purity of 99.8%. Fumed micro porous silica (purity 99%, Dongyang Chem. Co) with a median particle size of 2.5 μm was used as the silicate source for the synthesis of mesoporous silica. Sodium hydroxide (NaOH) and hydrochloric acid (HCl) were obtained from Sigma-Aldrich, while analytical grade absolute ethanol was obtained from Merck and used without purification.

Preparation

Production of NZVI involved the reduction of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ in aqueous solution by NaBH_4 [10]. After 30 min of agitation, the (NZVI/MSN), Nano composite were separated from the mixture and washed with acetone for three times and then vacuum dried at 60°C and stored in a desiccator for further use.

Characterization

The diffractograms of adsorbents were obtained by a Rigaku miniFlex II desktop X-ray diffractometer with $\text{Cu K}\alpha$ as a source at a tube voltage of 30 kV and a current of 15 mA. The diffractogram patterns were collected in 2θ range from 0° to 80° with step sizes of 0.02° and at a scanning speed of 1°/min. The surface area of adsorbent was determined from the adsorption isotherms of nitrogen at -196°C onto the catalyst using Micrometrics ASAP 2020. All the samples were degassed at 105°C prior to the analysis and the adsorption of N_2 was measured at -196°C. Brunner-Emmett-Teller (BET) equation was employed to calculate the specific surface area. The surface structure of adsorbent was observed by using FESEM (JEOL). FTIR spectra were collected by using PerkinElmer Spectrometry 100.

Adsorption study

Batch adsorption experiments were conducted by using the solution of chloroform dissolved in 2-propanol. The chloroform stock solution was prepared by dissolving accurately weighed chloroform in 2-propanol to the concentration of 1000 mg L^{-1} . The experimental solutions were obtained by diluting the chloroform stock solution in accurate proportions to required initial concentrations. A Genesys 10S UV-VIS spectrophotometer was used for the measurement of absorbance at the predetermined maximum absorbance wavelength ($\lambda_{\text{max}}=245 \text{ nm}$) of the chloroform to determine the concentrations of chloroform in the solution. The vertical error bars on the data points indicated the average deviation from triplicate the experimental data collection for the adsorbent.

Batch adsorption experiments were carried out to study the different parameters included contact time, pH of the solution, temperature and initial concentration of chloroform. The amount of NZVI/MSN was loaded into CHCl_3 solution in 250 ml flask sealed with the rubber stopper, then placed on a rotary shaker at 150 rpm during the entire experiment period. Equilibrium time of adsorption was determined by using 0.1 g of NZVI/MSN in 100 ml of 20 mg/L CHCl_3 solutions. The mixture was equilibrated by shaking thoroughly for different time intervals viz. 2, 4, 8, 15, 30, 60, 90, 120 and 180 min. At the end of the shaking period, the solution was sampled by a syringe. The sample was then filtered immediately through 0.22 μm membrane filters for further analysis. Effect of pH of the solution on the CHCl_3 adsorption was investigated by varying those from 2-12. Initial pH of the solution was adjusted by using 1 M HCl or 1 M NaOH . To study the effect of temperature on the adsorption of CHCl_3 by NZVI/MSN, adsorptions were performed at 30, 35, 40, 45 and 50°C. In order to study the effect of initial concentration of CHCl_3 on the adsorption performance, a series of adsorption experiments was carried out with different initial CHCl_3 concentration from 10 to 40 mg/L .

RESULTS AND DISCUSSION

Characterization

The XRD diffractograms of the unsupported and supported nanoscale particles are illustrated in Figure 1. The apparent peak in at the 2θ of 44.45° indicates the presence of zero-valent iron [11]. Because of the small size of the particles,

the peaks in the XRD pattern are relatively broad [12,13]. The NZVI without iron oxides was identified by the XRD spectrometer under alkaline conditions. No obvious reflections of Fe oxides were observed in the XRD pattern of prepared (NZVI) suggesting that their major surface species are Fe⁰ and no core-shell structure was observed. Obvious diffraction peaks at the 2θ of 35.07° and 53.89° were observed in NVZI/MSN. The XRD patterns of supported nanoparticles indicate the crystalline nature (iron silicon) of NVZI/MSN. It indicates that the sample possesses well-ordered tetragonal mesostructure in the pattern of NZVI/MSN, the (2 2 2) and (2 0 0) reflections still can be observed but the intensity decreases clearly [14], which is caused by the impregnation of iron nanoparticles (Figure 1).

Surface area and pore size of the adsorbent was summarized in Table 1. It can be observed that acid treatment has increased the surface area of fumed silica from 23 m²/g to 40.65 m²/g [7]; causing increased number of sorption sites toward NZVI on mesoporous silica nanoparticles (MSNs) as this procedure may disaggregate particles and eliminate impurities for the prepared sample [8]. It also leads to partial leaching of iron contents on mesoporous silica nanoparticles (MSN) [8]. In addition, the NZVI grafting on MSN caused by the surface area decreased from 125.87 m²/g to 72.38 m²/g for fumed silica purchased from Sigma.

Figure 2 illustrates the FESEM micrograph of the prepared adsorbent. As shown in Figure 2a, the FESEM image reveals that iron nanoparticles tend to form a chain-like aggregate due to the magnetic attractive force between particles. These chain-like nano iron aggregates were also observed by others [6]. On the other hand, when (NZVI) particles were loaded onto the surface of (MSNs), significant differences can be observed as shown in Figure 2b, which showed the porous structure of the prepared NZVI/MSN.

Figure 3, shows the FTIR spectra of adsorbent. Broad peak at wavenumber region 3000-3500cm⁻¹ is corresponding to OH stretching band. It may be also peak for carboxylic group as described in many studies [15]. Peak at wavenumber of 1653 cm⁻¹ corresponds to bending modes of NZVI and water [15]. The peaks between 1400 cm⁻¹ and 600 cm⁻¹ are characteristic bands of silicate corresponding to tetragonal sheet Si-O stretching modes and Fe-O deformation [16] (Figure 3).

Adsorption study

As illustrated in Figure 4, the equilibrium time of adsorption of CHCl₃ onto NZVI/MSN was determined by taking 0.1 g adsorbent with 100 ml of CHCl₃ solution (initial concentration, C⁰=20 mg/L). The removals of CHCl₃ by adsorption onto NZVI/MSN were found to be rapid at the initial period of contact time, and then to become slow with the increase of contact time. At first 10 min, the amount of 30.78% CHCl₃ was removed, and almost totally removed after 60 min adsorption. Therefore, it can be concluded that the equilibrium has been achieved at 60 min and the maximum removal 52.085% at 180 min.

The initial pH was varied from 2 to 9 to study the effect of initial pH on adsorption performance. The pH of the

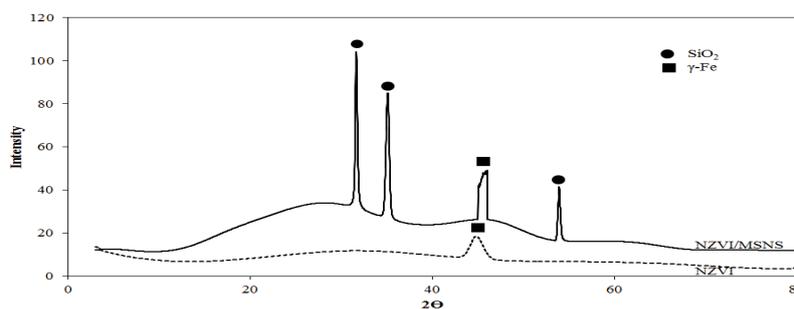


Figure 1: Diffractogram of NZVI and NZVI/MSN

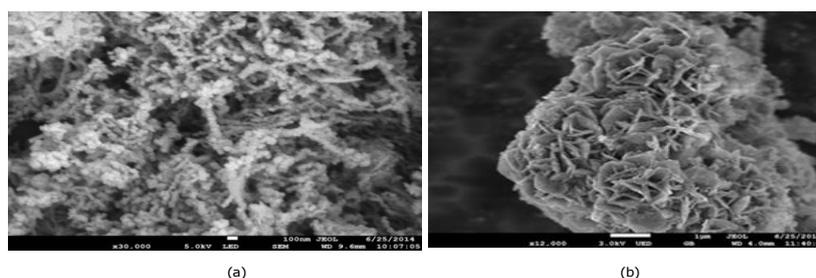


Figure 2: (a) FESEM micrograph of NZVI, and (b) pore shape of NZVI/MSNs

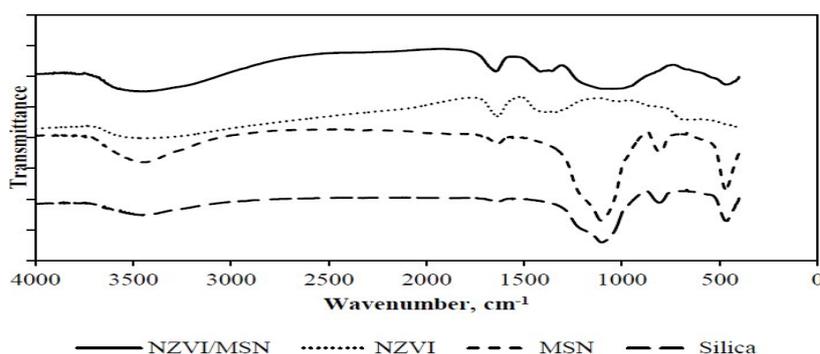


Figure 3: FTIR spectra of adsorbents

solution plays an important role in the whole adsorption process, particularly on the adsorption capacity. As observed in Figure 5, consistent increase in adsorption capacity of CHCl_3 was noticed as the pH increased from 2-7, whereas in 7-9, the adsorption amount was only slightly affected by pH. As pH of the system increased, the number of negatively charged adsorbent sites increased and the number of positively charged surface sites decreased, which did not favor the adsorption of negatively charged CHCl_3 related to the electrostatic repulsion [15] (Figure 5).

The effect of temperature on adsorption was studied by varying the adsorption temperature (30-50)°C as illustrated in Figure 6. The adsorption of CHCl_3 by NZVI/MSNs equilibrium was found to increase with increasing temperature. At the temperature of 30°C, the CHCl_3 uptake was 4.06 mg/g and slightly increased at a temperature of 35°C (12.398 mg/g). The CHCl_3 uptakes consistently increased to 13.916, 15.067 and 15.891 mg/g for adsorption temperature of 40, 45 and 50°C respectively. This fact indicates that the mobility of CHCl_3 molecules increased with the temperature. The trend also suggests the endothermic nature of the adsorption process. Similar results were also reported in the literature [2,4] (Figure 6).

The adsorption isotherm studies were conducted by series of batch adsorption at various initial concentrations of CHCl_3 . Langmuir and Freundlich isotherm models were used to investigate the type of chloroform adsorption data on to NZVI/MSN under laboratory conditions. Langmuir and Freundlich isotherm models were employed to describe the adsorption process in this study. Langmuir adsorption isotherm model was employed to fit the adsorption characteristic of the adsorbent. At equilibrium, the amount of target metal adsorbed onto the corresponding adsorbent, q_e (mg/g) was found by a mass balance relationship as explained in ‘equation (1)’ [17].

$$q_e = (c_o - c_e) \frac{V}{W} \tag{1}$$

Where C_o and C_e (mg/L) are the initial and the equilibrium liquid-phase concentration of CHCl_3 respectively. V (L) is the volume of the solution and W (g) is the weight of the adsorbent. The Langmuir isotherm model can explain by ‘equation (2)’ [17].

$$q_e = \frac{b q_m c_o}{1 + c_o c_e} \tag{2}$$

Where q_m (mg/g) and K_L (L/mg) are the Langmuir parameters, related to the maximum capacity of adsorption and the binding energy of adsorption, respectively. The values of q_m and K_L can be calculated from the intercept and slope of the linear plot of C_e/q_e against C_e as shown in Figure 7a. It was found that the maximum capacity of CHCl_3 adsorption onto NZVI/MSN was 38.314 mg/g. This value is comparable with some other adsorbent as shown in Table 2. Correlation coefficient obtained by the linear regression was 0.9892. This indicates that the Langmuir isotherm model properly describes the adsorption performance of CHCl_3 into NZVI/MSN. The linearized Freundlich isotherm equation that corresponds to the adsorption on heterogeneous surface is given as ‘equation (3)’ [17].

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \tag{3}$$

Where C_e is the concentration of solute at equilibrium (mg/L) and q_e is the adsorption capacity at equilibrium (mg/g), and K_F , n are the Freundlich parameters. The Freundlich isotherm constants K_F and n can be determined from the plot of $\ln q_e$ versus $\ln C_e$ as illustrated in Figure 7b. The slope $1/n$ measures the surface heterogeneity. Heterogeneity

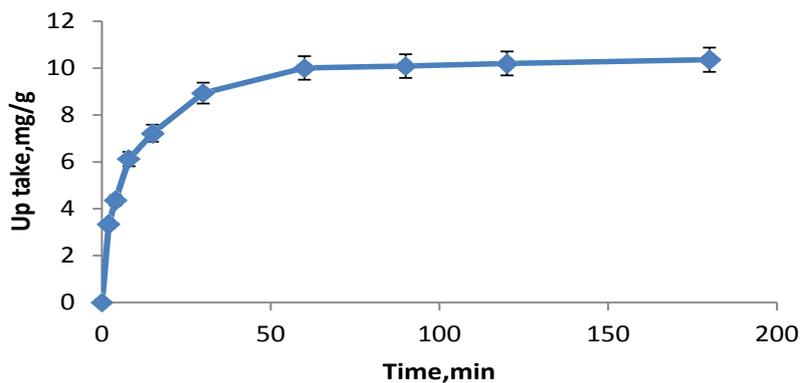


Figure 4: Equilibrium time of CHCl₃ adsorption on NZVI/MSN

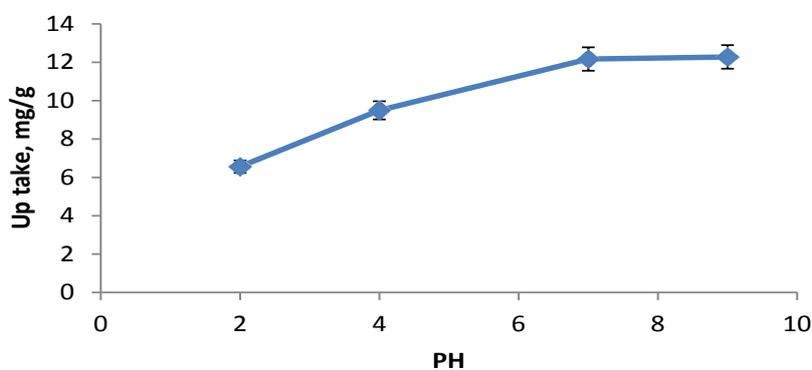


Figure 5: Effect of initial pH solution

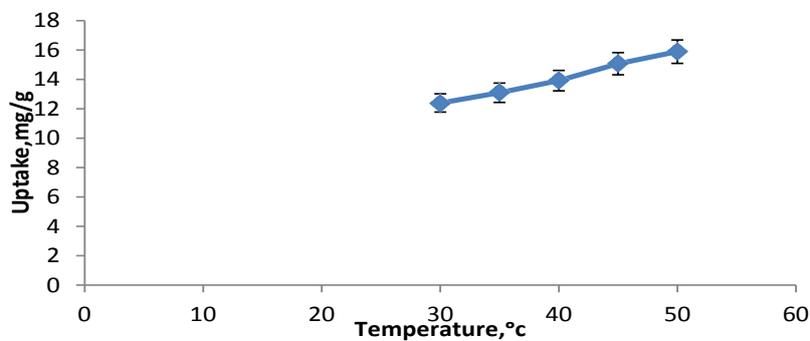


Figure 6: The effect of temperature onto CHCl₃ adsorption onto NZVI/MSN

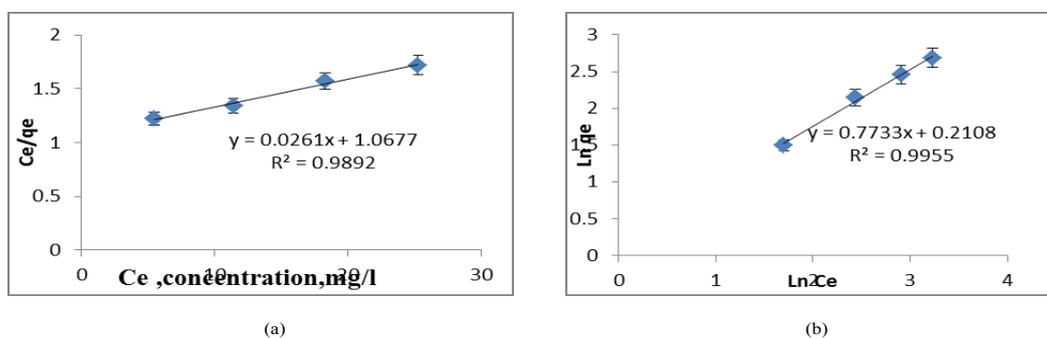


Figure 7: Linearization of adsorption isotherm plot for (a) Langmuir, (b) Freundlich model

becomes more prevalent as $1/n$ gets closer to zero [16]. Langmuir and Freundlich isotherm parameters for adsorption of CHCl₃ onto NZVI/MSNS are summarized in Table 2.

Adsorbent	BET surface area	BJH pore size, cm ³ /g
NZVI	41	0.165
MSN	126	1.051
NZVI/MSN	72	0.466

Table 1: Surface area and pore size of adsorbents

Absorbents	Langmuir			Freundlich			Reference
	K _L , L/mg	q _{max} , mg/g	R ²	K _F	1/N	R ²	
NZVI/MSN	0.0244	38.31	0.9892	0.2346	0.77	0.9991	This study
Activated carbon SKD515	5.47	9.69	0.9960	12.15	0.78	0.9500	[6]
Nano-TiO ₂	-	57.6	-	-	-	-	[4]
Rectorite/Chitosan	0.7	6.3	-	2.3	0.7	-	[7]

Table 2: Isotherm parameters of the adsorption of CHCl₃ onto NZVI/MSNs and for selected adsorbents from the literature

In overall, Freundlich isotherm characterized the adsorption process better than that of Langmuir isotherm as indicated by higher correlation coefficient value. The surface heterogeneity of the adsorbent became more prevalent since the 1/n value of Freundlich isotherm parameter of adsorption was nearly zero [16]. Hence, the adsorption of CHCl₃ onto NZVI/MSN can be considered as a multilayer adsorption rather than a monolayer adsorption.

CONCLUSION

The study concludes that NZVI/MSNs have been successfully synthesized in the laboratory. The adsorbent has the surface area and pore size of 72 m²/g and 0.466 cm³/g; respectively. The prepared adsorbents were characterized by X-ray diffraction (XRD). Fourier transforms infrared spectroscopy (FTIR), (BET) and Field Emission Scanning Electron Microscope (FESEM). The removal of chloroform from aqueous solutions by batch adsorption experiments were carried out. Adsorption of CHCl₃ into NZVI/MSN achieved the equilibrium in 60 min, with almost all of the CHCl₃ in the solution was totally removed. Uptake of the CHCl₃ in the solution was increased by higher temperature. Experimental result of CHCl₃ initial concentration variation indicated that the fitting of the results to Freundlich isotherm model and the adsorption process was considered as multilayer adsorption. Maximum capacity of CHCl₃ adsorption was 38.314 mg/g on NZVI/MSN and found to be comparable with the other adsorbent and can be considered as the promising adsorbent to be applied in industrial waste water remediation.

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