

Kinetic and thermodynamic studies of adsorption of 4-chloro-2-nitrophenol on nano-TiO₂

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ABSTRACT

Adsorption capacity of 4-chloro-2-nitrophenol (4C2NP) onto nano-TiO₂ from aqueous solutions was investigated in a batch system by considering the effects of various parameters like contact time, nano-TiO₂ dosage, initial pH and initial 4C2NP concentration. Optimum conditions for 4C2NP adsorption were found to be initial pH ≈ 2, nano-TiO₂ dose ≈ 0.01 g and equilibrium time ≈ 1 h. The adsorption kinetic data were analyzed using pseudo-first and pseudo-second order models. It was found that the pseudo-second-order kinetic model was the most appropriate model, describing the adsorption kinetics. The thermodynamic parameters such as ΔG° , ΔH° and ΔS° were computed from the experimental data. These values show that the adsorption of 4C2NP onto nano-TiO₂ is spontaneous and endothermic.

Keywords: Adsorption; Kinetic; Thermodynamic; 4-Chloro-2-nitrophenol; Nano-TiO₂

INTRODUCTION

Phenols are considered as priority pollutants since they are harmful to organisms at low concentrations and many of them have been classified as hazardous pollutants, because of their potential to harm human health. Chronic toxic effects due to phenols reported in humans include vomiting, difficulty in swallowing, anorexia, liver and kidney damage, headache, fainting and other mental disturbances [1]. While the World Health Organization (WHO) recommends the permissible phenolic concentration of 0.001 mg/L in potable waters, the maximum concentration of total phenols in drinking water is given as 0.5 $\mu\text{g}/\text{dm}^3$ by the European Union [2,3]. Phenol and its derivatives appear in the effluents from many industries, such as coking, synthesis rubber, pharmaceuticals, petrochemical, paper, textiles and wood [4].

In the last decade, various methods have been proposed to remove phenols, including advanced oxidation process [5], biological degradation [6],

ultrafiltration [7], ozonation [8] and adsorption [9,10]. The adsorption method appears to be the best strategy, especially for removal of the moderate and low concentration phenolic compounds from effluent. Various adsorbents were tested to adsorb the phenolic compounds in aqueous solutions in the past years. For example, Roostaei and Tezel investigated phenol adsorption on silica gel, activated alumina, activated carbon and zeolites, the latter two materials show a higher capacity for adsorption of phenol [11]. Gonzalez *et al.*, found that activated carbons are good adsorbents for phenol and 2,4,5-trichlorophenol [12]. Some other materials, such as calcined layered double hydroxides [13], sewage treatment plant biosolids [14] and mesoporous silicate [15] were tested to remove phenol and substituted phenols from aqueous solution. The use of

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nanomaterials as an adsorbent is a new field of interest. Nanoparticles have high adsorption capacity. In addition, the operation is simple and the adsorption process is rapid [16].

In this paper, nano-TiO₂ adsorbent was used to adsorption of 4-chloro-2-nitrophenol (4C2NP) from aqueous solutions. The study was carried out with the aim to optimize conditions for removal of 4C2NP by nano-TiO₂. The experimental kinetic data were evaluated by applying the pseudo-first and pseudo-second order models. Finally, thermodynamic parameters for 4C2NP adsorption process have been calculated.

EXPERIMENTAL

Nano-TiO₂ (Degussa P25) was purchased from Degussa, Germany. Particle size and surface area of nanoparticles were about 20 nm and 15-50 m²/g, respectively. 4-Chloro-2-nitrophenol (C₆H₄ClNO₃, M_w= 173.56 g/mol, λ_{max}= 219 nm at acidic pHs and 234 nm at alkaline pHs) was supplied by Fluka, Germany.

Adsorption of 4C2NP was carried out by a batch method to obtain equilibrium data. The variation of the 4C2NP concentration versus time in the aqueous solution was monitored under various conditions such as nano-TiO₂ dosage (0.005, 0.01, 0.05 and 0.1 g), initial pH (2, 4, 6, 8, 10 and 12) and initial 4C2NP concentration (2, 4, 6, 8 and 10 mg/L). A stock solution was prepared by dissolving the required amount of 4C2NP in ethanol (from Merck) and then diluted to the appropriate concentration by double distilled water. The initial pH was adjusted by adding either HCl or NaOH. Adsorption was achieved by adding a known amount of nano-TiO₂ into 250 mL of 4C2NP solution of known concentration and pH, and the mixture was shaken in a shaking water bath at a speed of 140 shakes/min. Samples were taken at predetermined time intervals, centrifuged (Hettich/UNIVERSAL 16-R) at 10000 rpm for 10 min and the analysis of 4C2NP remaining in the solution was done using a UV-160 Shimadzu spectrophotometer. The adsorbed 4C2NP amount onto the TiO₂ nanoparticles (mg/g) at any time and at equilibrium, were calculated from the following relations:

$$q_t = \frac{(C_0 - C_t)V}{M} \quad (1)$$

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

where C₀, C_t and C_e are the initial, at any time *t* and equilibrium 4C2NP concentration (mg/L), respectively. *V* is the solution volume (L) and *M* is the nano-TiO₂ mass (g).

RESULTS AND DISCUSSION

Effect of contact time

In order to find out the optimum contact time, 0.1 g of nano-TiO₂ was added to 250 mL of 4C2NP solution with concentration of 10 mg/L at 25°C. The working pH was that of solution (pH 5.7) and was not controlled. The mixture was shaken at different times and left for 180 min (Fig. 1). Rapid adsorption was observed during the first 30 min of contact time and it became slower at the later stages of contact time. Fig. 1, also indicates that the time required for equilibrium is 1 h. Thus, for all equilibrium adsorption studies, the contact period was kept 1 h.

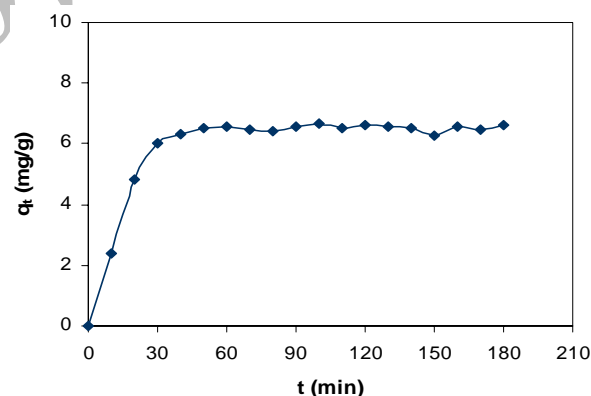


Fig. 1. Effect of contact time on 4C2NP adsorption onto nano-TiO₂ (nano-TiO₂ dose: 0.1 g, pH: 5.7, initial 4C2NP conc.: 10 mg/L, temp.: 25°C).

Effect of nano-TiO₂ dosage

To study the effect of nano-TiO₂ dosage on the adsorption of 4C2NP, the experiments were done under the conditions described at previous stage with contact time of 1 h and variable nano-TiO₂ dose (0.005, 0.01, 0.05 and 0.1 g). Fig. 2, shows the effect of nano-TiO₂ dosage on the removal of 4C2NP. A trend of increment in adsorption capacity with increasing of nano-TiO₂ dosage was observed from 0.005 to 0.01 g. Nano-TiO₂ recorded a maximum capacity of 77.78 mg/g at 0.01 g dose. The initial increment in adsorption

capacity with increase in adsorbent dosage was expected, since number of adsorbent particles increases and thus more surface areas were available. Further increment in nano-TiO₂ dosage beyond maximum adsorption capacity at 0.01 g resulted in a decline in capacity as shown in Fig. 2. This reduction in capacity had been explained as due to the overlapping of the adsorption sites as a result of overcrowding of adsorbent particles above 0.01 g dose [17]. As a result, the nano-TiO₂ of 0.01 g was used as an optimum dose in the subsequent experiments of this work.

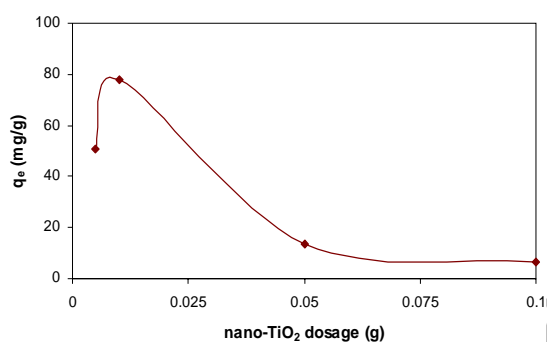


Fig. 2. Effect of nano-TiO₂ dosage on 4C2NP adsorption (pH: 5.7, initial 4C2NP conc.: 10 mg/L, temp.: 25°C, contact time: 1 h).

Effect of initial pH

In this study, the pH value was considered as an important parameter, because the pH of the solution controls the electrostatic interactions between the adsorbent and adsorbate [18]. The adsorbent surface charge is neutral at isoelectric point (IEP), where the pH_{IEP} for the Degussa P25 TiO₂ is ranged between 6.2 and 6.9 [19]. While the surface of the adsorbent carries positive charge at pH values lower than IEP, it carries negative charge at pH values higher than IEP [16].

In Fig. 3, the effect of initial pH on the adsorption of 4C2NP onto nano-TiO₂ at 25°C and initial 4C2NP concentration of 10 mg/L is depicted. As shown, it can be deduced the amount of 4C2NP adsorbed on nano-TiO₂ increased by decreasing the pH and the highest amount of 4C2NP adsorption was at pH 2 (86.3 mg/g).

At low pH of 6, nano-TiO₂ surface is positively charged and since there is no electrostatic repulsion between the unionized 4C2NP species and the positively charged surface, the adsorption is higher. On the other hand for pH > 6, the nano-

TiO₂ surface is negatively charged resulting in reduced adsorption due to electrostatic repulsion between the negative surface charge of TiO₂ nanoparticles and the ionized 4C2NP species. Similar result was reported for the adsorption of azo dye Reactive Red 195 on TiO₂ nanoparticles [20]. Therefore, the rest of the experiments were performed at pH 2.

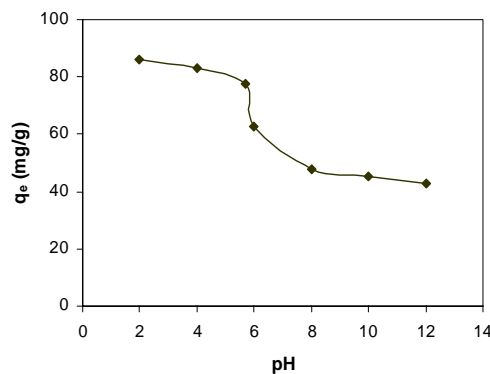


Fig. 3. Effect of pH on 4C2NP adsorption onto nano-TiO₂ (nano-TiO₂ dose: 0.01 g, initial 4C2NP conc.: 10 mg/L, temp.: 25°C, contact time: 1 h).

Effect of initial 4C2NP concentration

To determine the effect of initial 4C2NP concentration on its adsorption onto TiO₂ nanoparticles, 0.01 g of nano-TiO₂ was added to 250 mL of 4C2NP solution with initial concentrations in the range of 2 to 10 mg/L at pH 2 and 25°C. Based on results (data not shown here), when the initial 4C2NP concentration increased from 2 to 10 mg/L, the amount of 4C2NP adsorbed per unit weight of the nano-TiO₂ increased from 6 to 86.3 mg/g. This is obvious from the fact that the initial 4C2NP concentration provides an important driving force to overcome all of mass transfer resistance. Furthermore, the increase of loading capacity of nano-TiO₂ with increasing initial 4C2NP concentration may be due to higher interaction between 4C2NP and adsorbent.

Adsorption kinetic studies

Adsorption kinetic shows the evolution of the adsorption capacity through time and it is necessary to identify the types of adsorption mechanism in a given system. The kinetics of the adsorption of 4C2NP onto nano-TiO₂ was investigated by 250 mL of solution containing 10 mg/L 4C2NP in the range of 0-45 min. The

adsorption kinetic data were described according to the integrated rate equations of pseudo-first and pseudo-second order (3,4), respectively:

$$\ln(q_e - q_t) = -k_1 t + \ln q_e \quad (3)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (4)$$

where q_e and q_t are the amount of 4C2NP adsorbed (mg/g) at equilibrium and at time t (min). k_1 (min^{-1}) and k_2 ($\text{g/mg}\cdot\text{min}$) are the pseudo-first and pseudo-second order rate constants, respectively. In Fig. 4 (a and b), the plots of adsorption kinetic models is depicted. The results of the kinetic parameters for 4C2NP adsorption are listed in Table 1.

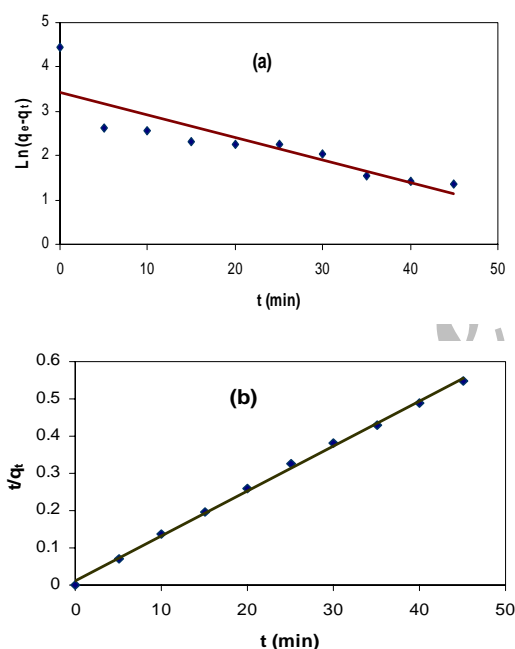


Fig. 4. Plots of pseudo-first-order (a) and pseudo-second-order (b) adsorption kinetics of 4C2NP onto nano-TiO₂ (nano-TiO₂ dose: 0.01 g, pH: 2, initial 4C2NP conc.: 10 mg/L, temp.: 25°C).

Table 1. Kinetic parameters for 4C2NP adsorption onto nano-TiO₂

Pseudo-first-order model		Pseudo-second-order model		
k_1	R^2	k_2	$q_{e,cal}$	R^2
0.050	0.751	0.011	83.333	0.998

The coefficient of determination, R^2 for the pseudo-second-order adsorption model has a high value (>0.99), and its calculated equilibrium adsorption capacity ($q_{e,cal}$) is consistent with experimental data ($q_{e,exp} = 86.306$ mg/g). These

facts suggest that the pseudo-second-order adsorption mechanism is predominant.

Adsorption thermodynamic studies

Thermodynamic studies were performed in the temperature range of 298-328 K, at an initial 4C2NP concentration of 10 mg/L to find the nature of adsorption process. The determination of equilibrium constant (K_C) is a key step to obtain the thermodynamic variables of adsorption process. Generally, K_C is calculated from experimental data by using the following relation:

$$K_C = \frac{q_e}{C_e} \quad (5)$$

Where q_e and C_e are the amount of 4C2NP adsorbed (mg/g) and concentration of 4C2NP (mg/L) at equilibrium, respectively. The standard Gibbs free energy (ΔG°) values were calculated from: $\Delta G^\circ = -RT \ln K_C$

where R is the gas constant (8.314 J/mol.K) and T is the absolute temperature (K). Standard enthalpy (ΔH°) and entropy (ΔS°) were calculated from the slope and intercept of the plot of $\ln K_C$ vs. $1/T$ (Fig. 5) using the following equation:

$$\ln K_C = -\frac{\Delta H^\circ}{R} \left(\frac{1}{T}\right) + \frac{\Delta S^\circ}{R} \quad (7)$$

Results were summarized in Table 2. As it can be seen, the negative values of ΔG° show a spontaneous nature of adsorption. The decrease in ΔG° with the increase of temperature indicates more efficient adsorption at higher temperature. The positive value of ΔH° indicate that the adsorption reaction of 4C2NP on nano-TiO₂ is endothermic. In the case of $\Delta S^\circ > 0$, the release of the attached water molecules took place as 4C2NP adsorbed on the substrate and contributed to the increase in the degree of freedom of the entire system.

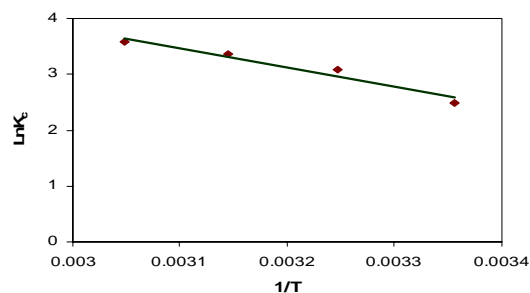


Fig. 5. Plot of $\ln K_C$ vs. $1/T$ (nano-TiO₂ dose: 0.01 g, pH: 2, initial 4C2NP conc.: 10 mg/L, contact time: 1 h).

Table 2. Thermodynamic parameters for 4C2NP adsorption onto nano-TiO₂

ΔG° (kJ/mol)				ΔH° (kJ/mol)	ΔS° (J/mol.K)	R^2
298 K	308 K	318 K	328 K			
-6.179	-7.911	-8.878	-9.745	28.688	117.784	0.951

CONCLUSION

The adsorption behavior of 4-chloro-2-nitrophenol on nano-TiO₂ was investigated. It was found that pH 2 is the best pH to have the maximum adsorption amount, also the best contact time was found to be 1 h and the optimum adsorbent dose is 0.01 g. In addition, the adsorption amounts increase with an increase of initial concentration. It was found that the pseudo-second order kinetic model was the most appropriate model, describing the adsorption kinetics. Negative free energy change of

adsorption (ΔG°), positive enthalpy change (ΔH°) and positive entropy change (ΔS°) indicate that the adsorption is a spontaneous and endothermic process.

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