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Effect of pH, Initial Concentration, Background Electrolyte, and Ionic Strength on Cadmium Adsorption by TiO_2 and γ-Al_2O_3 Nanoparticles

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ABSTRACT : The entrance of Cd (II) to aqueous environments causes a major problem to human health. The current article examines the efficiency of TiO_2 and γ-Al_2O_3 nanoparticles in Cd (II) removal from aqueous medium as influenced by different chemical factors, such as pH, initial concentration, background electrolyte, and ionic strength, in accordance with standard experimental methods. It conducts Batch experiments, fitting various isotherm models (Freundlich, Langmuir, Temkin, and Dubinin-Radushkevich) to the equilibrium data. Saturation indices (SI) of TiO_2 and γ-Al_2O_3 nanosorbents indicate that adsorption is a predominant mechanism for Cd (II) removal from aqueous solution, giving maximum Cd (II) adsorption rates of 3348 and 1173 mg/kg for TiO_2 and γ-Al_2O_3 nanoparticles, respectively, both obtained at the highest pH level (pH = 8) as well as the highest initial Cd (II) concentration (equal to 80 mg/ L). Cadmium removal efficiency with TiO_2 and γ-Al_2O_3 nanoparticles has increased by raising pH from 6 to 8. The Freundlich adsorption isotherm model could fit the experimental equilibrium data well at different pH levels. Also, it has been revealed that cadmium adsorption drops as the ionic strength is increased. The maximum Cd (II) adsorption (1625 mg/kg) has been attained at 0.01 M ionic strength in the presence of NaCl. Thermodynamic calculations demonstrate the spontaneous nature of Cd (II) adsorption by TiO_2 and γ-Al_2O_3 nanoparticles. The former (TiO_2) have high adsorption capacities, suggesting they are probably effective metal sorbents, compared to the latter (γ-Al_2O_3).

Keywords: Cadmium adsorption, Isotherm models, Removal efficiency, Speciation, Visual MINTEQ.

INTRODUCTION

Cadmium (Cd (II)) as one of the chemical pollutants in the surrounding environment, due to its non-degradable, immanent and accumulative essence even when present in trace concentrations, has engrossed a lot of attentions from past to recent (Tabesh et al., 2018; Kataria & Garg, 2018; Parvin et al., 2019). Cadmium pollution was considered as a serious problem for human health because it can introduce to the food chain from contaminated environments (Chen et al., 2017; Lin et al., 2018). The International Agency for Research of Cancer (IARC, 1974) classified the Cd (II) as toxic and carcinogenic heavy metal to human health. The efficiency of various body organs of living species are affected by Cd (II), and different drastic and torrid diseases also cause by Cd (II) exposure (Chen et al., 2017). The maximum acceptable levels of Cd (II) in drinking

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water are 0.003 mg/ L and 0.005 mg/ L according to WHO (2011) and USEPR (2012) respectively. Thus, it is very necessary to specify effective methods for control of Cd pollution and increase environmental protection.

Modern technologies have been expanded for decreasing heavy metals concentration from the environment. Several technologies including precipitation (Fan et al., 2017), advance oxidation (Cheng et al., 2016), flocculation (Folens et al., 2017), electrolysis (Li et al., 2016), adsorption (Yu et al., 2018; Vilardi et al, 2018; Sharma et al., 2019), ion exchange and membrance technology (Lu et al., 2018). However, most of these technologies are usually inconclusive and costly, because of diffusion restriction or the deficit of adequate active surface sites of them, particularly when the heavy metal concentration excesses of 100 ppm (Koju et al., 2018; Haq et al., 2019). Regarding all various technologies, adsorption is considered as a quick, simple, environmentally friendly, useful, economical and worldwide method. The nature of the adsorbent and efficient parameters for removal of metal from the aqueous and non-aqueous environments are important agents for the increase of adsorptive separation efficiency (Sharma et al., 2019).

Recently, success achievements in nanotechnology result in attention to produce novel nanoadsorbents for heavy metals removal from solutions. Several adsorbents including MgO nanoparticles (Lu et al., 2018; Parvin et al., 2019), magnetic biosorbent (Bonilla-Petriciolet et al., 2018), and Fe_2O_3 nanoparticles (Li et al., 2019) have been applied for removal of various heavy metals from aqueous solution. Because of nanoadsorbents unique physical and chemical properties, and high- performance specific surface area, there is great consideration to these adsorbents recently (Bashir et al., 2018; Musso et al., 2019; Sharma et al., 2019). If different metal oxides supplied and activated correctly, they can use as adsorbents. High consistency, appropriate dielectric properties and photocatalytic activity of TiO_2 lead to acceptable performance of this nanoparticle as an adsorbent (Lajayer et al., 2018), also, γ-Al_2O_3 nanoparticles has potentially high resistance to chemical factors, So the nanoparticles are capable of acting as a catalyst in different chemical reactions (Gatabi et al., 2016; Lu et al., 2018).

Although there are many previous reports about the removal of Cd (II) in the aqueous medium, there is little prior research on Cd (II) removal affected by different background electrolytes with various ionic strengths. So the basic goal of this study was to assess the efficiency of two common nanoparticles (TiO_2 and γ-Al_2O_3) in Cd (II) removal from solution, also the influence of pH, Cd (II) initial concentrations and background electrolyte with different ionic strengths factors on Cd (II) adsorption by various nanoparticles were identified in this study.

MATERIAL & METHODS

Nanostructured TiO_2 and γ-Al_2O_3 were analytical grade and used without further impurity (purity, 99%) from Nanopars Lima (www. Nanopars Lima co, Iran). Nanoparticles shape and morphology were recognized by using Scanning electron microscope X-ray (Genesis XM2, USA). BET- nitrogen gas (Brunauer-Emmett-Teller) analysis was performed for determining the specific surface area of nanoadsorbents (Quantachrome Nova 2000e, USA) at 77.4 K. Speciation

The Cd speciation and saturation indices (SI) in isotherm supernatants at the latest concentration (80 mg/ L) were computed using the chemical equilibrium model Visual MINTEQ version .3.1. Visual MINTEQ is a geochemical model to identify the metal speciation, solubility equilibria, etc. of natural or laboratory solutions (Allison et al., 1991). The saturation index (SI) is calculated

from the difference between the logarithm of the ion activity product (log IAP) and, the logarithm of the temperature corrected solubility constant (log K_s) for each solid compound of the experiment. Over-saturation, under-saturation and equilibrium conditions with the solid phase are occurred when SI > 0, SI < 0, and SI = 0 (or more accurately, - 0.5 < SI < 0.5) respectively (Allison et al, 1991).

A batch adsorption isotherm experiment was carried out using Cd^{2+} solutions at different initial concentrations (0, 2.5, 5, 10, 20, 40, and 80 mg/ L) at 25 ± 1 ˚C, with 0.1 g nanostructured materials and 5 mL of adsorbate at different concentrations. The background solution was 0.01 M sodium nitrate ($NaNO_3$) in order to neutralization of ionic strength, due to less competition of Na^+ ions with Cd^{2+} for active adsorption sites of minerals, mainly in low concentrations (Bhardwaj et al., 2019). Adjustment of pH was accomplished using either 1 N NaOH or 1 N HCl. Samples were shaken for 2 h (1000 rpm) and left for 24 h at room temperature for equilibration. The concentration of Cd (II) in solutions was measured by Flame Atomic Adsorption Spectrophotometer (AAS, Shimadzu AA- 6300, Japan) after separation of solid-liquid phases of nanoparticle suspensions by centrifugation for 30 min (10000 rpm) and filtered through No. 42 Whatman filter paper. All expressed adsorption experimental data were navigated as the mean of three replicates with less than 5% standard deviation. Cadmium removal efficiency (%) was calculated by the following equation (Kataria & Garg, 2018):

$$\text{Removal Efficiency}(\%) = (C_0 - C_e)/C_0 \times 100 \quad (1)$$

where C_0 (mg/L) and C_e (mg/ L) are the initial and equilibrium Cd (II) concentrations respectively.

The Freundlich empirical equation, especially for founding the monotonous energy distribution and the heterogeneity of the sorbent surface, is expressed as (Freundlich, 1906):

$$Q_m = K_F \times Ce^{\left(\frac{1}{n}\right)} \quad (2)$$

where Q_m is the amount of metal ion adsorbed (mg/ kg), K_F is the Freundlich constant representing the adsorption capacity (L/ mg), C_e is metal equilibrium concentration (mg/ L), and the adsorption intensity was expressed by n as a constant value (dimensionless). The Langmuir equation is intended for a homogeneous surface of the adsorbent, is described as (Langmuir, 1916):

$$Q_m = \left(K_L \times C_e \times S_m\right)/\left(1 + K_L \times C_e\right) \quad (3)$$

where Q_m and C_e have the same definitions as in Equation (3), K_L is a constant of the Langmuir equation, that is related to adsorption affiliation of binding sites for ion adsorption (L/mg), and S_m is the maximum adsorption capacity with monolayer coverage (mg/ kg).

The Temkin equation that is leaning of the linear decrement of adsorption energy due to adsorbent/ adsorbate interactions is represented as (Temkin & Pyzhev, 1940):

$$Q_m = A + K_T \times Ln\left(C_e\right) \quad (4)$$

where Q_m and C_e are the same as above mentioned, A is the constant and intercept of equation (L/g), and K_T is the constant value of the Temkin equation that is represented the sorption heat (J/ mol).

The adsorption mechanism was usually expressed by using Dubinin–Radushkevich equation that is related to Gaussian energy distribution onto a heterogeneous surface. It can be expressed as Dubinin-Radushkevich (Dubinin, 1960):

$$Q_m = q_{DR} \exp(-\beta_{DR} \times \varepsilon_{DR}^2) \quad (5)$$

where Q_m is the adsorbed ion amount per unit weight (mmol/g), q_{DR} (mmol/ g) and β_{DR} (mol^2/ J^2) are the empirical constants of the equation and ε_{DR} is related to the Polanyi potential that expressed as RT ln (1+ (1/C_e)), where R and T are the gas constant (8.314 J/ mol. K) and absolute temperature (K)

respectively. The adsorption free energy (*E*) generally is related to the value of β_{DR} that can be computed from the following equation (Dubinin, 1960):

$$E = 1/\sqrt{2\beta_{DR}} \quad (6)$$

The type of adsorption mechanism is related to adsorption free energy (kJ/ mol). Physisorption, ion exchange and, chemisorption mechanisms have adsorption energy in the range of 1-8 kJ/ mol, 8- 16 kJ/ mol, and 20-40 kJ/ mol respectively.

Different concentrations (0.01, 0.1, and 0.5 M) of chloride salts ($CaCl_2$ and NaCl) were added to 5 mL of 80 mg/ L Cd (II) solution with 0.1 g nanoparticles. The pH of each sample was monitored at the end of each experiment to verify any changes which were statistically negligible. The suspensions were shaken for 2 h and left overnight for equilibration. Equilibrium Cd (II) concentration in solution samples were measured by Atomic Adsorption Spectrophotometer, after centrifuging at 10000 rpm for 30 min (Sharma et al., 2019).

Adsorption of Cd (II) onto nanoadsorbents base on thermodynamic studies was calculated at constant temperature (298 K). The probability of spontaneous adsorption was determined by the thermodynamic parameter such as Gibb's free energy (ΔG^0). The parameter was calculated by the following equation (Vilardi et al., 2018):

$$\Delta G^0 = -RT\, ln(K_L \times 10^6) \quad (7)$$

where *R*, *T* and K_L are commonly gas constant (8.314 J/ mol K), absolute temperature (K), and the constant of the Langmuir equation (dimensionless, due to multiple at 10^6) respectively. The Arrhenius equation was used to determine kinetic of adsorption reactions. It can be expressed as the following equation (Laidler, 1984):

$$K(T) = (K_B \times T/h \times C_0)\, exp^{-\Delta G^0/RT} \quad (8)$$

K_B is the Boltzmann constant (1.380×10^{-23} J/ K), *T* is the absolute temperature (K), *h* is the plank constant (6.626×10^{-34} J/S), C_0 is the concentration (mol/ L), *R* is the gas constant (8.314 J/ mol K), and ΔG^0 is Gibb's free energy (KJ/ mol) respectively.

The coefficient of determination (R^2) and the root mean square error (RMSE) statistics were used to evaluate the goodness of fit and absolute error measures respectively. The RMSE is expressed as (Wang et al., 2019):

$$RMSE = \sqrt{\sum_{i=1}^{n} (P_i - O_i)^2 / n} \quad (9)$$

where P_i and O_i are the predicted and measured values of Cd (II) concentrations sorbed to nanoadsorbents and *n* is the number of initial Cd (II) concentrations applied in sorption experiment respectively. Root mean square error (0 to + ∞) was used as an index of absolute error. A lower RMSE and higher R^2 values show better goodness of fit between measured and estimated data.

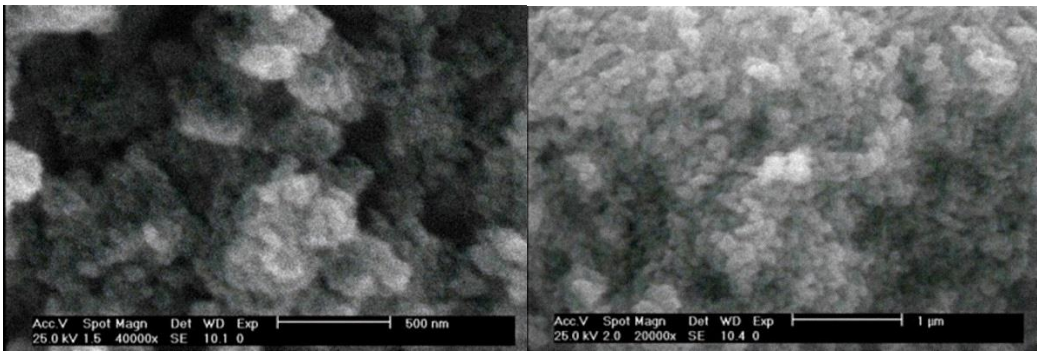
Statistical evaluation was performed using SAS 9.3 (SAS Institute, 2011), speciation of Cd (II) in aqueous was accomplished by Visual MINTEQ 3.1, and bar chart, line graphs and surface plot were drawn using Microsoft Office Excel 2015 software. Optimization of various parameters of adsorption models were performed using Solver 2015.

RESULTS AND DISCUSSION

The mean diameters of TiO_2 and γ-Al_2O_3 nanoparticles were 10 nm and 20 nm respectively and both nanoparticles showed the spherical shape prior to adsorption (Fig. 1). Based on nanoadsorbents SEM images, although TiO_2 nanoparticles were homogeneous in size, γ-Al_2O_3 nanosorbents showed a high surface homogeneity. The BET equation was applied to calculate the specific surface area of nanomaterials. According to results, the TiO_2 nanoparticles had a greater surface area (200 m^2 /g) than γ-Al_2O_3 (150

m^2/ g). Nanoparticles diameter and specific surface area significantly affect the adsorption capacity (Lajayer et al., 2018).

Metal speciation in solution results from competition between different metal complexes, metal chelates, and free metal ions. Table 1 shows the frequencies of various Cd species at different pH with TiO_2 and γ-Al_2O_3 nanosorbents. Free metal ions (Cd^{2+}) were predominant in solutions with two nanoparticles at different pH, but the proportion of other Cd species were negligible. Several studies showed that the prominent chemical form of Cd was Cd^{2+} in pH ranging from 6 to 8 (Koju et al., 2018; Haq et al., 2019; Li et al., 2019). Saturation indices of different Cd^{2+} minerals were all below zero and undersaturated in solutions with TiO_2 and γ-Al_2O_3 nanoparticles at various pH (Table 2). According to geochemical modeling data, no precipitation was occur in solution with the nanoparticles (Table 2). So the physical adsorption on nanoparticle surfaces was the predominant mechanism for Cd (II) removal from aqueous solution.



(A) (B)

Fig. 1. SEM images of (A) TiO_2, (B) Al_2O_3 nanoparticles

Table 1. Speciation of Cd in equilibrium solution in contact with the nanoparticles at different pH using Visual MINTEQ model (Ionic strength 0.01M Na (NO_3))

Species	Frequency (%)		
	pH 6	pH 7	pH 8
Cd^{2+}	98.4	98.0	97.9
$Cd(NO_3)^+$	1.5	1.9	2.1
$Cd(OH)_2$	0.05	0.07	0.4
$Cd(OH)^+$	0.02	1.2	1.3
$CdCl^+$	1.4	1.8	2.4

Table 2. Saturation indices of minerals in equilibrium solution in contact with nanoparticles at different pH using Visual MINTEQ (Ionic strength 0.01M Na (NO_3))

Adsorbent	Cd minerals	pH 6	pH 7	pH 8
TiO_2	$Cd(OH)_2$	-2.4	-1.3	-1.4
	$Cd(NO_3)_2$	-1.5	-2.5	-1.2
	Lime	-22.9	-20.4	-18.3
	Portlandite	-12.9	-10.2	-8.9
γ-Al_2O_3	$Cd(OH)_2$	-5.0	-2.8	-1.0
	$Al(OH)_3$	-1.5	-2.3	-1.1
	Boehmite	-1.2	-3.4	-2.6
	Diaspore	-2.9	-1.2	-1.2
	Lime	-22.9	-20.5	-18.9
	Portlandite	-12.9	-8.7	-8.9

The adsorption capacity of TiO_2 and γ-Al_2O_3 nanoparticles was evaluated at various initial concentrations. As can be seen in Fig. 2, the adsorption capacity of Cd (II) continuously increased with the increase of equilibrium concentration at different pH. Increasing of Cd (II) adsorption with nano-oxides was attributed to the pH-dependent charge of these adsorbents (Chen et al., 2017; Tabesh et al., 2018). Electrostatic repulsion between positively charge Cd (II) ions and positively nanoparticle surfaces generated at the pH less than pH_{ZPC}, causes to diminish the adsorption of Cd ions as outer sphere complexes (Razzaz et al., 2016). However, inner sphere complexes are responsible for metal adsorption at $pH > pH_{ZPC}$.

In order to determine the maximum Cd (II) adsorption and adsorption parameters, four equilibrium models were fitted to the experimental data, including Freundlich, Langmuir, Temkin, and Dubinin Radushkevich equations (Tables 3 and 4). By comparing the statistical parameters, it was found that the Freundlich model could well fit the experimental equilibrium data at different pH (Table 3). This indicated the surface heterogeneity of nanoparticles, uniform energy distribution and reversible Cd (II) adsorption during the sorption process.

Adsorption parameters of the Langmuir model indicated the maximum Cd (II) adsorption capacity (S_m) with TiO_2 nanoparticles was 2733, 2981, and 3348 mg/kg at pH 6, 7, and 8 respectively. For γ-Al_2O_3 the maximum adsorption capacity was in the fallowing order: 1173 mg/ kg (pH 8) > 918 mg/ kg (pH 7) > 368 mg/ kg (pH 6). Comparing of the results with various previous studies shows that experimental data of the present study was found to be lower than those of many corresponding nanosorbents in the literatures (lslam et al., 2018; Szatyłowicz et al., 2018; Wang et al., 2019).

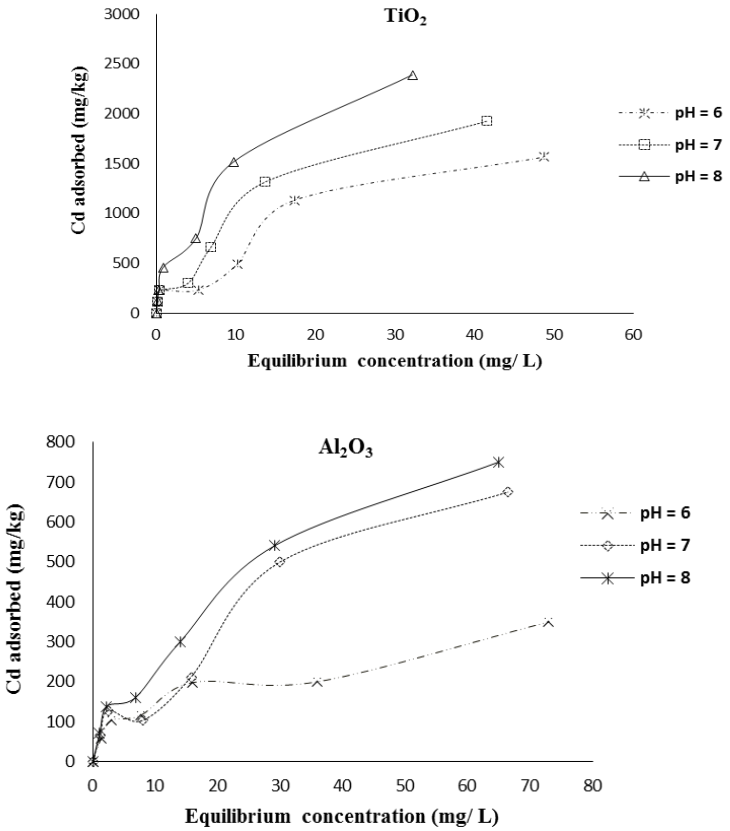


Fig. 2. Effect of pH on Cd (II) adsorption by nanoadsorbents

The Dubinin Radushkevich equation was fitted to specify the chemical or physical adsorption mechanisms. The adsorption free energy of the Dubinin Radushkevich equation was less than 8 kJ/mol with both nanoparticles at different pH which is evidence of physically adsorption mechanism of Cd (II) onto nanoparticle surface (Table 3). In physical adsorption, the individuality of the adsorbate and the adsorbent are preserved. In return, chemisorption occurs as a chemical reaction between the adsorbate and the surface. Also new chemical bonds are generated at the adsorbent surface (Rahmani et al., 2010). The Temkin model failed to fit the Cd (II) isotherms with both studied nanoadsorbents in compare with other isotherm models (Table 3).

Table 3. Isotherm equation parameters for adsorption of Cd (II) by TiO_2 and γ-Al_2O_3 nanoparticles

Adsorbent	pH	Freundlich				Langmuir				Temkin				Dubinin–Radushkevich				
		K_F	n	R^2	RMSE	S_m	K_L	R^2	RMES	A	K_T	R^2	RMSE	q_{DR}	β_{DR}	E	R^2	RMSE
		(L/mg)				(mg/kg)	(L/mg)			(g/L)	(J/ mol)			(g/mmol)	(J^2/ mol^2)	(kJ/ mol)		
TiO_2	6	154	1.65	0.95	0.04	2733	0.02	0.95	0.13	270	243	0.85	0.22	0.010	2.02×10^{-5}	1.57	0.93	0.18
	7	242	1.77	0.95	0.06	2981	0.04	0.97	0.11	407	298	0.77	0.32	0.002	7.15×10^{-4}	2.64	0.94	0.15
	8	425	1.99	0.98	0.08	3348	0.07	0.94	0.36	657	382	0.86	0.65	0.002	6.33×10^{-6}	4.32	0.92	0.39
γ-Al_2O_3	6	53	1.35	0.95	0.01	368	0.06	0.90	0.08	20.83	64	0.90	0.03	0.002	1.71×10^{-5}	1.70	0.92	0.08
	7	58	1.50	0.95	0.03	918	0.08	0.91	0.07	15.31	130	0.88	0.08	0.006	2.03×10^{-5}	1.56	0.95	0.05
	8	69	1.73	0.98	0.03	1173	0.11	0.96	0.03	7.62	153	0.92	0.07	0.006	2.63×10^{-5}	1.37	0.92	0.02

K_F is the Freundlich equation constant; n is the empirical constant of the Freundlich equation; S_m is maximum adsorption capacity; K_L is the Langmuir equation constant; A is the empirical constant; K_T is the constant value of the Temkin equation; q_{DR} and β_{DR} are the empirical Dubinin-Radushkevich equation constants; and E is the adsorption free energy.

Table 4. Cadmium adsorption capacity by TiO_2 and γ-Al_2O_3 nanoparticles at different pH

Adsorbent	pH	Freundlich		Langmuir		Temkin		Dubinin–Radushkevich	
		Q_e	Q_m	Q_e	Q_m	Q_e	Q_m	Q_e	Q_m
		(mg/kg)		(mg/kg)		(mg/kg)		(mg/kg)	
TiO_2	6	1566	1615	1566	1607	1566	1214	1566	1650
	7	1925	1984	1925	1962	1925	1518	1925	1930
	8	2391	2422	2391	2392	2391	1985	2391	2310
γ-Al_2O_3	6	350	559	350	307	350	295	350	290
	7	675	950	675	781	675	561	675	693
	8	750	769	750	1037	750	650	750	710

Q_e and Q_m are the maximum equilibrium Cd (II) concentration and predicated by the model respectively.

Cadmium removal from solution increased as the initial pH increased from 6 to 8 for both nanoparticles (Fig. 3). The significant low removal efficiency at pH 6 for TiO_2 (54 %) and γ-Al_2O_3 (25%) nanoparticles can be related to the fact that in lower pH medium, nanoparticles has the predominance of positive charges on their surface due to their high pHzpc 6.9 (TiO_2) and 7.2 (γ-Al_2O_3) and the high electrostatic repelling forces inhibits the contact of Cd^{2+} and the nanoparticles surface (Saleh et al., 2016; Vilardi et al., 2018). Same results were found by Song et al (2011) and Huang et al (2016). A continuous increase in removal efficiency was found by increasing the pH range from 6 to 8. Previous studies have shown that pH of 7–7.5 was optimum for Cd^{2+} adsorption on TiO_2 and γ-Al_2O_3 nanoparticles (Tabesh et al., 2018; Sharma et al., 2019). Obtained results showed the significant differences in Cd (II) removal efficiency with TiO_2 and γ-Al_2O_3 nanoparticles at different pH (Fig. 3). Higher surface area and specific adsorption sites are effective to increase nanoparticles ability to heavy metals removal from aqueous solution (Saleh et al., 2016).

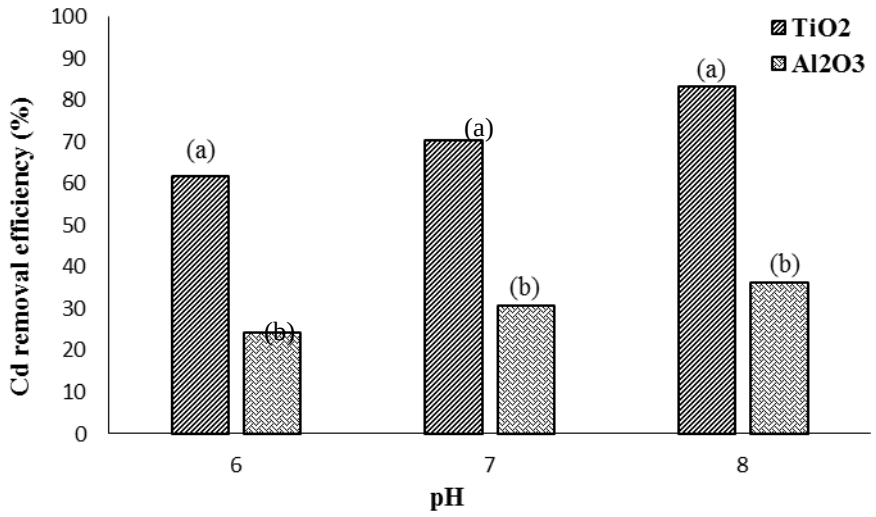


Fig. 3. Effect of pH on Cd (II) removal efficiency with TiO_2 and Al_2O_3 nanoparticles

***Same letters indicate no significant difference at the $\alpha < 5\%$ level (The comparison between the removal efficiency of each nanoparticle in a given pH is done)**

As shown in Fig. 4, the amount of Cd (II) adsorbed with both nanoparticles increased significantly by increasing of Cd (II) concentration from 2.5 to 80 mg/ L. The maximum Cd (II) adsorption on TiO_2 and γ-Al_2O_3 nanoparticles were 2500 mg/kg and 2390 mg/ kg at the highest initial Cd (II) concentration and pH respectively, which is higher than that of many other adsorbents reported in literature (Haq et al., 2019). In this study, optimum initial concentration for Cd (II) adsorption with TiO_2 and γ-Al_2O_3 nanoparticles cannot be determined exactly, but it is more than 80 mg/L certainly, because Cd (II) adsorption increased up to 80 mg/L continuously by increasing of initial concentration. Various range of optimum initial Cd (II) concentration were reported in other studies (Cheng et al., 2012; Zadeh et al., 2018; Sharififard et al., 2019). More than 200 mg/ L was reported as the optimum initial Cd (II) concentration with TiO_2 nanoparticles (Razzaz et al., 2016). Increasing the initial concentration leads to a strong tensile force between dissolved ions and solid phase, results in increase of adsorption (Huang et al., 2016). However, at higher initial concentrations most of the active sites are occupy which results in partial deactivation of the nanoparticle surfaces, so available surface sites have decreased that decline the adsorption capacity of nanoadsorbents (Tabesh et al., 2018; Kataria & Garg, 2019).The higher Cd (II) adsorption capacity of TiO_2 nanoparticles in different initial concentrations can be attributed to the lower particle diameter and surface properties of the nanoparticle (El-Deen & Zhang, 2016; Kow et al., 2017). The results are consistent with previous studies (Park et al., 2017; Kim et al., 2019).

The Cd (II) removal efficiency with TiO_2 and γ-Al_2O_3 nanoparticles as affected by various range of initial Cd (II) concentrations and pH is shown in Fig. 5. The Cd (II) removal efficiency of both nanoparticles was decreased by increasing of initial concentration. The maximum Cd (II) removal efficiency (95%) with TiO_2 was obtained at minimum initial Cd (II) concentration (2.5 mg/ L) at the highest pH. However, the removal efficiency increased by increasing pH from 6 to 8, as the lowest Cd (II) removal efficiency (38%) was obtained at the highest initial concentration and the lowest pH (Fig. 5). Same results were found with γ- Al_2O_3 nanoparticles as well. The Cd (II) removal

efficiency of γ-Al_2O_3 at 2.5 mg/ L initial concentration was 46%, 52%, and 56% at pH 6, 7, and 8 respectively. Decreasing the Cd (II) removal efficiency by increasing of initial Cd (II) concentration can be due to the lack of the total amount of available active sites for binding of metal ions onto adsorbents (Kim et al., 2019).

Considering the higher capacity of TiO_2 nanoparticles in Cd (II) adsorption, the effect of different ionic strengths and background electrolytes on Cd (II) adsorption capacity with the nanoparticle were assessed. As shown in Fig. 6, the Cd (II) adsorption was decreased as increasing of ionic strength from 0.01 to 0.5 M at a constant pH, indicating competitive adsorption between the background cations and Cd (II) (Fig. 6). Several studies have been reported the reverse effect of ionic strength on Cd (II) adsorption (Tajali Rad et al., 2019; Wang et al., 2019). The effect of ionic strength on electrostatic potential and the maximum adsorption is demonstrated by previous researches (Li et al., 2019; Musso et al., 2019). Negatively charges on surface nano oxides and zeta potential increase by increasing of ionic strength which decrease the adsorption capacity (Bashir et al., 2018).

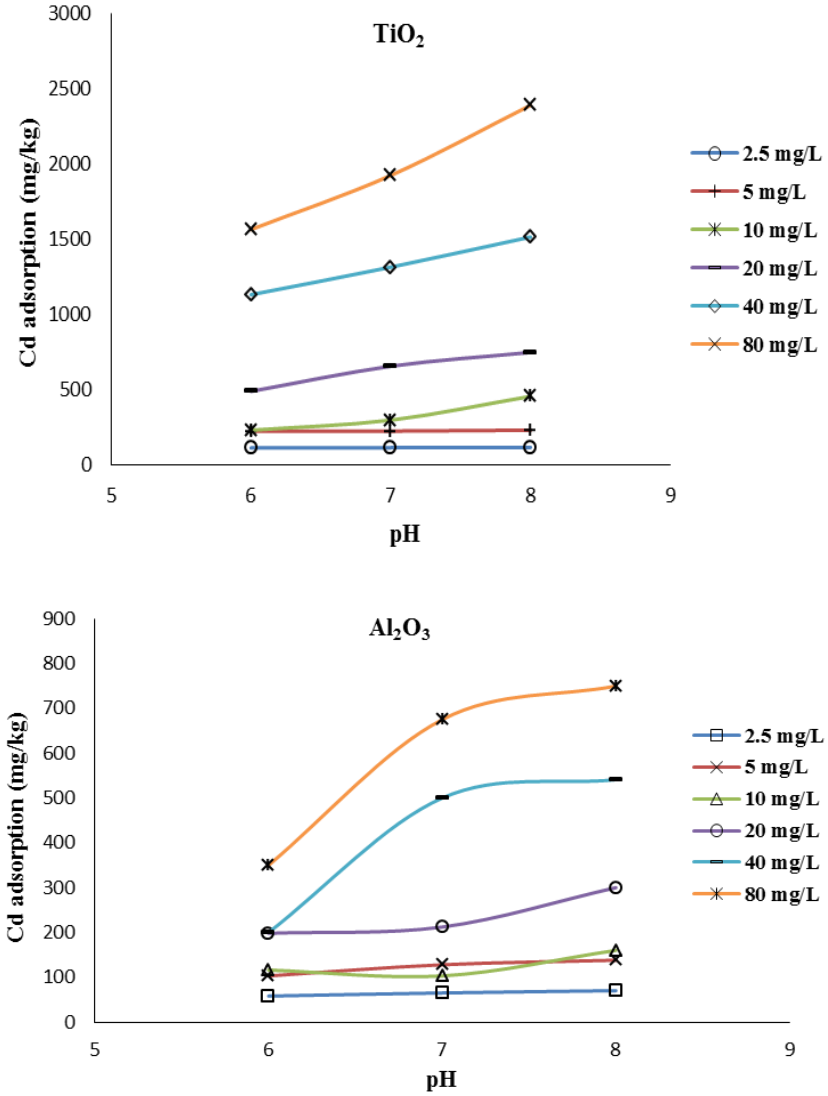


Fig. 4. Effect of different Cd (II) initial concentration on adsorption

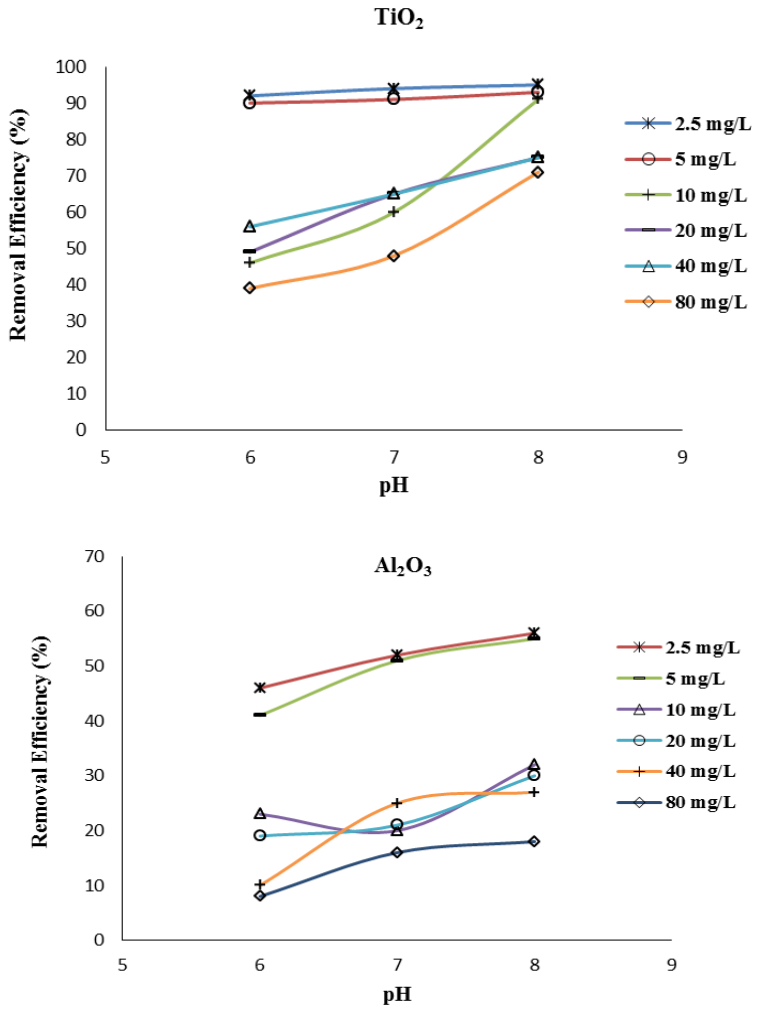


Fig. 5. Effect of Cd (II) initial concentration on removal efficiency

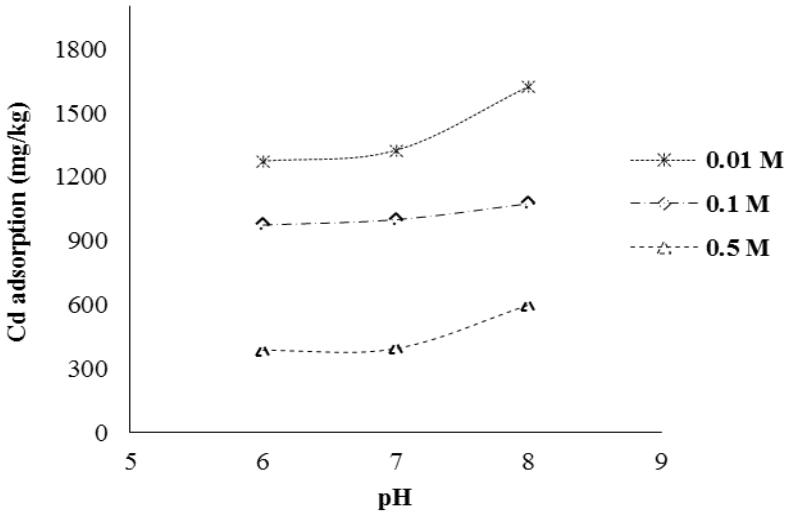


Fig. 6. Effect of ionic strength on Cd adsorption with TiO_2 nanoparticles

Presence of different ions in solution affects the surface charge of nanoparticles and results in the variation of the adsorption (Bonilla-Petriciolet et al., 2018). The competitive effect of some ions on Cd (II) adsorption with TiO_2 nanoparticles was investigated in presence of $CaCl_2$ and NaCl as various background electrolytes at a constant ionic strength (0.01 M). It is found that the Cd (II) adsorption ranged from 1225 to 1500 mg/ kg and 1275 to 1625 mg/ kg in presence of $CaCl_2$ and NaCl respectively (Table 5). This may be due to the higher competition of Ca^{2+} ions with Cd (II) for adsorption on active surface sites. The results of Li et al. (2016) showed the significant decrease of Cd (II) adsorption using various nanoparticles by increasing of Ca^{2+} concentration in solution.

Table 5. Cadmium adsorption (mg/kg) in presence of 0.01 M $CaCl_2$ and NaCl as background electrolytes with TiO_2 nanoparticles

Electrolyte	pH	Cd adsorption (mg/ kg)	Mean adsorption (mg/ kg)
$CaCl_2$	6	1225	1400
	7	1475	
	8	1500	
NaCl	6	1275	1408
	7	1325	
	8	1625	

Thermodynamics was studied to determine spontaneous nature of Cd (II) adsorption by nanoparticles at different pH. The Gibbs's free energy (ΔG^0) has been calculated in constant temperature (25 ˚ C) and pressure using thermodynamic relationship. Gibbs's free energy of Cd (II) adsorption reaction with TiO_2 nanoparticles were -25.48, -26.62, and -27.90 kJ/mol at pH 6, 7, and 8 respectively. For γ-Al_2O_3 the following result was as; -27.57 (pH 6), -27.97 (pH 7) and -28.76 (pH 8). The more negative amounts of ΔG^0 demonstrated the spontaneous nature of Cd (II) adsorption by nanoparticles and feasibility of the process. The result of kinetic calculation at 298 K shows the following orders with TiO_2 and γ-Al_2O_3 nanoparticles by increasing pH respectively;

ΔG^0 (kJ/mol), TiO_2: 1.81×10^{-51} (pH 6) < 2.86×10^{-51} (pH 7) < 4.80×10^{-51} (pH 8)

ΔG^0 (kJ/mol), γ-Al_2O_3 : 3.70×10^{-51} (pH 6) < 4.91×10^{-51} (pH 7) < 6.64×10^{-51} (pH 8)

The kinetic of adsorption reactions increased by increasing pH with both nanoparticles. It can be mentioned that the spontaneous adsorption reactions occur slowly at the lowest pH than the highest.

CONCLUSION

Experimental studies revealed that TiO_2 and γ-Al_2O_3 nanoparticles have high efficiency in removing of Cd (II) from aqueous solution. The maximum adsorption capacity of TiO_2 nanoparticles was higher than γ-Al_2O_3. Modeling study showed that adsorption was the predominant mechanism for removal of Cd (II) from aqueous solution with the nanoparticles. Cadmium adsorption increased with increasing pH and initial Cd (II) concentration. Maximum removal efficiency increased by increasing pH. Cadmium adsorption decreased by increasing of ionic strength. Cadmium adsorption decreased in the presence of 0.01 M $CaCl_2$ background electrolyte. Thermodynamic results demonstrated the spontaneous nature of Cd (II) adsorption onto TiO_2 and γ-Al_2O_3 nanoparticles at different pH. TiO_2 nanoparticles have high

adsorption capacities due to their increased surface area, suggesting they may be effective metal sorbents.

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