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Thermodynamic and kinetic studies for the adsorption of Cd (II) using nanoparticles of Tio_2 from aqueous solution

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ABSTRACT

Cadmium is a toxic, stable and non-biological heavy metal causing numerous adverse effects on the environment and animals. It is one of the most important primary contaminants of drinking water. The aim of this study was to evaluate the efficiency of titanium dioxide nanoparticles as adsorbent for the removal of Cd^{2+} from aqueous solutions. The effects of varying parameters such as pH, temperature, initial metal concentration, adsorbent dosage and contact time on the adsorption process were examined. The equilibrium adsorptiondata were analyzed using two isotherm models (Langmuir and Freundlich), two kinetics models (pseudo-first order and pseudo-second order) andthermodynamic parameters (ΔG°, Δ*H*° and Δ*S*°). The highest uptake was observed incondition of pH = 6, absorbentamount 1 g, contact time 120 minutes, initial metal concentration 10 mg/L, and temperature 25°C. The results indicate that Langmuir model provide better correlation of experimental data, and the pseudo-second order kinetic equation could better describe the adsorption kinetics of considered heavy metal. Thermodynamic parameterswere calculated and the negative value of ΔGÏ indicate the process was spontaneous, positive value of Δ*H*° confirms the reaction to be endothermic and positive value of Δ*S*° show that the degree of freedom increase at the solid-liquid interface during the adsorption process. The shape and dimensions of adsorbents were determinedbyScanning Electron Microscope (SEM), the kind of structure and phase identification of adsorbent powders was determined by X-ray diffraction (XRD). Fourier transform infrared spectrometer (FTIR)was used to find participating functional groups in adsorption.

KEYWORDS

Cadmium;
Adsorption;
Nano particles of titanium dioxide;
Aqueous solutions.

INTRODUCTION

In recent years, heavy metal pollution is considered to be one of the main sources of the environmental problems,since they have severe toxicological effects on the ecological systems. Heavy metals are widely distributed in nature and easily enter the food chain through a number of pathways, and tend

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to accumulate in living organisms causing various diseases[4, 20]. Cadmium is a toxic, stable and non-biological heavy metal causing numerous adverse effects on the environment,animals, and humans. It causes kidney damage, bone diseases and cancer[13, 11]. Elevated environmental levels of cadmium may come from a variety of sources such as smelting industries, impurities in the agricultural chemicals, sewage sludge, and attrition of automotive tires[5]. Currently, the US Environmental Protection Agency regulates at least ten metals, including Cd, Pb and Cu as primary contaminants in drinking water[7]. Cadmium is one of six substancesthat were banned by the European Union's Restriction on Hazardous Substances (RoHS) directive, which bans certain hazardous substances in electrical and electronic equipment, but allows for certain exemptions and exclusions from the scope of the law[22]. Nanoparticles loosely defined as manufactured materials that are smaller than 100 nanometers in at least one dimension. Nano-sorbents have emerged as a new area of research with potential application, due to their large surface areas, in removal of heavy metal ions from liquid solutions. In addition, synthesis of nano-sorbents is simple, their adsorption process is rapid, they provide a high number of surface active sites, and they are nontoxic; these attributes lead to high adsorption efficiency[9]. In recent years, nano-sized inorganic oxides like Tio_2 has been used as solid sorbents due to their special physical and chemical properties such as high adsorption capacity, great adsorption speed, and low temperature modification[12]. Heavy metal ions could be eliminated by several traditional techniques, including chemical precipitation, reverse osmosis, electrochemical treatment techniques, ion exchange, membrane filtration, coagulation, extraction, irradiation, and adsorption[24]. Adsorption is currently considered the best method for wastewater treatment because it is inexpensive, widely applicable, and efficient, and it generates relatively low amounts of sludge[1, 21]. The aim of this work is to study the evaluation of Tio_2, best condition of adsorption, isotherm models, thermodynamic and kinetic in adsorption of Cd^{2+} fromaqueous solution in batch experiments.

EXPERIMENTAL

Materials and instrumental

A stock solution (1000 mg/L) of Cd (II)was prepared by dissolving appropriate amounts of $Cd(NO_3)_2.4H_2O$(Merck, Germany) in double distilled water[2]. Batch experiments were carried out in 100 ml conical flasks,[11]. Double distilled water was used for all dilutions[23]. A pH meter) Taiwanese- AZ86552 (was employed for measuring pH values,0.1 M HNO_3 and 0.1 M NaOH were used to adjust pH of the solution in the range of 4–9,Shaker incubator (IKA KS 4000 ic) was used to dissolve absorbent and adsorbent in a particular temperature. Centrifugation(HE RMLE Z3000) was usedfor separation of unsolved Particles[23, 9, 11]. Nanoparticles of Tio_2indimensions of 20 to25 nmwere purchased (purity,99%) fromIranian Nano Material Pioneerscompany (http://parscenter.com/nanosunny), the residual concentration of cadmium in solution was analyzed using atomic absorption spectrophotometer (Unicam-919)[11]. The shape and dimensions of adsorbents were determinedbySEM (Scanning Electron Microscope),Thekind of structure andphaseidentification of adsorbent powders was determined by X-ray diffraction (XRD)[17]. Fourier transform infrared spectrometer (FTIR)was used to find participatingfunctional groups in adsorption[11].

Adsorption method

The optimum conditions of adsorption were considered in pH--6, temperature 25°c, contact time 60minutes, adsorbent dosage 0.1 g,initial metal concentration 10 mg/L. The effects of pH (between 4and 9), temperature (between15Úc and 40°c), initial concentration ofCd (II) (10mg/L to 50 mg/L),contact time(15 min to 120 min), and adsorbent dosage(0.1 to 1g) wereinvestigated. All experiments were performed at least three times. The suspension was mixed on shaker incubator in 100 rpm in 25°c. the mixturewas centrifuged at 5000 rpm for 5 min to separate the solidadsorbents from the solution. The final concentration of the metalions were determined by flame atomic absorption spectroscopy(AAS). The percent adsorptionof metal ions werecalculated as follows[18]:

$$\text{Adsorption (\%)} = \left(\frac{C_i - C_e}{C_i}\right) \times 100 \quad \textbf{(1)}$$

Where C_i and C_e(mg/L) are the initial and final metal ionsconcentrations, respectively. The cadmiumconcentration retained in the adsorbent phase was calculated according to:

$$q_e = \frac{(C_i - C_e) \times V}{M} \quad \textbf{(2)}$$

Whereqe (mg/g) isthe amount of ions adsorbed per unit mass ofadsorbent,C_i and C_e(mg/L) are same as in Eq. (1), v (L) is the volumeof Cd(II) solution, and M (g) is themass of the adsorbent[2, 11].

Characterization of Tio2

XRD analysis

The structure of nano-Tio_2were studied by X-ray diffraction (XRD) analysis,Figure 1 shows the presence of strong diffraction peaks at 25 and 48 indicating nanoparticles of Tio_2 in the anatase phase[20]. The intensity of XRDpeaks of the sample reflects that the formed nanoparticles are crystalline and broad diffraction peaks indicate very small size crystallite and it confirmed the structure of Tio_2 is crystalline.

SEM analysis of Tio_2

Scanning electron microscope (SEM) was used for morphological study of nanoparticles of Tio_2. Figure 2 shows the surface cellular morphology of nanoparticles of Tio_2 andthis structure can increase the surface area of adsorbent thereby improving the adsorption of heavy metals. Figure 2c showsdimension of Tio_2 between 20 and 25 nanometer. Figure 2ashows a lot of empty space on the surface of Tio_2 before adsorption and Figure 2bshows cadmium on the surface of Tio_2 and empty spaces without cadmium so it can be concluded that adsorbent has more ability to adsorb.

FTIR analysis

FT-IR spectroscopy method was used torepresent the information about the nature of the presentbondsand the functional groups such as carboxyl, sulfonate,hydroxyl, and amino groups on the surface of Tio_2 and the possibleinteraction between metals and the functional groups, it isin the range of 400-4000 cm^{-1}[14, 9, 3]. It is clear that the strong and broad band at 3376 $cm^{-1}$and 3248 cm^{-1}might be related to –OH groups and peak in1600.41 related to c=o groups, so itis concluded that carboxylic acid groups play a main role in adsorption by Tio_2[3].

RESULT AND DISCUSSION

Effect of pH

Adsorption studies have indicated that pH of the solution strongly affects heavy metal removal because both density andsign of charges on the adsorbent surface varies with pH of the solution. The adsorption experimentsinvolved adding 0.1 g of $Tio_2$to series of 100 ml Erlenmeyer flaskscontaining of Cd

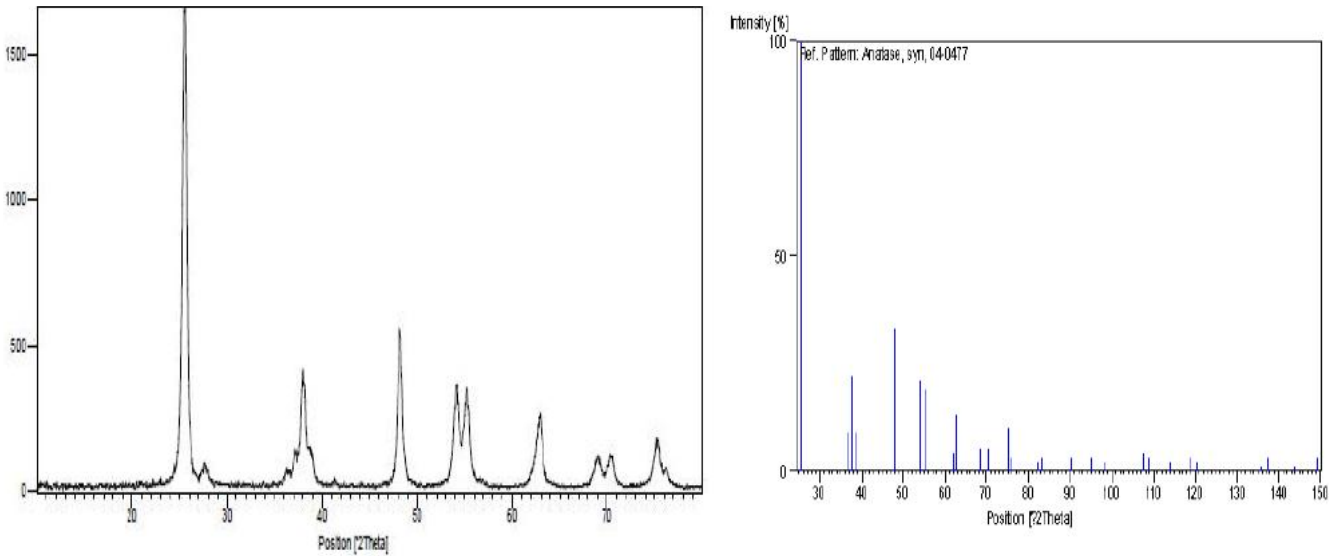

Figure 1 : The XRD patterns of pure nano-Tio_2

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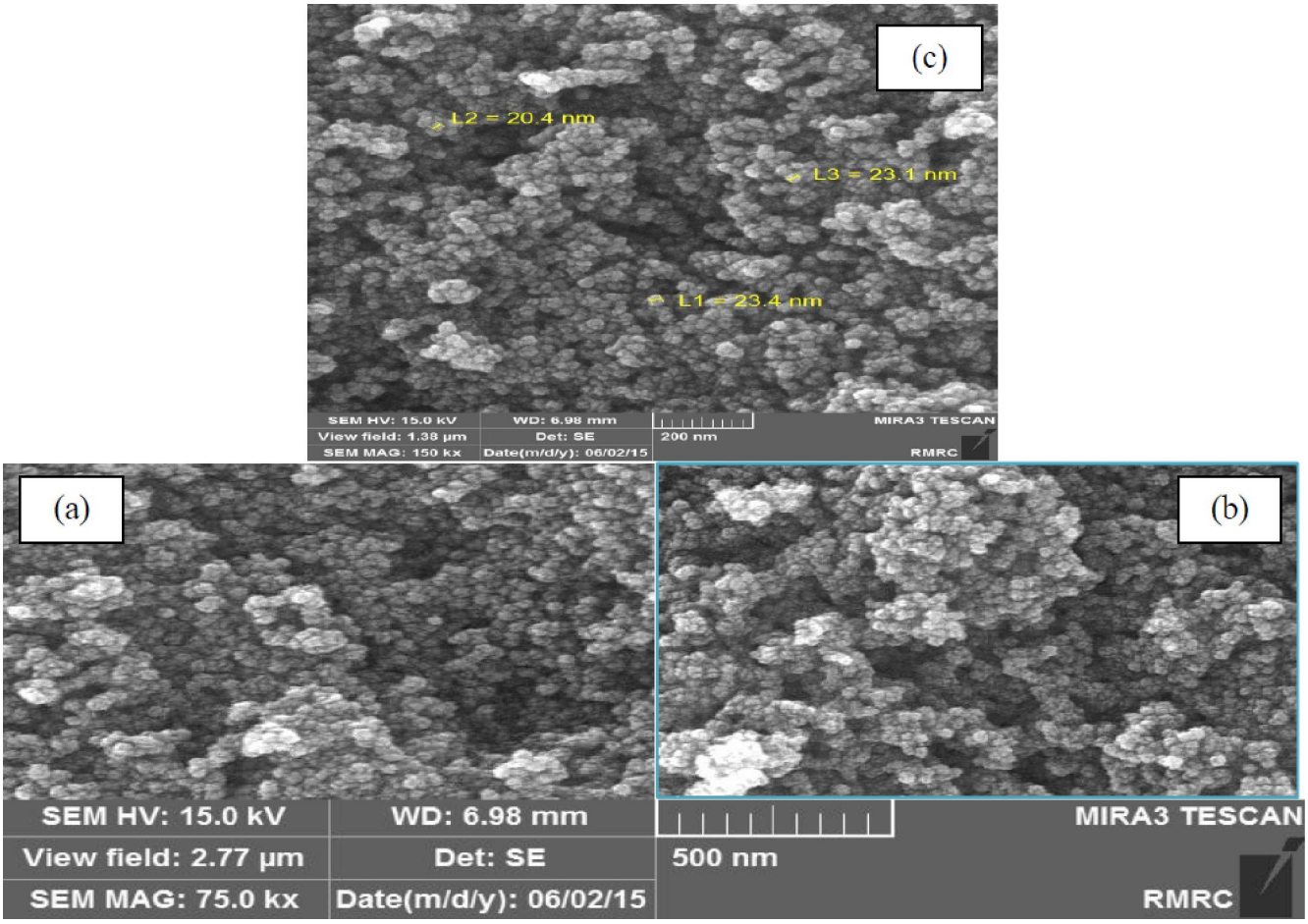

Figure 2 : SEM images of (a) pure Tio_2, (b) SEM image of Tio_2 after adsorption of cadmium,(c) Thedimension of nanoparticles of Tio_2

(II) solution with initial concentration of 10 mg/L. The suspensionswere mixed onshaker incubator for 60 minutes in 25°c,pH of Cd(II) solution was adjusted to a rangeof values from 4 to 9 with appropriate volume of buffer solutions,all other parameters was kept constant[2, 9]. The Ph_{pzc} values (the pH pointof zero charge) oftitanium dioxides is 6.3[6], thismeans that the Tio_2 surface is positively charged ($Ti–OH_2^+$)when the pH is lower than this value and negatively charged(Ti–O-) when the pHis higher than PZC. Interactions are goingto accelerate or retard the degradation[6, 17]. Therewas also competitiveadsorption between H^+ ions and strongly competing heavymetals in solution. Nano-adsorbent binding sites were dominated by H^+ions at lowpH, heavy metal ions decreased with an increase in the number of protonatedmetal-bindingadsorbent groups. The competing effect of H^+ ions decreased as pH increased, whichled to greater heavy metal ion adsorption onto the adsorbent. Figure.4shows that the maximum removal was found at pH 6[6, 7, 17].

Effect of initial concentration

The initial concentration of Cd(II) solution was varied from 10 to 50 mg/Landall other parameters were kept constant in optimum conditions. The removal of cadmium decreased with an increase in the initial Cd(II) concentration due to lack of binding sites for the adsorption of Cd(II) ions. However, amount of metal adsorbed per unit mass of adsorbentq_e,is higher at high concentrations, as shown in Figure 5. The maximum removal was found atinitial concentration of 10 mg/L. A larger driving force for mass transfer at higher concentrations of metal ions is responsible for the increase in loading capacity of the adsorbent as concentration of metal ion increases, the probability of surface adsorption increases because more ions are available per unit surface area[9].

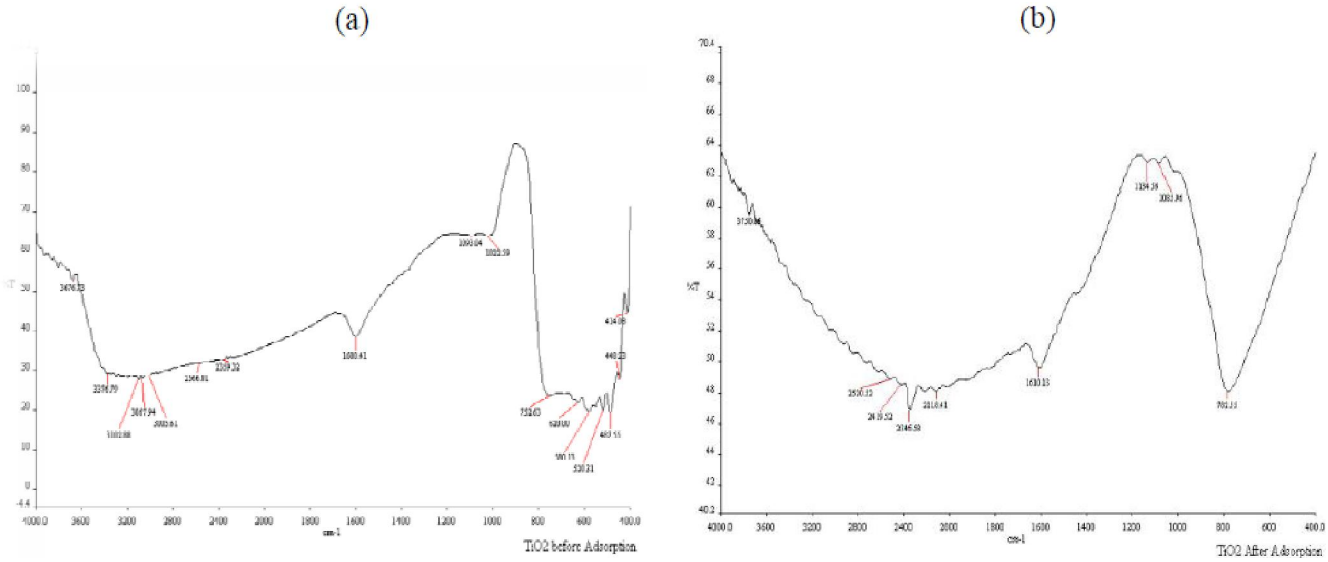

Figure 3 : FTIR patterns ofTio_2 (a) before adsorption ofcadmium, (b) after adsorption ofcadmium

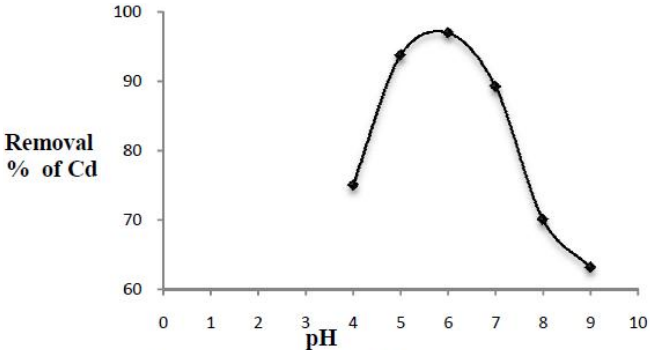

Figure 4 : Effect of pH on the Cd(II) removal by nano-Tio_2

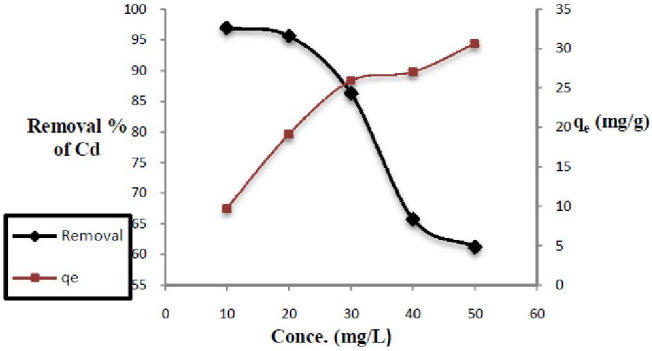

Figure 5 : Effect of initial concentrationon the Cd(II) removal by nano-Tio_2

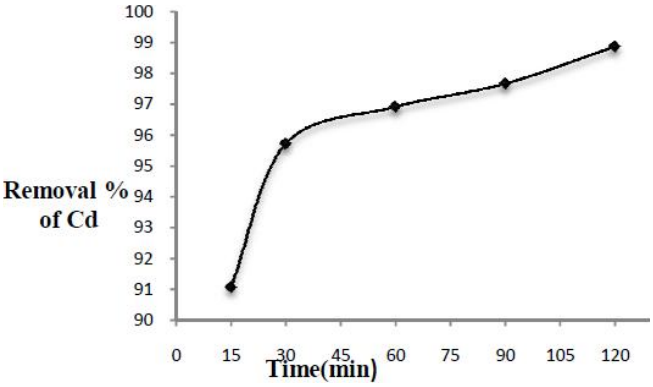

Figure 6 : Effect ofcontact time on the Cd(II) removal by nano-Tio_2

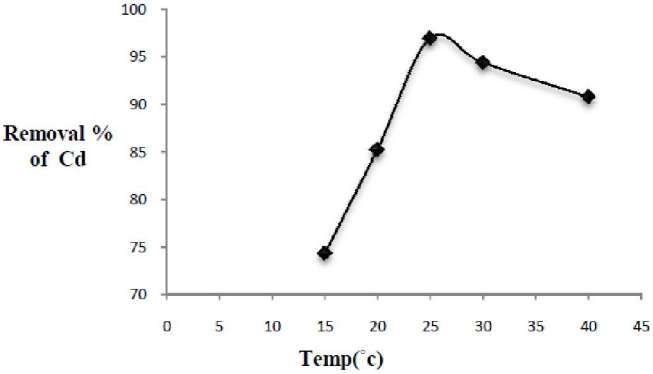

Figure 7 : Effect of temperature on the Cd(II) removal by nano-Tio_2

Effect of contact time

Contact time is one of the important parameters for successful adsorption[23]. Batch experimental procedures were prepared with different shaking times of 15, 30, 60, 90, and 120 min, while other conditions remained constant[17]. Figure 6shows the maximum adsorption amount of 99% in time of 120 minutes.

Effect of temperature

The effect of temperature on adsorption of Cd(II) ions by nanoparticles of $Tio_2$was investigated at a range of 15 to 40°c. This may be due to the effect of

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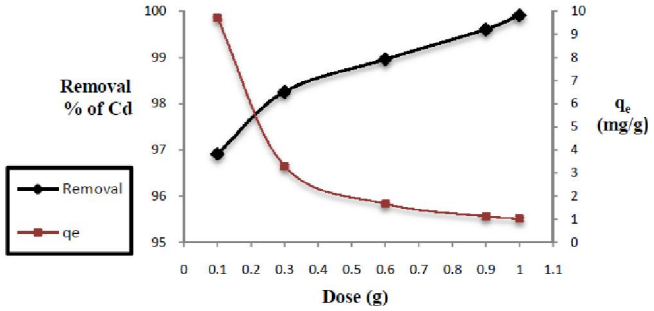

Figure 8 : Effect ofadsorbent dosageon the Cd(II) removal by nano-Tio_2

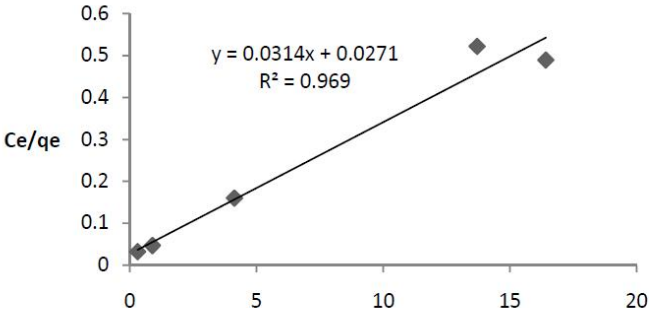

Figure 9 : Langmuir isotherm for adsorption of Cd(II) at pH 6, time 60 min, 25Úc, 1 g Tio_2

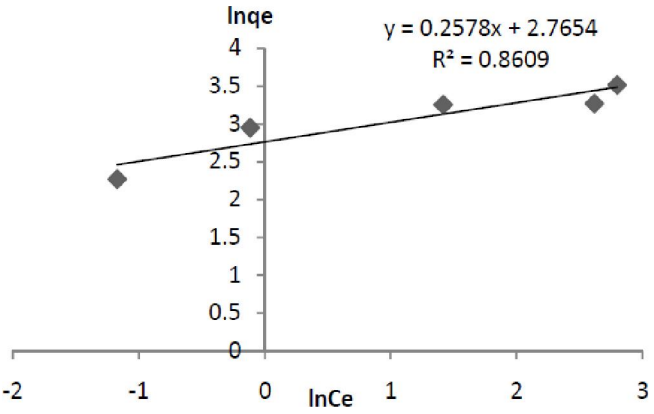

Figure 10 : Freundlich isothermfor adsorption of Cd(II) at pH 6, time 60 min, 25Úc, 1 g Tio_2

temperature on the number of active sites on the surface of the absorbent. The maximum adsorption was observedin 25°c. It iswell recognized that the characteristic of the adsorbent surfaceis a critical factor in adsorptionand it is proven that active sites on the surface by increasing temperature is increased[25], but thedecrease of adsorption efficiency with the increase of temperatureis due, most probable, to the desorption tendency of heavy metalsfrom adsorbent surface because ofthe nature of heavy metal[4].

Effect of adsorbent dosage

Differentadsorbent dosage ranged from 0.1 to 1g was applied to study the effect of adsorbent dose on the adsorption of Cd(II), the adsorption of Cd(II) ion were increased with subsequent increasing the adsorbent dose[3]. It is obviously because ofincreasing the number of active sites on the surface of the absorbent. Figure 8 shows the effect ofadsorbent dosage in adsorption;The maximum adsorption was observedin 1 g tio_2, butthe optimum dosage is 0.1 g, because more than 97% adsorption was observed in this dosage and it is economically affordable.

Adsorption isotherm

Adsorption isotherm givesimportant information about the mechanism of adsorption and shows the relationbetween the amount adsorbed and the equilibrium concentrationof ions in the liquid phase therefore helps us in the design of new adsorbing systems[25, 19, 24, 17]. From these isotherms, several adsorption parameters could be calculated. The most widely used adsorption isotherms are Langmuir model and Freundlich model[24]. Adsorption isotherm experiments were prepared using Cd (II)solution at different initial heavy metal concentrations (10,20,30,40,50 mg/L) at 25°c in pH 6, absorbentamount 1 g, contact time 60 minutes.

Langmuir andFreundlichisotherms models

The most widely used Langmuir equation, which is validfor monolayer sorption on a surface with a finite number ofidentical sites[16], and all surface sites are energeticallyidentical and surface itself is homogeneous. It also assumes thatintermolecular forces decrease rapidly with the distance from theadsorption surface[9]. Langmuir isotherm is expressed as:

$$q_e = \frac{q_{max} \times C_e b}{1 + C_e b} \quad (3)$$

The Langmuir isotherm in the linear form is as follows[16, 20]:

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

q_e (mg/g) is the amount of metal ions adsorbed by the nano-Tio_2, and C_e (mg/L) is the equilibrium concentrations of metals ions,q_{max} (mg/g) is the maximum adsorption capacity of adsorbent at monolayer and b is the Langmuir constant,When Ce/q_e was plot-

ted against C_e, a straight line with a slopeof $1/q_{max}$ was obtained. Figure 9 indicating that the adsorptionof Cd(II) metal ions on the Tio_2 nanoparticles follows theLangmuir isotherm[8, 20]. The Langmuir constants b and q_{max} werecalculated from this isotherm and their values are listedin TABLE 1.

The Langmuir isotherm can be expressed in terms of a dimensionlessconstant called equilibrium parameter, R_L which is definedas[16]:

$$R_L = \frac{1}{1+bc_i} \quad (5)$$

Where C_i is the initial metal concentration and the value of R_L indicatesthe type of isotherm to be favorable ($0 < R_L < 1$), unfavorable($R_L > 1$), linear ($R_L = 1$), or irreversible ($R_L = 0$)[7, 20]. R_L values for Cd (II) was calculated and its value was less than 1, and greater than zeroindicating favorable adsorption (TABLE 1)[9]. The Freundlich isotherm model is an empirical relationshipdescribing the adsorption of solutesfrom a liquid to asolid surface, and assumes that different sites with severaladsorption energies in multilayeron energetically heterogeneous surfaces[9, 8]. The Freundlich isotherm is written as:

$$q_e = K_{f(Ce)^{1/n}} \quad (6)$$

The linear form of the equation becomes:

$$\text{Ln } q_e = \text{Ln}K_f + \frac{1}{n}\text{Ln } C_e \quad (7)$$

Where q_e (mg/g) is the amount of metal ions adsorbed by the nano-Tio_2, and C_e (mg/L) is the equilibrium concentrations of metals ions. The slope 1/nranging between 0 and 1 is a measure of adsorption intensityor surface heterogeneity, becoming more heterogeneous as itsvalue gets closer to 0[8]. Designates the amount of cadmium adsorbed atequilibrium in mg/g, C_e is the solute equilibrium concentration inmg/L, K_f and n are Freundlich constants related to the adsorptioncapacity and intensity of adsorption,respectively,K_f and n weredetermined from plot of Lnq_e vs. Ln C_e as shown in Figure 10.

TABLE 1 and comparing the results of two modelsshows that the adsorption of Cd (II)metal ions follow the Langmuir isotherm.

TABLE 1 : Isotherm parameters for removal of Cd (II) by Tio_2

Isotherms	Parameters	Results
Langmuirq_{max}	(mg/g)	31.847
b	(l/mg)	1.158
R_L		0.07
R^2		0.969
FreundlichK_f	(mg/g(l/mg)1/n)	15.885
n	3.878	
	R^2	0.8609
	1/n	0.257

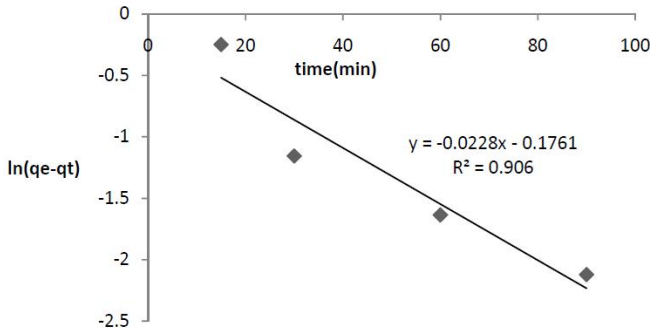

Figure 11 : Pseudo-first-order kinetics of Cd (II) ion adsorption on nano-Tio_2

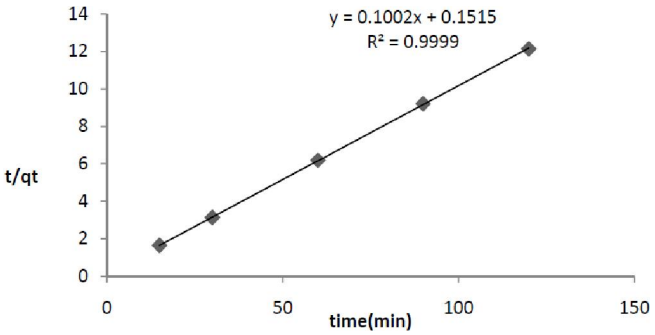

Figure 12 : Pseudo-second-order kinetics of Cd (II) ion adsorption on nano-Tio_2

Adsorption kinetics

Adsorption kinetics study is important in order to determine the uptake rate of adsorbate at the solid-phase interface[8]. The dynamics of the adsorption process in terms of theorder and the rate constant can be evaluated using the kinetic adsorption data. The kinetics of removal of metal ions are explicitly explained in the literature using pseudo-first-orderand pseudo-second-order kinetic models. The pseudo-firstorder kineticmodelof Lagergrenassumes that the binding is originated from physical adsorption and the equation is given as[17]:

$$\text{Log}(q_e - q_t) = \text{log}q_e - \frac{k}{2.303}t \quad (8)$$

Or is givien as[23]:

$$\ln (q_e - q_t) = \ln q_e - k_1 t \quad (9)$$

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TABLE 2 : kinetics parameters for removal of Cd (II) by Tio_2

Kinetics models	Parameters	Results
Pseudo-first-orderk_1	(min)	0.022
q_{exp}	(mg/g)	9.885
$q_{(theor)}$	(mg/g)	0.835
R^2		0.906
Pseudo-second-orderK_2	(min)	0.066
q_{exp}	(mg/g)	9.885
$q_{(theor)}$	(mg/g)	9.98
R^2		0.999

Where q_e and q_t (mg/g) are the amounts of Cd (II) ion adsorbed ontonano-TiO2 at equilibrium and time t, k1 (min^{-1}) is the rate constant. The plot of ln ($q_e - q_t$) against t was employed to obtain the k_1 andq_e; see Figure 11. The pseudo-second-ordermodel of Ho is based on chemical adsorption (chemisorption) and theequation can be expressed as[10, 9]:

$$\frac{t}{qt}=\frac{1}{k_2 q_e^2}+\frac{t}{q_e} \quad (10)$$

Where k_2 (g/(mmol min)) is the adsorption rate constant of pseudosecond-order reaction. The straight-line plots of t/q_t vs. t have beenused to determine rate parameters; see[8], Figure 12. Kinetic parameters for adsorption of Cd (II) ions by nanoparticles of Tio_2 are given in TABLE2.

TABLE 2 and comparing the results of two kinetics models shows that the adsorption of Cd (II)metal ions follow the pseudo-second-orderkinetic.

Determination of thermodynamic parameters

Three thermodynamic parametersincluding the change in freeenergy change (ΔG°),enthalpy change (Δ*H*°) and entropy change (Δ*S*°) were used todescribe thermodynamic behavior of the adsorption of Cd(II)ions onto nanoparticles of Tio_2, These parameters were calculated fromthe following equations[23, 2, 9]:

$$\Delta G = -RT\ln K_c \quad (11)$$

Where, R is the universal gas constant (8.314 J/mol K), T istemperature (K) and K_c is the distribution coefficient[9]:

$$k_c = \frac{C_a}{C_e} \quad (12)$$

By considering the following equation, the enthalpy (Δ*H*°) and entropy (Δ*S*°) of adsorption were estimated from the slopeand intercept of the plot of ln K_C versus 1/T yields, respectively.

TABLE 3 : Thermodynamicparameters for removal of Cd (II) by Tio_2

T(°C)T	(K)ΔG	(kJ mol^{-1})	Δ*H*°(kJ mol^{-1})	Δ*S*°(J×mol^{-1}× K^{-1})
15	288	-2543.3	37426.30	143.95
20	293	-4266.1		
25	298	-8532.78		
30	303	-7095.79		
40	313	-5945.12		

$$\ln k_c = -\frac{\Delta H}{R}\frac{1}{T}+\frac{\Delta S}{R} \quad (13)$$

The negative sign ofΔG valuesfor the adsorption of Cd(II) by nanoparticles of Tio_2indicts spontaneousnature of the reaction, while positive Δ*H* values of confirm itsendothermicity. The positive Δ*S*value of indicates an overall entropyincrease and show the degrees of freedom increased at the solid-liquid interface during the adsorption of the metal ions onto the adsorbents[2, 9].

CONCLUSIONS

The study indicated that nanoparticles of Tio_2 could be used as an efficient adsorbent material for the removal of cadmium ions from aqueous solutions. Optimization of the adsorption parameters, such as solution pH, initial metal ionconcentration, contact time, adsorbent amount, and temperature were carried out to elucidate the sorption characteristics of Tio_2. The highest uptake was observed incondition ofpH 6, absorbentamount 1 g, contact time 120 minutes, initial metal concentration 10 mg/L and temperature 25. The Langmuir and Freundlich adsorption models were used for themathematical description of the adsorption equilibrium of cadmium ions to Tio_2 and the obtained results showed that the

adsorption equilibrium datafitted very well to the Langmuir model. The values of thermodynamic parameters (ΔH, ΔS and ΔG) indicate that the sorption process is spontaneous for all studied temperaturesand endothermic. The process followed pseudo-second order kinetics, indicating that one of themechanism of the process is chemisorption. Base on the results it can conclude that titanium dioxide nanoparticles are cost-effective for the removal of heavy metals from aqueous solutions because of low maintenance costs,high efficiency in adsorption, ease of use, the nature of the renewable.

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