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Cadmium removal from wastewater using nano-clay/TiO_2 composite: kinetics, equilibrium and thermodynamic study

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A B S T R A C T

In this research, commercial nano-clay (NC) was modified with TiO_2 functional groups and characterized via XRD and FTIR methods. The modified nano-clay was applied as an adsorbent for the removal of cadmium from wastewater solutions. The effects of the operating parameters including initial pH, cadmium concentration and adsorbent concentration were analyzed by the Taguchi method. The optimum conditions for cadmium removal by the nanoclay/TiO_2 composite were an initial feed pH of 6, an initial concentration of 30 mg/L, and an adsorbent concentration of 4.5 g/L. Under these conditions, nearly 90% of the cadmium ions were removed by modified nano-clay after one hour. The equilibrium results showed that the Freundlich model could well fit the experimental data, and this indicated the multilayer adsorption process. The adsorption capacity of the nano-clay for cadmium improved from 8.92 mg/g to 16.20 mg/g by modification with TiO_2. The kinetic data were analyzed using the pseudo-first order, pseudo-second-order, and intraparticle kinetics models. Thermodynamic studies indicated the exothermic and spontaneously nature of the adsorption process.

1. Introduction

The adsorption process has attracted much attention in recent years because of its outstanding performance, easy control, and reduced operating costs [1-2]. Among the different adsorbents, clay and bentonite have received considerable attention due to their high mechanical and chemical stability, low cost, eco-friendliness, and natural abundance. Also, these materials have a high cation exchange capacity, a moderate surface area, and are applied as the adsorbent for various separation targets [3-6]. Due to the increased application of the adsorption process, the improvement of the adsorption ability of natural adsorbents such as bentonite and clay is essential. Today, nanoparticles are applied to synthesize different nanocomposite such as TiO_2 nanoparticles. TiO_2 nanoparticles have recently received much attention because of its high reactivity [7]. TiO_2 is a well-known photoactive structure that has properties such as low cost, high oxidizing ability, eco-friendly, non-toxic, and chemical inertness. TiO_2 particles are widely used today as a photo-catalyst in the advanced oxidation process for the removal of various contaminants from wastewater. Nowadays, with the development of nanotechnology and nanostructures, TiO_2 nanoparticles are considered as a photo-catalyst or adsorbent for the separation of organic and heavy metals from wastewater either on its own or in combination with other materials such as bentonite, chitosan, silica, graphite oxide, zinc oxide nanoparticles, polymers, etc. [8-17]. A review of the literature shows that the TiO_2 composite with nano-clay has not been studied as an adsorbent for heavy metal removal up until now. Today, water contamination with different pollutants is a major environmental problem. Heavy metals are major water pollutants that are widely distributed in the environment and are harmful due to their toxicity. They are non-biodegradable, and their concentration in living organisms is accentuated through bioaccumulation via the food chain. Their accumulation causes different diseases and dysfunctions. Cadmium is a toxic metal found in several industrial discharges and effluents. It is released into the

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environment through the combustion of fossil fuels, metal production (zinc, iron and steel production), cement production, electroplating, and the manufacturing of batteries and pigments. The presence of cadmium (II) in water, even at low concentrations, is extremely harmful to the aquatic environment; it can also cause muscular cramps, chronic pulmonary problems, renal degradation, proteinuria, skeletal deformity, and testicular atrophy in humans. The World Health Organization (WHO) guideline has set its maximum concentration at 0.003 mg/L for drinking water [18-19]. Among the various separation technologies, adsorption is more advantageous due to its high separation efficiency, low cost, and easy operation [1]. Recently, the use of natural materials as the adsorbent for heavy metal removal from wastewater has gained considerable importance in the adsorption process [1]. This research analyzed the separation efficiency of nano-clay modified with TiO_2 for heavy metal removal from dilute solution. The adsorption ability of this composite was investigated for Cd (II) removal from dilute solutions under different adsorption conditions. Also, the equilibrium and kinetics of the adsorption process were analyzed in order to understand the adsorption mechanism.

2. Material and methods

2.1. Materials

The commercial nano-clay was purchased from Southern Clay Products Incorporated. The nano TiO_2 particles were purchased from Evonik Industries. The Cd $(NO_3)_2$. $4H_2O$ was supplied by the Merck Company, and deionized water was used for the preparation of the metal solutions. The initial pH of the solution was adjusted with HCl (37%) and NaOH that was supplied by the Merck Company. The ethanol (99.9%) and NaCl were also supplied by the Merck Company.

2.2. Modification of nano-clay with nano TiO_2 particles

Initially, 10 g of nano-clay was mixed with 500 ml of deionized distilled water and stirred for 3 h at 80 °C. In another container, 5 g of the TiO_2 particles and 50 ml of ethanol were added; then, 125 ml of hydrochloric acid was added, and it was stirred for 3 h at room temperature. These two mixtures were then combined and mixed for 10 h at 80 °C. The resulting mixture was filtered and washed several times with water and ethanol (50/50); subsequently, it was dried in an oven and then milled. The modified nano-clay was donated as TiMNC.

2.3. Adsorbents characterization

To determine and detect the presence of titanium nanoparticles on the nano-clay surface, XRD and FTIR analyses were performed. In order to determine the distribution of titanium on the clay surface, EDS microanalysis and element mapping were used. The pH_{ZPC} of the adsorbent was measured according to the following procedure. First, 50 mL of NaCl solution (0.1 N) was poured into 24 glass Erlenmeyer flasks (100 mL). The initial pH of the solutions was adjusted in the range 1-12. Then, 0.1 g of the dried material was added to each glass, and the suspension was shaken for one day. Next, the solutions were filtered, and the pHs of the filtrates were measured. The point at which the pH of the solution did not change after one day of contact with the adsorbent is expressed as pH_{ZPC}.

2.4. Removal experiments

In this study, the effects of three operating parameters including solution pH, initial metal concentration, and concentration of TiMNC were investigated in four levels for the removal of Cd (II) from the single solution. Based on the Taguchi method, a standard orthogonal array L16 with sixteen rows and three columns was applied to these removal experiments [20]. Table 1 shows the experimental layout of these experiments. The kinetic experiments for Cd (II) ions removal were performed at a pH = 6.0, a temperature of 25 ˚C, an adsorbent concentration of 3 g/L, and an initial concentration 50 mg/L. The contents of the flasks were agitated on an orbital shaker (200 rpm) for prescribed periods of time (5-200 min). Then, the adsorbent was separated with Wattman filter paper, and the solution concentration was analyzed using an inductively coupled plasma (ICP) analyzer; next, the metal uptake capacity of the adsorbent, *q*, was calculated [20]. In order to assess the adsorption equilibrium and determine the adsorption capacity of the nano-clay and TiMNC, adsorption equilibrium was performed under the following conditions: a pH = 6.0, an adsorbent concentration of 3 g/L and a 24 h time for reaching equilibrium. The initial concentrations of Cd (II) were 10–50 mg/L. The equilibrium tests were performed at 25 ˚C, 35 °C and 45 °C. The metal solution was filtered after equilibrium, and the residual concentration of the metal ions was determined and used to calculate *q*.

Table 1. Experimental layout for removal tests

Run No.	pH	Initial concentration	Adsorbent dosage
1	1	5	1
2	1	10	1.5
3	1	30	3
4	1	50	4.5
5	2	10	1
6	2	5	1.5
7	2	50	3
8	2	30	4.5
9	4	30	1
10	4	50	1.5
11	4	5	3
12	4	10	4.5
13	6	50	1
14	6	30	1.5
15	6	10	3
16	6	5	4.5

3. Results and discussion

3.1. Characterization results

Figure 1 presents the FTIR results of the nano-clay and TiO_2 modified nano-clay. In order to detect the TiO_2, the recognition of the Ti-O bond is sufficient. The graph in Figure 1 shows the peaks in the range of 400-900 cm^{-1}. X-ray diffraction (WAXS) was used to confirm the formation of the TiO_2 groups, and the results are shown in Figure 2. The absorption peaks at 25.8, 37.5 and 55.4 are related to TiO_2 characteristic peaks. Figure 3 presents the results of the element mapping, which indicates the good distribution of titanium on the clay surface.

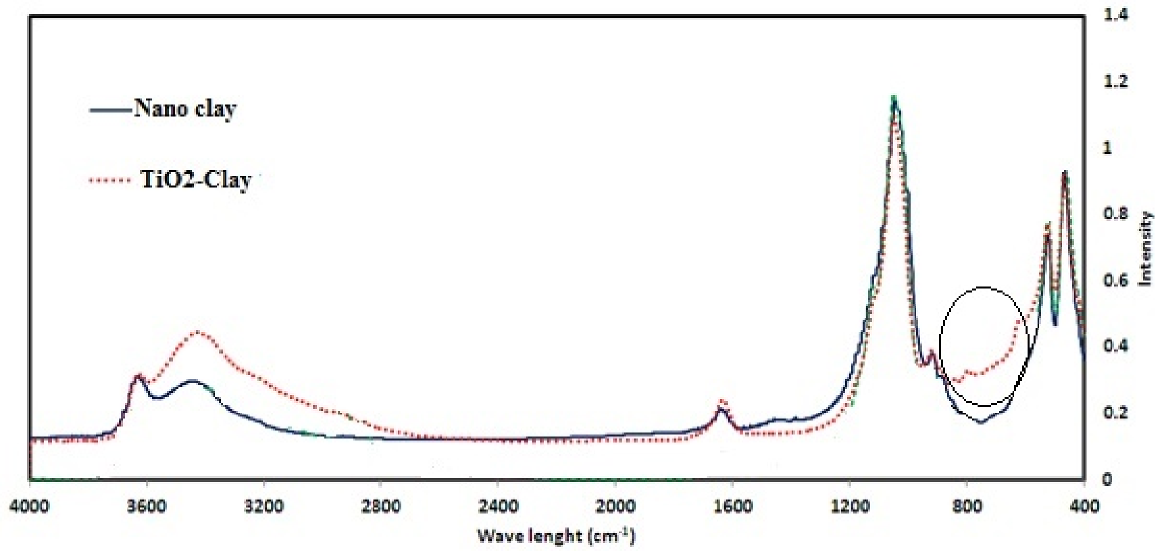

Fig. 1. FTIR spectra of nano-clay and modified clay

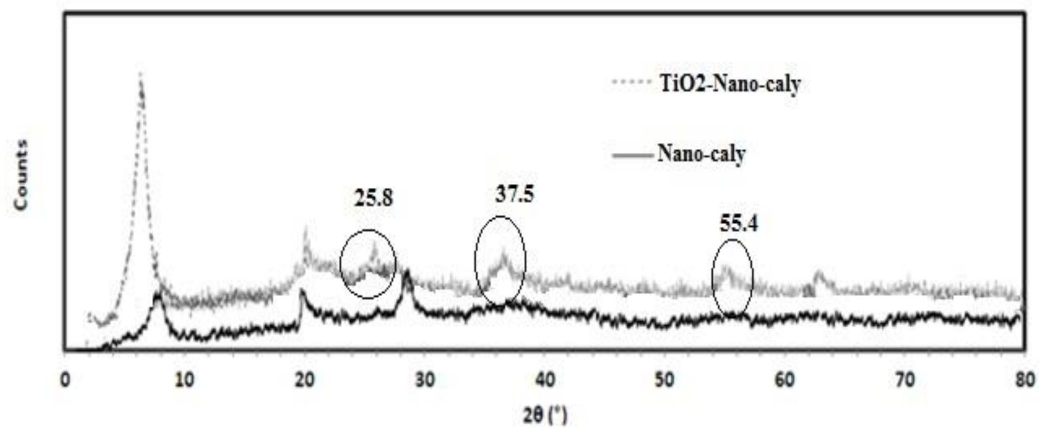

Fig. 2. WAXS spectra of nano-clay and modified clay

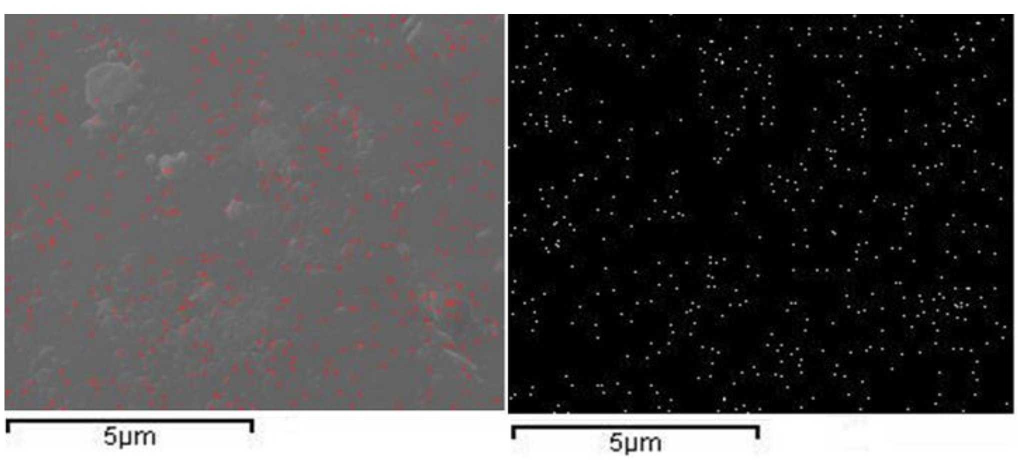

Fig. 3. Element mapping results for TiMNC composite

3.2. Separation results

3.2.1. Taguchi analysis of results

To analyze the results in the Taguchi method, the percentage of Cd (II) removal was selected as the efficiency of the process, and the optimum conditions were estimated based on this parameter. The observed results for the effect of the pH solution, dosage of adsorbent and initial concentration on cadmium removal using TiMNC are shown in Figure 4. The results indicated that the optimum operating conditions were a pH=6, a dosage of adsorbent =4.5 g/L, and an initial concentration = 30 mg/L. Under these conditions, about 90% of the cadmium was removed from the dilute solution using TiMNC after 1 h. The pH_{zpc} of the TiMNC was 4.6. At a pH < 4.6, the surface charge of TiMNC was positive and could not attract Cd^{2+} cations; however, at higher pH values, the surface of the adsorbent had a higher negative charge which resulted in a higher cadmium attraction. The adsorption ability of TiMNC is a result of its functional groups. These functional groups containing oxygen can attract the Cd^{2+} ions via two mechanisms: ion-exchange and sharing the electron pair.

As shown in Figure 4b, the removal percentage increased with increasing the concentration of the adsorbent. This result was expected; the number of adsorption sites for the cadmium ions increased as the concentration of the adsorbent increased. Therefore, more metal ions could be removed from the solution. According to Figure 4c, the removal efficiency increased with increasing initial concentration, and then decreased. The initial increase was due to the high start driving force. Then, the driving force was reduced by the saturation of the adsorption sites of the adsorbent surface, and the removal percentage decreased.

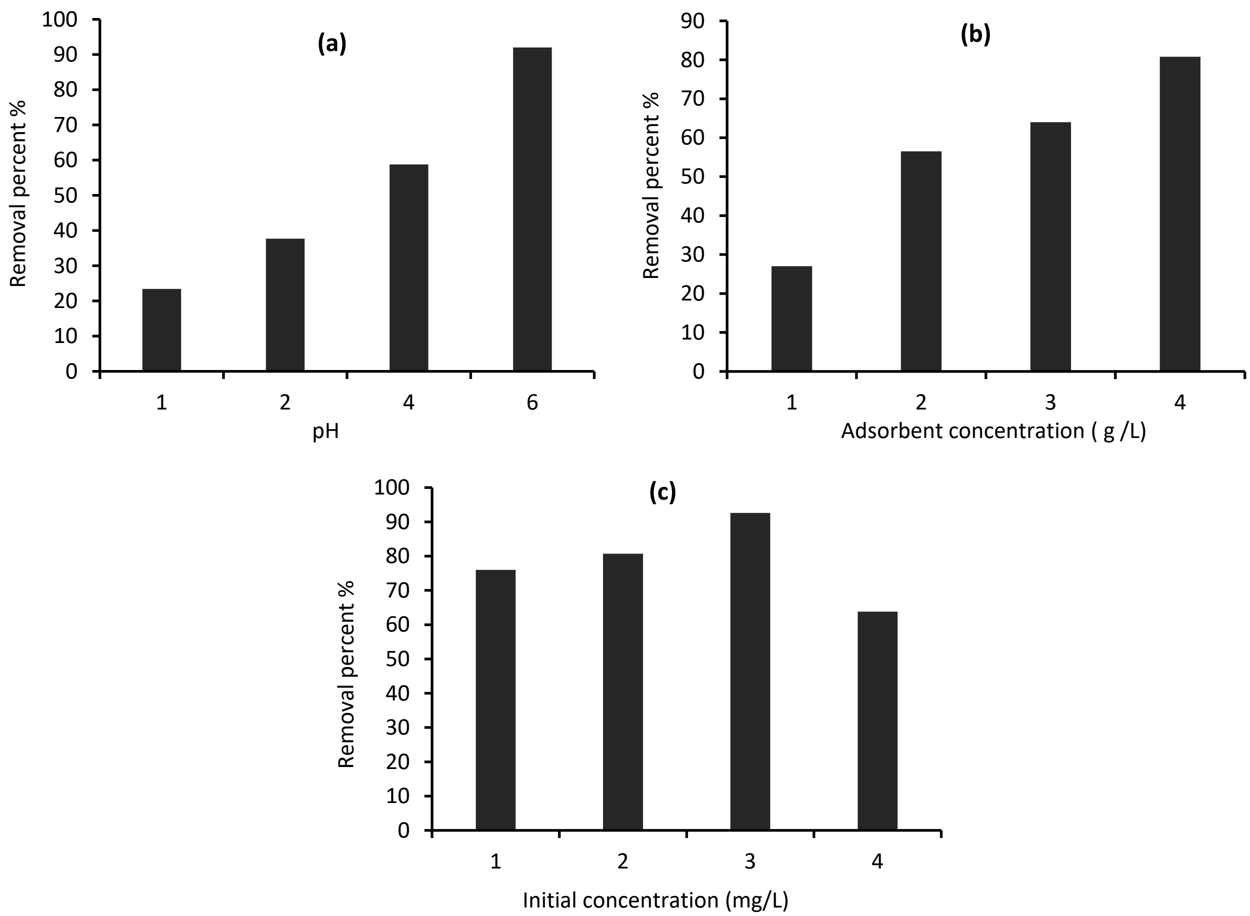

Fig. 4. Removal efficiency of cadmium using TiMNC as a function of: (a): initial pH (initial concentration: 23.75 mg/L, adsorbent concentration: 2.5 g/L); (b): adsorbent concentration (pH: 3.25, initial concentration: 23.75 mg/L); (c): Initial concentration of cadmium (pH: 3.25, adsorbent concentration: 2.5 g/L)

The importance of each operating parameter is estimated using ANOVA analysis. The F-ratio parameter of the ANOVA analysis is applied to estimate the importance of the parameters. For each parameter, the calculated F-ratio value (in the ANOVA table) is compared with the standard F-value of 3.29 (for $F_{0.1, 3,6}$) from the Fischer tables [21]. According to this value and the ANOVA data (Table 2), the F-value for all the parameters is greater than the standard F-value (3.29); therefore, the tests are reliable with a 90% confidence, and these parameters have great effects on the performance of the adsorption process for cadmium removal using TiMNC.

Table 2. ANOVA data for cadmium removal

Removal parameters	Degree of Freedom	Var (V)	F-ratio	Percent of contribution
Initial pH	3	1980.99	39.83	39.19
Adsorbent concentration	3	525.88	11.57	27.06
Initial Conc.	3	284.67	18.71	24.83
Error	6	49.74		8.92

3.2.2. Kinetics and equilibrium of removal process

Figure 5 presents the kinetic adsorption data for cadmium removal using nano-clay and TiMNC from a single solution. These kinetic data were analyzed in terms of the pseudo-first-order, pseudo-second-order, and intra-particle diffusion equations; the parameters of these equations are given in Table 3 for NC and TiMNC adsorbents.

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \quad \text{pseudo-first order} \quad (1)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad \text{pseudo-second order} \quad (2)$$

$$q_t = k_{id} t^{1/2} + \theta \quad \text{Intra-Particle diffusion} \quad (3)$$

Based on the data presented in Table 3, the pseudo-first-order was the best model to predict the kinetic behavior of Cd (II) removal using nano-clay. But for Cd (II) removal using TiMNC, the data was best described with the pseudo-second order kinetics model. This suggested that the main adsorption mechanism was a physical adsorption for the removal of this metal using nano-clay and chemical adsorption for removal using TiMNC. It can be said that by modifying the nano-clay surface, titanium functional groups have been formed on its surface that act as an absorption site. The value of θ indicates the importance of both the film and internal diffusion stages in the adsorption of cadmium from the solution with the adsorbents.

Table 3. Kinetics parameters for Cd(II) removal using NC and MiNC

Kinetics models	Parameter	NC	MiNC
$q_{e,exp}$ (mg/g)		4.60	11.28
Pseudo-first order	k_1	0.0202	0.037
	q_e	4.47	2.45
	R^2	0.998	0.93
Pseudo-second-order	k_2	0.034	0.008
	q_e	1.5	11.210
	R^2	0.85	1
Intra-particle diffusion	k_{id}	0.138	0.139
	θ	5.944	9.79

R^2	0.90	0.75

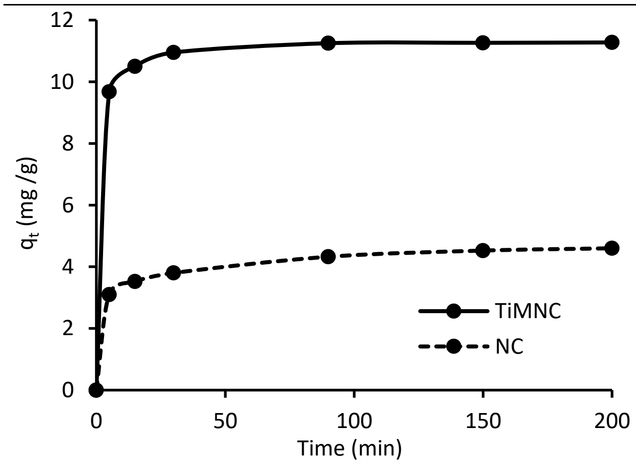

Fig. 5. The kinetics data for Cd (II) removal using NC and TiMNC

The adsorption equilibrium isotherms obtained for Cd (II) ions removal using NC and TiMNC are shown in Figure 6(a). It was found that the adsorption ability of the nano-clay improved by modification with the titanium nanoparticles, which occurred because of the new adsorption site created onto the TiMNC surface. The equilibrium data were analyzed with the Langmuir and Freundlich isotherms, and the constants of these models are summarized in Table 4. The results showed that the Langmuir isotherm best fitted with the equilibrium data of Cd (II) ions adsorption onto the NC and TiMNC, and these results indicated the monolayer nature of the adsorption process. The maximum adsorption capacity of TiMNC was 16.2 mg/g, which was comparable with the data reported for other adsorbents such as commercial activated carbon (10.3 mg/g), chitosan (10 mg/g), turkish fly ashes (0.29 mg/g), coffee grounds (15.65 mg/g), bamboo charcoal (12.08 mg/g), pen shells (37.63 mg/g), freshwater mussel shells (28.6 mg/g), and sweet potato peels (18 mg/g) [22-28].

$$q_e = q_{max} \frac{K_L C_e}{1 + K_L C_e} \quad \text{Langmuir} \quad (4)$$

$$q_e = K_f (C_e)^{\frac{1}{n}} \quad \text{Freundlich} \quad (5)$$

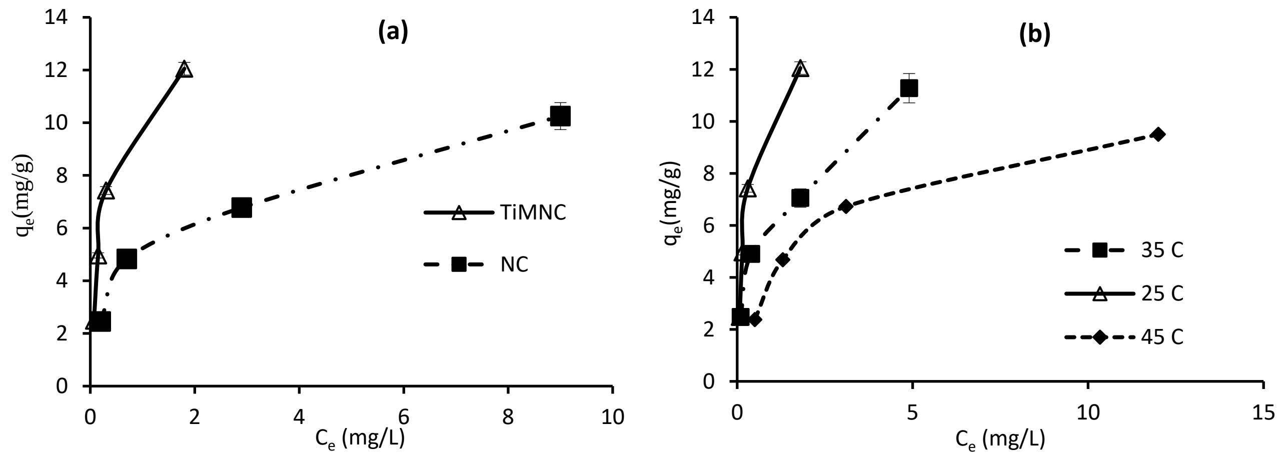

Fig. 6. (a): Equilibrium isotherms for Cd (II) removal using NC and TiMNC; (b): Adsorption isotherms for Cd (II) removal using TiMNC at various temperatures

Table 4. Equilibrium parameters for Cd (II) adsorption using NC and TiMNC

Isotherm models	Parameter	NC	TiMNC
	q_{max}	8.92	16.20
Langmuir	K_L	1.067	2.523
	R^2	0.988	0.995
	K_f	1.96	2.76
Freundlich	n	2.77	2.17
	R^2	0.925	0.901

Figure 6(b) presents the adsorption isotherms of the cadmium adsorption onto the TiMNC composite at various temperatures. The amount of cadmium adsorbed decreased by increasing the temperature, and it confirmed that the adsorption process was exothermic. The equilibrium data at various temperatures was applied to estimate the thermodynamic parameters of the adsorption process including the changes in Gibbs free energy (ΔG° (kJ/mol)), enthalpy (ΔH° (kJ/mol)) and entropy (ΔS° (kJ mol^{-1} K^{-1})), respectively, by the following relation [2]:

$$\begin{cases} \Delta G^\circ = -RT\ln(K_L) \\ \ln(K_L) = \dfrac{-\Delta H^\circ}{RT} + \dfrac{\Delta S^\circ}{R} \\ T.\Delta S^\circ = \Delta H^\circ - \Delta G^\circ \end{cases} \tag{6}$$

Table 5 presents the thermodynamic data. The value of these parameters is negative, and it indicates the spontaneous and exothermic nature of adsorption process, and this process is feasible.

Table 5. Thermodynamic data for Cd (II) removal using TiMNC composite

Temp. (K)	K_L	Ln (K_L)	ΔG	ΔH	ΔS	T. ΔS
298	283613	12.555	-31.106	-38.129	-0.023	-6.928
308	193122.1	12.171	-31.166			-7.161
318	107464.9	11.584	-30.628			-7.393

4. Conclusions

In this paper, commercial nano-clay was modified with TiO_2 nanoparticles. The FTIR and WAXS analysis confirmed the existence of TiO_2 bonds on the clay surface. The modified nano-clay was used as an adsorbent for Cd (II) removal from dilute solutions. The Taguchi analysis of the experimental data showed that the solution pH, initial concentration and concentration of adsorbent had significant effects on the efficiency of the removal process. Under optimum operation conditions, about 90% of the Cd (II) was removed using the modified clay after 1 h. The Langmuir isotherm provided the best fit with the equilibrium data for Cd (II) removal. The results showed that the adsorption capacity of the nano-clay increased after modification with the titanium groups. It was observed that the adsorption of Cd (II) using TiMNC was exothermic.

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