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Adsorption of chloroform from aqueous solution by nano -TiO₂

ABSTRACT

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In this study, nano-TiO₂ was employed for the adsorption of chloroform from aqueous solution in batch equilibrium experiments to investigate its adsorption properties. The effects of pH, initial chloroform concentration and nano-TiO₂ dosage were also investigated. Optimal conditions for chloroform removal by nano-TiO₂ have been then identified. Results of equilibrium experiments showed that the solution pH was the key parameter affecting the adsorption characteristics. It was found that the adsorption efficiency of chloroform was more at pH 8.0. Results showed that the initial adsorption rate was increased with the increasing nano-TiO₂ dosage and decreasing initial chloroform concentration. Equilibrium data were fitted to Langmuir, Freundlich and Temkin isotherms. The Langmuir isotherm was found to be the best fitting isotherm model. The adsorption kinetic data were analyzed using pseudo-first-order and pseudo-second-order. It was found that the pseudo-second-order kinetic model was the most appropriate model, describing the adsorption kinetics.

Keywords: Chloroform, Nano-TiO₂, Adsorption, Kinetics, Isotherm

INTRODUCTION

It is well known that trace amounts of chloroform are contained in tap water and ground water. Production of chloroform in tap water is caused by reaction between residual chlorine and organic compounds [1]. Also, chloroform has been used in a wide range of industrial processes and to produce industrial products, for example, lubricants, cleaning solvents, paper bleaching, and intermediates for pharmaceuticals, herbicides and fungicides [2]. Unfortunately, emissions of this compound are harmful to the environment, and in particular it is an important contributor to the destruction of the ozone layer [3]. Also it is toxic or carcinogenic and thus represents a direct health risk such as liver and kidney cancer, nervous system and reproductive effects [4-6].

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It is important to find reliable methods to convert it to less harmful compounds. Several treatment alternatives have been proposed for the removal of THMs. Removal can be performed with adsorption on activated carbon, oxidation, stripping and biological treatment [7]. Extensive studies of photocatalytic degradation of chlorinated hydrocarbons on TiO_2 have been reported [8]. In a research, the effectiveness of granular activated carbon (GAC) and air stripping (AS) packed column for the removal of chloroform (CHCl_3) (as THMs basic indicator compound in many resources) from drinking water was studied [7]. Razvigorova et al. studied chloroform adsorption onto activated carbons made from apricot stones, lignite's, and anthracite [9]. Also, adsorption of chloroform and trichloroethylene onto charcoals was investigated [10]. One effective removal method is adsorption using different adsorbents with high surface area capacity such as nano materials.

The use of TiO_2 catalyst for environmental cleanup has been of great interest since TiO_2 is stable, harmless, and inexpensive [11]. Chloroform has been reported to be mineralized completely in aqueous TiO_2 suspensions [12] and has been often selected as a model compound among chlorinated organic pollutants in water [13, 14]. In this study, adsorption of chloroform from aqueous solutions on nano- TiO_2 was investigated. Batch adsorption studies were carried out to investigate the effect of various parameters like adsorbent dose, pH, and initial concentration and contact time. Langmuire, Freundlich and Temkin adsorption isotherms were used to model the equilibrium adsorption data for chloroform. The adsorption kinetic data were analyzed using pseudo-first-order and pseudo-second-order.

MATERIALS AND METHODS

Nano- TiO_2 (Degussa P25) used as adsorbent in this study was provided from Degussa (Germany), its particle size and surface area was about 20 nm and 15-50 m^2/g , respectively. Chloroform was purchased from Merck (Germany). The adsorption experiments were carried out in a 1000 mL Erlenmeyer flask containing 0.1 g nano- TiO_2 and 1000 mL of 0.1 mg/L chloroform solution

at the desired pH. For equilibrium, the system was stirred by a magnetic stirrer for 2.0 h. The pH value of the solution was adjusted with 0.1 mol/L HCl or 0.1 mol/L NaOH. The variation of the chloroform concentration versus time in the aqueous solution was observed under various conditions such as adsorbent dosage (0.01, 0.05, 0.1 and 0.5 g), initial pH (2, 4, 6, 8 and 10) and initial chloroform concentration (0.2, 0.4, 0.6, 0.8 and 1 mg/L). After regular intervals of time, suitable aliquots were analyzed for the chloroform concentration. The mixture was centrifuged for the removal of solid catalyst and the concentration of chloroform remaining in the solution was determined by the gas chromatography (GC-ECD, model 3800, Varian-cp, USA), an Injector (model 1177) and a capillary column (CP Sil 13 CB).

Adsorption isotherm studies were carried out with different initial concentrations of chloroform while maintaining the adsorbent dosage at a constant level. Kinetic experiments were conducted using a known mass of adsorbent dosage. The rate constants were calculated using the conventional rate expression. The adsorption yield (%), the adsorbed chloroform amount onto the TiO_2 nanoparticles (mg/g) at any time and at equilibrium, were calculated from the following equations (1-3), respectively:

$$\text{Adsorption yield (\%)} = \frac{C_t - C_0}{C_0} \times 100 \quad (1)$$

$$q_t = \frac{(C_0 - C_t)V}{M} \quad (2)$$

$$q_e = \frac{(C_0 - C_e)V}{M} \quad (3)$$

Where C_0 , C_t and C_e are the initial, final and equilibrium chloroform concentration (mg/L), respectively. V is the solution volume (L) and M is the adsorbent mass (g).

RESULTS AND DISCUSSION

Effect of contact time on chloroform adsorption

Contact time is one of the main factors in batch adsorption process. In order to establish

equilibration time, the adsorption of chloroform on nano-TiO₂ adsorbent was studied as a function of contact time and results are shown in Figure 1.

Figure 1 indicates that the time required for equilibrium adsorption is 80 min and the optimal removal efficiency was reached within about 80 min to 82.6 %. There was no significant change in the equilibrium concentration after 80 min and the adsorption phase reached to equilibrium. Thus, for all equilibrium adsorption studies, the equilibration period was kept 80 min.

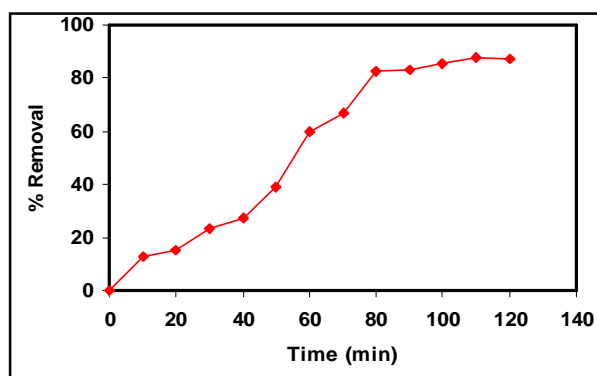


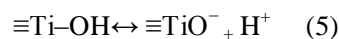
Fig.1. Effect of contact time on the adsorption of chloroform on nano-TiO₂ adsorbent dose: 0.1 g/L; pH: 8; initial CHCl₃ conc.: 0.1 mg/L; temp.: 25°C

Effect of pH on chloroform adsorption

Since the pH of the aqueous solution is a key parameter that controls the adsorption process, it is important to examine the influence of pH on chloroform adsorption. During the experiments, the parameters such as temperature (25°C), agitation speed, contact time (80 min), adsorbent dose (0.1 g/L) and initial chloroform concentration (0.1 mg/L) were kept constant. pH of solution was changed and the chloroform removal was investigated. Adsorption experiments were carried out at pH 2, 4, 6, 8 and 10. The acidic and alkaline pH of the solution was maintained by adding 0.1 N hydrochloric acid and sodium hydroxide. The effect of initial pH on the adsorption is shown in Figure 2. As it is shown, the optimum pH of solution was observed at pH = 8.

Adsorption of chloroform on nano-TiO₂ varies with the pH of solution, a fact that can be assigned to the strong dependence of catalyst surface phenomena on pH. It is well established a fact that upon hydration, the TiO₂ surface develops

hydroxyl groups, which can undergo a proton association or dissociation reaction:



Where $\equiv\text{Ti}-\text{OH}_2^+$, $\equiv\text{Ti}-\text{OH}$ and $\equiv\text{TiO}^-$ are positive, neutral and negative hydrous TiO₂ surface functional groups, respectively [15]. On the other hand, interactions with cationic electron donors and electron acceptors will be favoured for heterogeneous chemisorptions at high pH under conditions in which $\text{pH} < \text{pH}_{\text{IEP}}$ [16]. The adsorbent surface charge is neutral at isoelectric point (IEP) and it can be used to qualitatively assess the adsorbent surface charge. The empirical isoelectric point, pH_{IEP} , of TiO₂ reported in the literature ranges from 2 to 8.9 [17]. Note, however that the broad range of pH_{IEP} for TiO₂ nanoparticles depends on phase, method, preparation, hydration of the material and ionic strength of the solution [18]. However, the pH_{IEP} for TiO₂ in this paper is ranged between 7.2 and 8.9. Since chloroform is a kind of unionizable compound, the adsorption density is consistent with the concentration of the surface sites which can support the adsorption of chloroform. It implies that chloroform will be adsorbed by the greatest extent on catalyst surface under conditions in which $\text{pH} = \text{pH}_{\text{IEP}} = 8$. The working pH was that of solution (pH:8) and was not controlled. So, the experiments were done at pH:8.

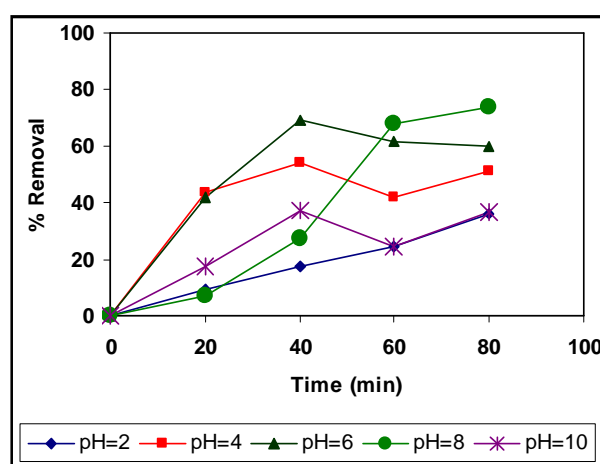


Fig.2. Effect of initial pH on the adsorption of chloroform on nano-TiO₂ adsorbent dose: 0.1 g/L; initial CHCl₃ conc.: 0.1 mg/L; temp.: 25°C

Effect of nano-TiO₂ dosage on chloroform adsorption

Adsorption of the chloroform investigated as a function of nano-TiO₂ dosage (Figure 3). The parameters like chloroform concentration, temperature and pH were kept constant while carrying out the experiments. The various doses (0.01, 0.05, 0.1 and 0.5g) of the adsorbent were mixed with the chloroform solutions and the mixture was stirred in a magnetic stirrer. The adsorption capacities for different doses were determined at definite time intervals by keeping all other factors constant.

The adsorption percent (%) of TiO₂ for chloroform is 97, 96.28, 48.62 and 43.66% for 0.5, 0.1, 0.05 and 0.01 g/L of adsorbent dosage, respectively (Figure 3). As expected, the removal efficiency increased with increasing the adsorbent dose, since number of adsorbent particles increases and thus more surface areas were available [19,20].

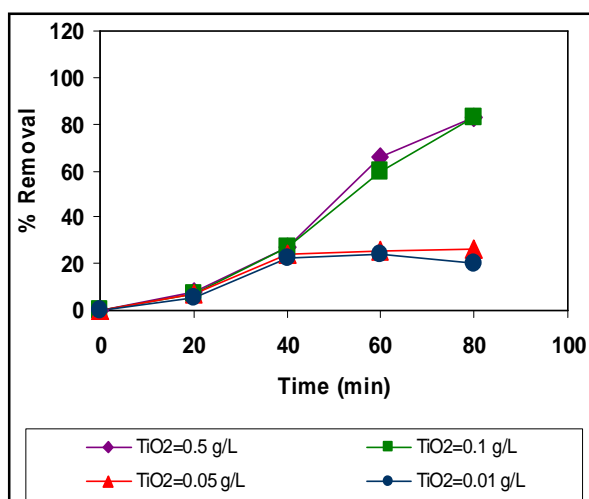


Fig.3. Effect of adsorbent dose on the adsorption of chloroform on nano-TiO₂ initial CHCl₃ conc.: 0.1 mg/L; pH: 8; temp.:25°C

Effect of initial chloroform concentration on its adsorption

The effect of initial chloroform concentration (0.2, 0.4, 0.6, 0.8 and 1 mg/L) on the adsorption of it onto nano-TiO₂ particles was investigated and results are shown in Figure 4. As Figure 4 is shown, chloroform removal efficiency decreased with the increase in initial chloroform concentration. The adsorption (%) of TiO₂ after 80 min of contact time and for initial chloroform concentration of 0.2, 0.4, 0.6, 0.8 and 1 mg/L were

found as 82.46, 78.69, 76.51, 69.42, and 50.48%, respectively. The observed lower adsorption percent at higher chloroform concentrations are due to the saturation of adsorption sites on TiO₂. However, at higher concentrations, the available sites of adsorption become fewer, and hence the percentage removal of chloroform which depends upon the initial concentration decreases [21].

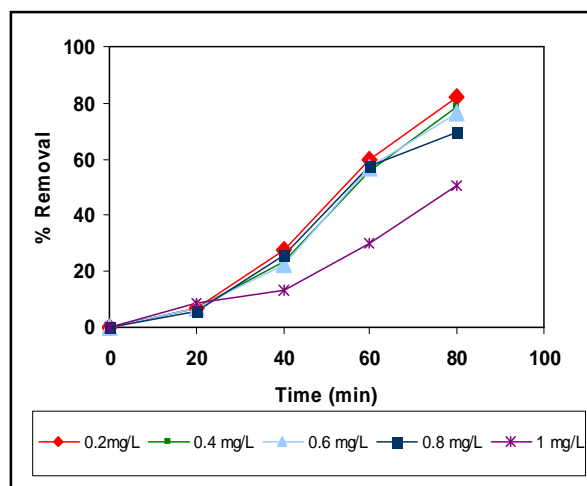


Fig.4. Effect of initial chloroform concentration on the adsorption of chloroform on nano-TiO₂ adsorbent dose: 0.1 g/L; pH: 8; temp.: 25°C

Equilibrium isotherms

Equilibrium data known as adsorption isotherms are basic requirements for the design of adsorption systems [22]. Equilibrium data can be analyzed using commonly known adsorption isotherms, which provide the basis for the design of adsorption systems [23]. An accurate isotherm is important for the design purposes [22]. Linear regression is commonly used to determine the best fitting model and to determine isotherm constants [24]. Several mathematical models can be used to describe the experimental data of adsorption isotherms. Equilibrium data are fitted to various isotherms like Langmuir isotherm, Freundlich isotherm, Radke and Prausnitz isotherm, Temkin isotherm and Redlich and Peterson isotherm. In this study, Langmuir, Freundlich and Temkin isotherms were used to describe the equilibrium characteristics of chloroform adsorption on nano-TiO₂.

• Langmuir theory

Langmuir isotherm is on the supposition that the surface of the adsorbent is a homogeneous

surface and that a monolayer surface coverage is formed with no interactions between the molecules adsorbed [25].

The Langmuir equation:

$$\frac{1}{q_e} = \left(\frac{1}{K_L q_m}\right) \frac{1}{C_e} + \frac{1}{q_m} \quad (6)$$

Where C_e (mg/L) is the equilibrium concentration of chloroform, q_e (mg/g) is the amount of chloroform adsorbed at equilibrium, q_m (mg/g) is the maximum adsorption at monolayer and K_L (L/mg) is the Langmuir constant related to energy of adsorption. To confirm the favourability of the adsorption process, the dimensionless separation factor (R_L) of equilibrium parameter was calculated, which is defined by:

$$R_L = \frac{1}{1 + K_L C_0} \quad (7)$$

Where K_L is the Langmuir constant and C_0 is the initial concentration of nano-TiO₂. The value of R_L indicates the type of the isotherm to be either unfavourable ($R_L > 1$), linear ($R_L = 1$), favourable ($0 < R_L < 1$) or irreversible ($R_L = 0$) [26].

• Freundlich theory

As known, Freundlich isotherm is applied to the adsorption process on a heterogeneous surface and is described as follows:

$$\ln q_e = \left(\frac{1}{n}\right) \ln C_e + \ln K_F \quad (8)$$

Freundlich equation is an empirical equation that was originally developed to overcome some limitations of the Langmuir theory, by taking into account the surface heterogeneity and that there might exist intermolecular interactions between the adsorbate molecules [27]. Here, C_e (mg/L) is the equilibrium concentration of CHCl₃, K_F [(mg/g)(L/mg)^{1/n}] and n are the Freundlich constants indicating adsorption capacity and

intensity, respectively. If n lies between one and ten, this indicates a favourable sorption process [28].

• Temkin isotherm

Temkin and Pyzhev considered the effects of some indirect sorbate/adsorbate interactions on adsorption isotherms and suggested that because of these interactions the heat of adsorption of all molecules in the layer would decrease linearly with coverage [29]. The Temkin isotherm has been used in the following form:

$$q_e = B_1 \ln C_e + B_1 \ln K_T \quad (9)$$

Where C_e (mg/L) is the equilibrium concentration of CHCl₃, K_T is the equilibrium binding constant (L/g), and B_1 is related to the heat of adsorption. Figure 5 (a), (b) and (c) are Langmuir, Freundlich and Temkin adsorption isotherms of CHCl₃ adsorption on nano-TiO₂, respectively. The values of the regression constants, parameters K_L , K_F , K_T and n , as well as the correlation coefficient R^2 are calculated and the results for isotherms are summarized in Table 1.

As it is seen from the Table 1, the Langmuir model exhibited better fit to the adsorption data than the Freundlich and Temkin models, since coefficient relation for Langmuir isotherm is 0.996. The constant q_m , which is measure the monolayer adsorption capacity of CHCl₃, can be as high as 9.69 mg/g. The fact that Langmuir adsorption fits the data well may be due to the homogenous distribution of active sites on the adsorbent surface [30]. The constant K_L , which denotes adsorption energy, is equal to 5.74 L/mg. To confirm the favourability of the adsorption process, the separation factor (R_L) was calculated. R_L values for CHCl₃ adsorption onto nano-TiO₂ was found to be 0.63 (less than 1 and greater than zero). This indicated that the adsorption of CHCl₃ onto nano-TiO₂ was favourable [31]. The value of n , the Freundlich parameter, which was greater than one (1.27) indicating the adsorption is much more favourable [32]. It is shown that Langmuir isotherm is suitable for characterizing the experimental adsorption isotherms.

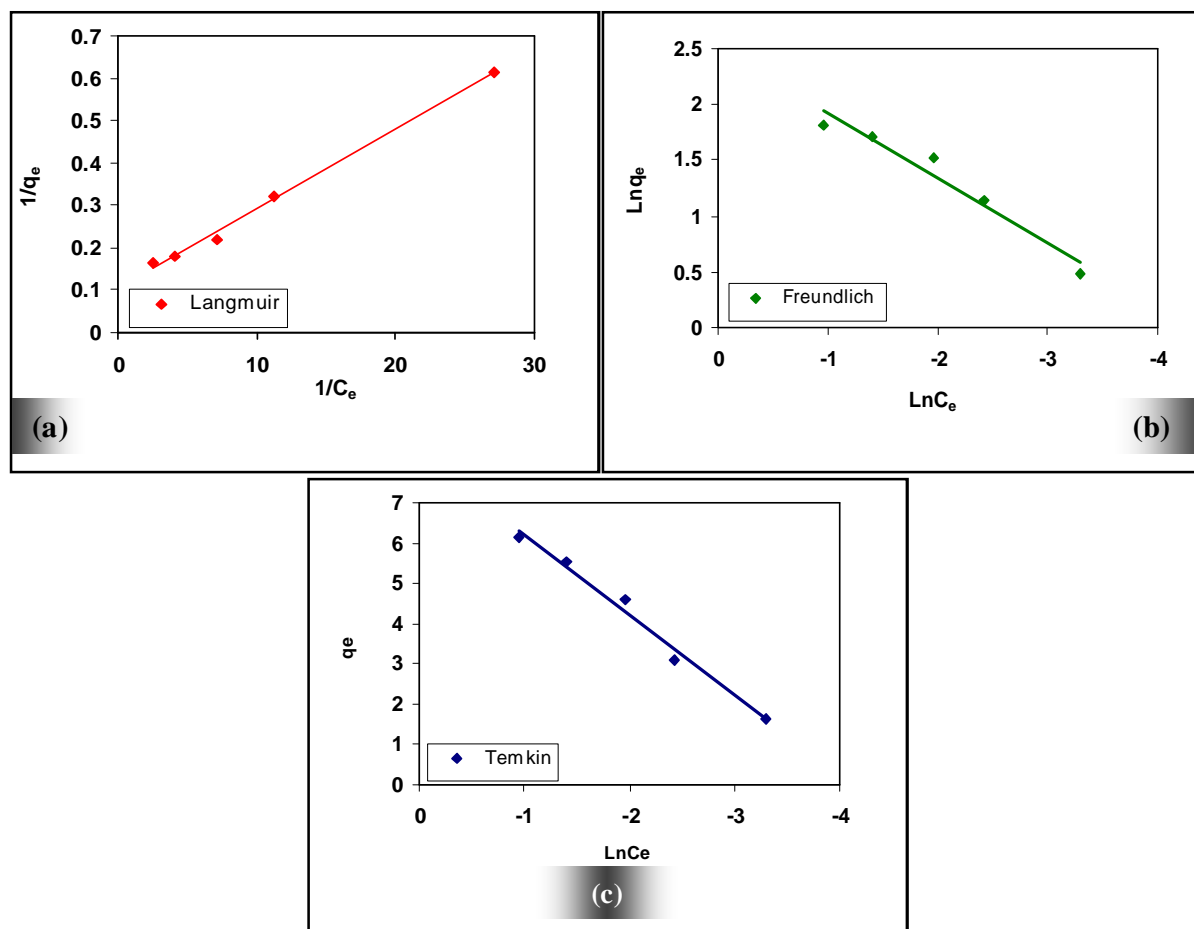


Fig.5. Plots of linearized Langmuir (a), Freundlich (b) and Temkin (c) adsorption isotherms of chloroform onto nano-TiO₂; adsorbent dose: 0.1g/L; pH: 8; temp.: 25°C

Table 1. Langmuir, Freundlich and Temkin Parameters for the adsorption of chloroform onto nano-TiO₂

Langmuir isotherm			Freundlich isotherm			Temkin isotherm		
q_m	K_L	R^2	K_F	n	R^2	K_T	B_1	R^2
9.69	5.74	0.996	12.15	1.27	0.95	60.40	2.008	0.98

Kinetics Studies

In order to investigate the mechanism of adsorption of the CHCl₃ on TiO₂ nanoparticles, kinetic models have been used to test experimental

data. Two kinetic models, pseudo-first-order and pseudo-second-order models, were used to investigate the adsorption process of CHCl₃ on TiO₂ nanoparticles.

• Pseudo-first-order model

The pseudo-first order rate expression, popularly known as the Lagergren equation, is generally described by the following equation [33]:

$$\frac{dq}{dt} = k_1(q_e - q_t) \quad (10)$$

The integrated rate law for a pseudo-first order rate expression [34] is given as:

$$\ln(q_e - q_t) = -k_1 t + \ln q_e \quad (11)$$

Where q_e and q_t (mg/g) are the amounts of CHCl_3 adsorbed on adsorbent at equilibrium and at time t , respectively, and k_1 is the pseudo-first order adsorption kinetic constant (1/min). The k_1 of pseudo-first order rate constant were calculated from the slopes of the respective linear plots of $\ln(q_e - q_t)$ versus t .

• Pseudo-second-order model

The sorption data were also analyzed in terms of a pseudo-second order mechanism [35] given by:

$$\frac{dq}{dt} = k_2(q_e - q_t)^2 \quad (12)$$

The integrated rate law for the pseudo-second-order kinetic model [36] may be expressed by the following equation:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (13)$$

Where, k_2 is the pseudo-second-order rate constant (g/mg.min) and q_e and q_t represent the amounts of CHCl_3 adsorbed (mg/g) at equilibrium and at given time t (min).

Figures 6 and 7 present the plots for the adsorption of CHCl_3 onto the nano TiO_2 applying the pseudo-first-order kinetic model and the pseudo-second-order kinetic model, respectively.

The slopes and intercepts of these curves were used to determine the values of k_1 and k_2 , and the equilibrium capacity (q_e) as well. The calculated values of the kinetic constants and the corresponding linear regression correlation are listed in Table 2. It is observed that the pseudo second- order model yields a somewhat better fit than the Lagergren model by comparing the results of correlation coefficients.

As it is seen from the Table 2, the best fit to the kinetic data arising from the studies of the adsorption of CHCl_3 onto the nano- TiO_2 was provided by the pseudo-second-order rate expression. This suggests that the CHCl_3 /nano TiO_2 system may involve an activated or chemisorption process [36].

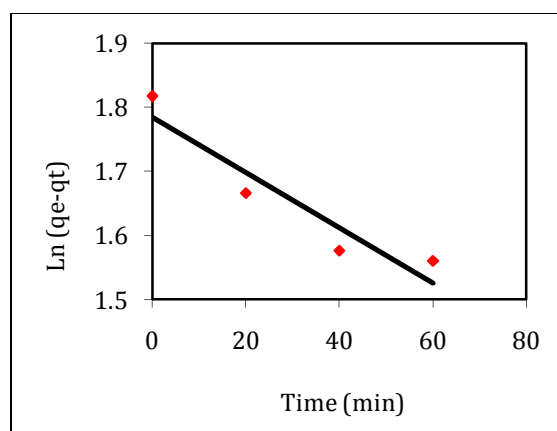


Fig.6. Pseudo-first-order kinetic model plots for adsorption of chloroform onto nano- TiO_2 .adsorbent dose: 0.1g/L; pH: 8; initial CHCl_3 conc. : 0.1 mg/L; temp.: 25°C

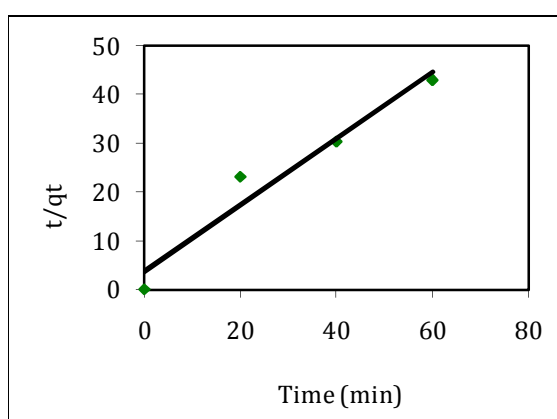


Fig.7. Pseudo-second-order kinetic model plots for adsorption of chloroform onto nano- TiO_2 .adsorbent dose: 0.1g/L; pH: 8; initial CHCl_3 conc. : 0.1 mg/L; temp.: 25°C

Table 2. Kinetic parameters for adsorption of chloroform onto nano-TiO₂

Pseudo-first-order model		Pseudo-second-order model		
K_1	R^2	K_2	$q_{e,cal}$	R^2
0.0043	0.88	0.12	1.46	0.949

CONCLUSION

The adsorption equilibrium and kinetics of chloroform onto nano-TiO₂ have been studied in the present work. Nano-TiO₂ is identified to be an effective adsorbent for the removal of chloroform from aqueous solution. The adsorption is highly dependent on various operating parameters such as adsorbent dose, contact time, pH and the initial chloroform concentrations. It has been observed that the percentage adsorption increases with an increase in the agitation time and becomes gradual after 80 min. The percentage adsorption is maximal at pH value of 8 and decreases with acidic and or basic strength of the chloroform solution. The percentage adsorption increased by increase the adsorbent dose and decreased by increase the initial chloroform concentrations. The adsorption kinetic data have been analyzed by the Lagergren first-order model and the pseudo-second order model, respectively. Adsorption kinetic follows pseudo-second-order kinetics. The equilibrium data are analyzed against Langmuir, Freundlich and Temkin isotherm equations. The result shows that the experimental data are best correlated with Langmuir isotherm.

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