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Milled goethite nanocrystalline for selective and fast uptake of cadmium ions from aqueous solution

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ABSTRACT

The purpose of the present study was to evaluate the performance of milled goethite as an effective nanomaterial for the removal of Cd(II) ions from aqueous solutions. Goethite nanocrystallines powders were prepared by high-energy ball milling with a balls-to-powder mass ratio of 10:1 and for 40 h of milling. X-ray diffraction, Rietveld analysis, and vibrating sample magnetometer are used to characterize the obtained nanopowders followed by tests for toxic metals removal from aqueous solutions. In addition, batch of experiments were performed to determine the adsorption equilibrium, kinetics, and thermodynamic parameters of toxic heavy metal ions by milled goethite. Adsorption data were modeled using Langmuir model, Freundlich equation, pseudo-first-order and pseudo-second-order equations. The adsorption process was found to be highly pH dependent. The adsorption of heavy metal ions reached a maximum value rapidly within 6 min and the adsorption parameters were in good agreement with both the Langmuir and Freundlich isotherms. A maximum Cd(II) ion adsorption capacity was estimated to be 167 mg g^{-1} at 328 K and a pH of 7. The kinetics of the adsorption process was found to follow the pseudo-second-order rate law. The evaluation of the thermodynamic parameters of milled goethite revealed a spontaneous endothermic adsorption process. Besides, the positive values of the entropy suggest an increase of randomness at the solid–solution interface during the heavy metal ions adsorption.

Keywords: Nanoparticles; Goethite; Ball milling; Heavy metal; Adsorption; Kinetics

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1. Introduction

The use of nanocrystalline iron oxides for adsorption of heavy metals from aqueous solution has attracted increasing attention in the last decades. They are widely explored as highly efficient absorbents for heavy metal removal from water/wastewater due to their fast kinetics, high-capacity, and preferable sorption toward heavy metals in water and wastewater. For adsorption of heavy metals from aqueous solution, the most widely studied magnetic nanocrystalline materials include iron oxides, manganese oxides, aluminum oxides, and titanium oxides. They are present in different forms: as particles, tubes, and other shapes. Both size and shape of these nanocrystallines have been reported as very important factors to determine as well as affecting their adsorption performances [1–7]. Several groups studied the removal of heavy metals from water/wastewater using different nanocrystalline iron oxides. Grossl et al. [4] studied the adsorption/desorption of Cu(II) on goethite (α-FeOOH). He et al. [5] showed that hematite (α-Fe_2O_3) is a very promising adsorbent to remove Pb^{2+} and Cd^{2+} ions. Roye and co-investigators [6] used maghemite (γ-Fe_2O_3) nanotubes for the removal of Cu^{2+}, Zn^{2+}, and Pb^{2+} ions from water. Recently, our group investigated the adsorption of heavy metal ions from aqueous solution by nanocrystalline Ni doped α-Fe_2O_3 obtained by mechanical alloying [7]. We showed that the obtained nanocrystalline powders are highly efficient adsorbents for Cd, Co, and Ni ions from aqueous solutions.

In this paper, the efficiency of milled nanocrystalline goethite for the removal of various metals ions from aqueous solutions was investigated. The nanopowders were prepared by high-energy ball milling and their structural and magnetic properties were investigated by X-ray diffractometer (XRD), Rietveld analysis, and vibrating sample magnetometer (VSM). The effect of initial pH, temperature, and initial concentration in Cr(VI), Cd(II), Co(II), and Ni(II) are particularly studied. The adequacy of different models is also investigated, including Langmuir's and Freundlich's models for the sorption isotherm data, first- and second-order equations for the kinetic data. Kinetic parameters as well as thermodynamic values (ΔH°, ΔS°, and ΔG°) are also evaluated and discussed.

2. Materials and methods

2.1. Samples' preparation and characterizations

Commercial goethite powder (usually represented by FeO(OH) formula) was used as starting material. The powder was introduced into a stainless steel vial with stainless steel balls (12 and 6 mm in diameter) into a SPEX 8000 mixer mill. A milling time of 40 h was considered with a balls-to-powder mass ratio fixed to 10:1.

Structural characterization was performed using Rigaku Ultima IV high-resolution XRD equipped with Cu-Kα radiation ($\lambda = 1.5418$ Å).

The crystallite size is calculated from the well-known Scherrer formula:

$$D = \frac{K\lambda}{B \cos \theta} \tag{1}$$

where B is the integral width of the sample (in rad), K a constant (approximately equal to 0.89), θ is the Bragg's angle, and λ the X-ray wavelength ($\lambda = 1.5418$ Å).

Magnetic characterization was carried out using a VSM type MicroMag Model 3900 with a sensitivity of 0.5 μemu using step field of 25 Oe and an averaging time of 1 s. Magnetization-field (M-H) curves were measured at room temperature ($T = 294$ K) in the field range +1 to −1 T.

2.2. Adsorption study

2.2.1. Preparation of heavy metal ions

A stock solutions (1,000 mg L^{-1}) of Ni(II), Cd(II), Co(II), and Cr(VI) were prepared by dissolving nickel nitrate ($Ni(NO_3)_2$), cadmium nitrate ($Cd(NO_3)_2$), cobalt nitrate ($Co(NO_3)_2$), and potassium dichromate (KCr_2CO_3), respectively, in distilled water. Experimental solutions at the desired concentration were then obtained by successive dilutions. All the reagents were of analytical grade or highest purity available, and used without further purification.

2.2.2. Analysis of heavy metal ions adsorption

The batch mode experiments were conducted by mixing 10 mg of milled goethite with 25 ml of different heavy metal ions solution having a known concentration, pH, and temperature in a 50 ml Erlenmeyer flask. The mixtures were stirred by a magnetic stirrer (600 rpm) for 12 h according to our preliminary tests (no significant adsorption was observed after 12 h reaction). 15 ml of suspension are sampled from each flask and filtered using 0.25 μm cellulose acetate syringe filters then centrifuged at 6,000 rpm for 10 min. The concentrations of Cd(II), Ni(II), Co(II), and Cr(VI) in the filtrate are measured by inductively coupled plasma-atomic emission spectrometry.

The parameters varied in the above experiments are: the heavy metal ions concentration in the solution (ranging from 5 to 100 mg l^{-1}), the pH value (4.0, 6.0, 7.0, and 8.0), and the temperature (25, 40, and 55°C). The initial pH is adjusted with 0.1 M HNO_3 or NaOH solutions. All the experiments were performed in duplicate and only the mean values are reported in this paper. The maximum deviation observed is less than 5%.

The amount of adsorbed solute q_e was determined as follows:

$$q_e = \frac{(C_0 - C_e) \cdot V}{m} \tag{2}$$

In Eq. (2), C_0 is the initial concentration (mg l^{-1}), V the volume of the pollutant solution (l), and m the mass of the milled nanopowder.

The sorption data of heavy metal ions were correlated to the theoretical models of Langmuir and Freundlich:

$$\frac{C_e}{q_e} = \frac{1}{Q_0} C_e + \frac{1}{Q_0 \cdot b} \qquad \text{Langmuir equation} \tag{3}$$

$$\ln(q_e) = \frac{1}{n} \ln(C_e) + \ln(k) \qquad \text{Freundlich equation} \tag{4}$$

where q_e is the amount of metal ions adsorbed per unit mass of adsorbent (mg g^{-1}); C_e is the equilibrium concentration of solute in the bulk solution (mg l^{-1}); Q_0 is the solid phase concentration corresponding to the complete monolayer coverage of adsorption sites [8]; and b is the constant related to the free energy of adsorption. Values of Q_0 and b can be graphically determined from the linearized and rearranged Langmuir equation (Eq. (3)); k and n are constants that can be related to the strength of the adsorptive bond and the bond distribution, respectively [9]. The values of k and n are, respectively, obtained from the intercept and the slope of the linear plot of ln (q_e) vs. ln (C_e) (Eq. (4)). The constant k can be defined as a sorption coefficient which represents the quantity of adsorbed metal ions for a unit equilibrium concentration (i.e. $C_e = 1$). The slope $1/n$ is a measure of the sorption intensity or surface heterogeneity [10]. For $n = 1$, the partition between the two phases is independent of the concentration. The situation $n > 1$ is the most common and corresponds to a normal Langmuir isotherm i.e. of *L*-type, while $n < 1$ is indicative of a cooperative sorption [11], which involves strong interactions between the molecules of adsorbate themselves. The essential characteristics of a Langmuir isotherm can be expressed in terms of a dimensionless separation factor, R_L, which describes the type of isotherm:

$$R_L = \frac{1}{1 + b \cdot C_0} \tag{5}$$

C_0 being the initial concentration of the pollutant in solution. The R_L value implies the adsorption to be either unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$), or irreversible ($R_L = 0$).

In order to predict the adsorption data of Cd(II) vs. time, two kinetic models were proposed and tested: a pseudo-first-order and a pseudo-second-order. The first-order model can be linearly expressed as follows:

$$\ln(q_e - q_t) = \ln(q_e) - k_1 \cdot t \tag{6}$$

where q_e and q_t (in mg g^{-1}) are the Cd(II) amounts adsorbed at equilibrium up to time t (min), respectively, and k_1 (min^{-1}) is the first-order adsorption rate constant.

The values of k_1 and q_e are determined from the slope and the intercept of the plot of In$(q_e - q_t)$ vs. t, respectively.

The linearized form of pseudo-second-order model is expressed as:

$$\frac{t}{q_t} = \frac{1}{k_2 \cdot q_e^2} + \frac{t}{q_e} \tag{7}$$

where k_2 is the pseudo-second-order rate constant (g mg^{-1} min^{-1}). If the pseudo-second-order kinetics is

Table 1
Rate adsorption constants for first- and second-pseudo-order kinetic models at 298 K and pH of 7

		First-order			Second-order		
$t_{1/2}$ (s)	$q_{e\ (exp)}$[a] (mg g^{-1})	k_1 (min^{-1})	$q_{e(cal)}$[b] (mg g^{-1})	r^2	$k_2 \times 10^3$ (g mg^{-1} min^{-1})	$q_{e(cal)}$[b] (mg g^{-1})	r^2
173	125	0.017	32.46	0.751	3.12	112	0.998

[a]Experimental data.

[b]Calculated data from models.

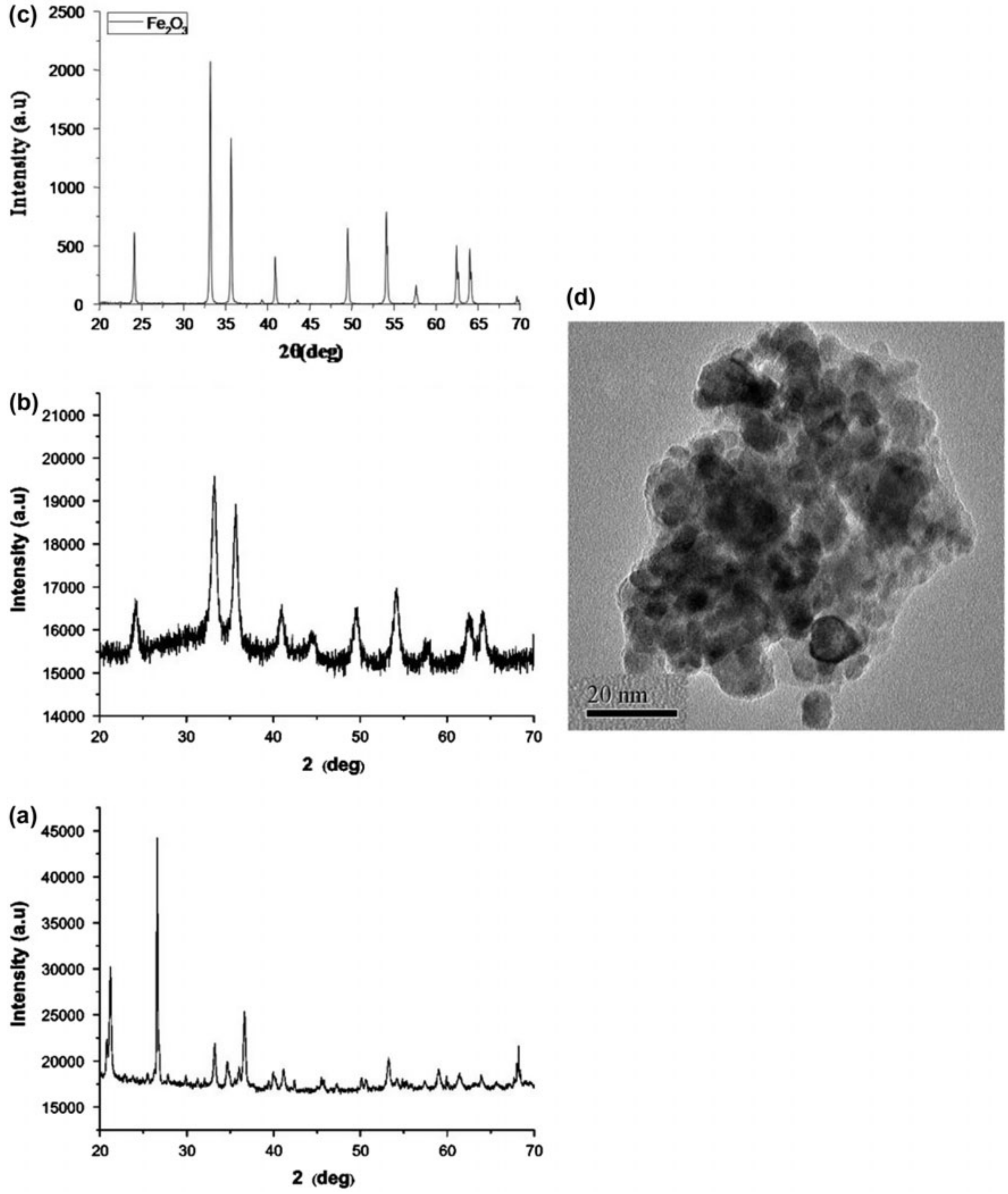

Fig. 1. XRD patterns (a) goethite powder as received, (b) milled for 40 h, (c) standard hematite α-Fe_2O_3 and (d) TEM image of the milled sample.

adequate, the plot t/q_t vs. t should be linear. The value of q_e is easily deduced from the slope, whereas the value of k_2 can be obtained either from the intercept or from the half-absorption time, $t_{1/2}$. The half-adsorption time, characteristic of the adsorption rate, is the time required to uptake half of the maximal amount of Cd(II) adsorbed at equilibrium.

The value of $t_{1/2}$ is calculated in the case of a pseudo-second-order process by the following relationship and listed in Table 1:

$$t_{1/2} = \frac{1}{k_2 q_e} \tag{8}$$

The thermodynamic proprieties (i.e. ΔH°, ΔS°, and ΔG°) of cadmium adsorption by milled goethite are calculated from the following equations:

$$\Delta G^\circ = -R \cdot T \cdot \ln K_a \tag{9}$$

$$\Delta S^\circ = \frac{\Delta H^\circ - \Delta G^\circ}{T} \tag{10}$$

The equilibrium constant of adsorption process is calculated by the equation $K_a = Q_0 \cdot b$. The value of enthalpy change ΔH° is determined from the slope of the linear curve of $\ln K_a$ vs. the reciprocal temperature ($1/T$) (Fig. 8). The free energy change (ΔG°) and entropy change (ΔS°) values are calculated from Eqs. (9) and (10), respectively.

3. Results and discussion

3.1. Structural and magnetic characterizations

Fig. 1 shows XRD patterns for initial goethite powder as received and milled for several milling periods of time. The pattern of unmilled goethite powder shows a series of strong and narrow peaks characteristic for high-quality crystals. The diffraction peaks become very broader and their relative intensity decreases with increasing milling time. This is mainly due to crystallite size reduction and accumulation of microstrain during mechanical milling. It can be seen that after 40 h of milling, the major peaks of the initial powder totally disappeared and some new peaks appeared. This result can be explained by the transformation of goethite under milling to another phase, the XRD pattern shows reflections that can be indexed mainly as hematite (α-Fe_2O_3).

Qualitative/quantitative phase analysis using the Rietveld method has been performed using PDXL program. The refinements of XRD patterns allow distinguishing between the iron phases. Fig. 2 shows the pattern fitting for the sample milled for 40 h. Phase identification confirmed the formation of nanocrystalline α-Fe_2O_3 phase after 40 h of milling with a small percentage of Fe phase (12%).

The average crystallite size of the 40 h milled powder in nanometric size according to TEM image

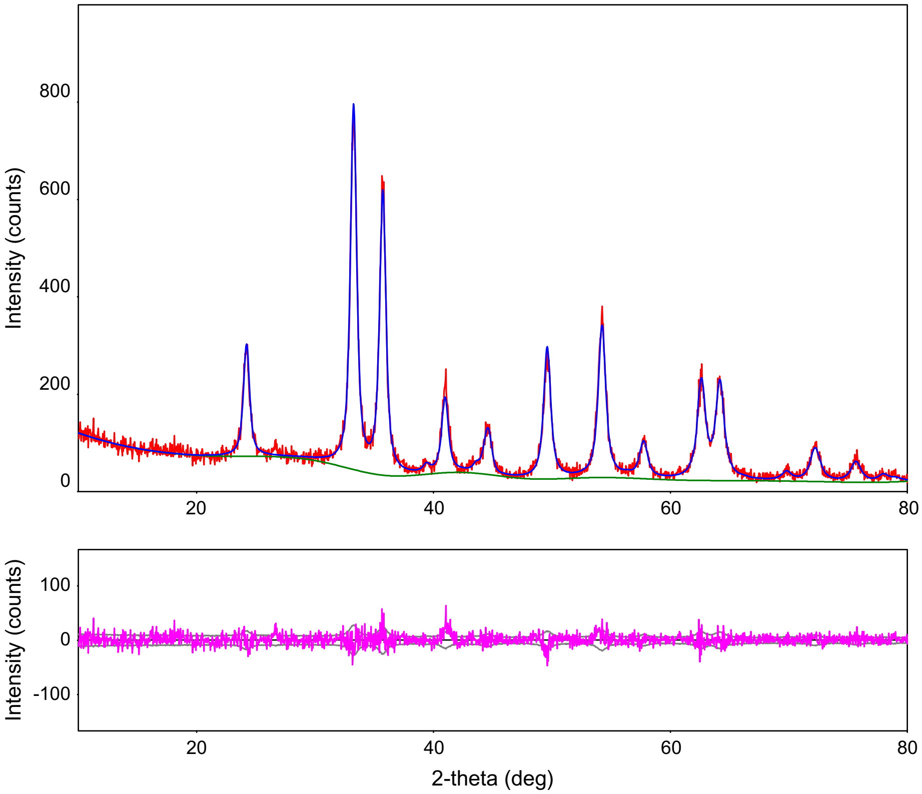

Fig. 2. A pattern fitting obtained by Rietveld refinements for the powder milled for 40 h. The net difference between the observed and measured profile is given on bottom of the plot.

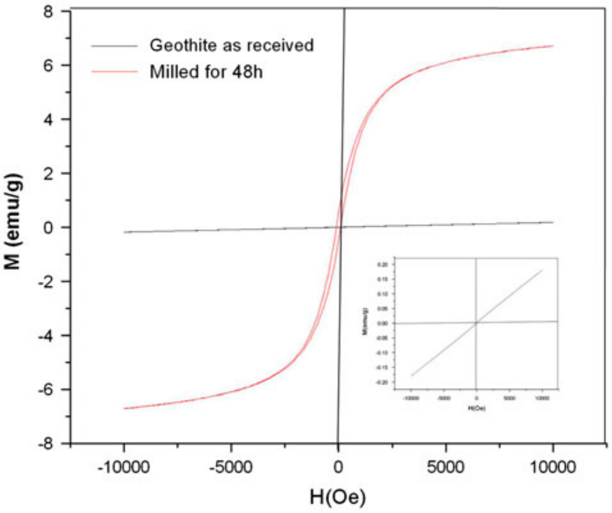

Fig. 3. Magnetic hysteresis loop curves of the powder as-received milling for 40 h. The inset shows the as-received goethite nanocrystallines which is paramagnetic.

(Fig. 1(d)) and the value is around 15 nm estimated from Scherer formula using the most intense (3 1 1) reflection.

Hysteresis M–H loop curves of as-received and milled for 40 h goethite powders are shown in Fig. 4. It can be seen that the as-received powder shows a paramagnetic behavior, whereas after 40 h of milling it becomes totally ferromagnetic with a saturation magnetization of 8.509 emu/g. The obtained para–ferro magnetic transition for the milled powders confirms that the phase transformation already observed with XRD analysis and Rietveld refinements. It is important to highlight that the above obtained phase/magnetic transformation will have a direct effects on the adsorption properties.

3.2. Adsorption of heavy metals ions

3.2.1. Adsorption capacity tests

The selective removal of four toxic heavy metal ions (Cd(II), Ni(II), Co(II), and Cr(VI)) from aqueous solutions were investigated at room temperature and a pH value fixed to 7.0 ± 0.2. 10 mg of 40 h milled goethite are mixed with 25 ml of 50 mg L^{-1} solution of each metal ion and stirred for 12 h in 50 ml Erlenmeyer flask. Fig. 4 illustrates the experimental data of adsorption capacities of the four heavy metals ions by milled goethite. It is obvious from this figure that the adsorption of milled goethite for Cd(II) is higher than that for Co(II), Ni(II), and Cr(VI), i.e. the adsorption capacity of Cd is about 66.50 mg g^{-1}, which was significantly higher than the values 53.91, 53.11 and 45.38 mg g^{-1} observed for Co, Ni, and Cr, respectively. In our previous study [7] on the removal of these above heavy metals by nanocrystalline Ni-doped α-Fe_2O_3, lower adsorption capacities were obtained essentially for Co(II) and Ni(II) than Cr(VI) metal ions under the same experimental conditions. Furthermore, numerous investigations carried out on the removal of Cd(II), Ni(II), and Co(II) by iron oxides nanomaterials showed that maximum adsorption capacities are obtained at pH values ranging from 5 to 8 [12]. Whereas, the maximum adsorption capacities of Cr (VI) are obtained at lower pH range of 2–3 [12]. In addition, the authors achieved much lower adsorption capacities for Ni(II) about 27 mg g^{-1} compared to the milled goethite used in the present study, i.e. 53.11 mg g^{-1} (almost half) [12]. More recently, Meng and Shibao [13] reported a similar adsorption capacity to that found with milled goethite while studying the removal of Cd(II) by functionalized Fe_2O_3 (α and γ phases) nanoparticles. Subsequently, owing to the raison that the milled goethite is highly efficient for

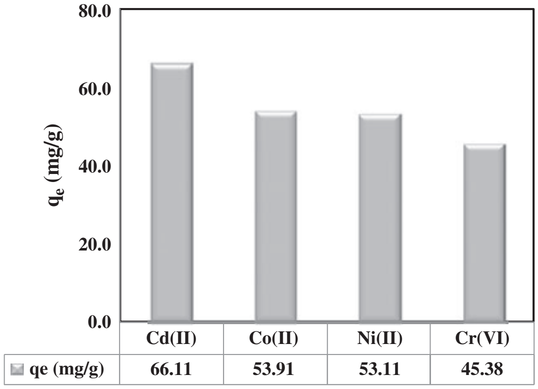

Fig. 4. Adsorption capacities of milled goethite nanocrystallines for heavy metal ions: Cd(II), Co(II), Ni(II), and Cr (VI).

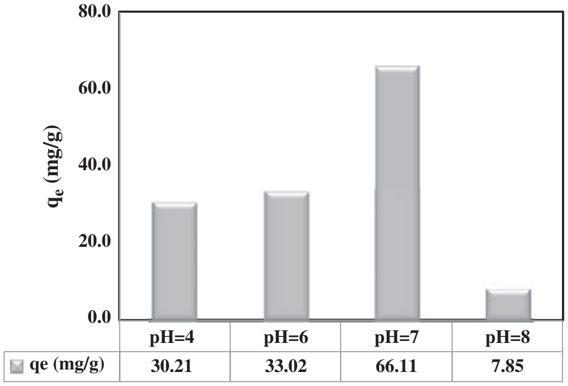

Fig. 5. The initial solution pH effect on the removal of Cd (II) by milled goethite nanocrystallines at room temperature and $C_0 = 50$ mg L^{-1}.

Cd ions than the remaining metal ions, the next part of this study will be devoted only to Cd(II) removal from aqueous solution. It is very important to note that this toxic heavy metal Cd(II) is present in the wastewater of a number of industries such as metallurgy, ceramics, electroplating, photography, pigments, textiles as well as synthetic chemicals.

3.2.2. Effect of initial pH on adsorption process

The effect of pH on the removal of Cd(II) is investigated by testing four values of pH 4, 6, 7, and 8 at a temperature of about 25 ± 1˚C and for concentrations of Cd(II) ranging from 5 to 100 mg L^{-1}. The contact time has been fixed to 12 h for all the experiments. The experimental results are presented in Fig. 5. It can be seen that the adsorption efficiency of Cd(II) increases with increasing the pH of the solution and attained a maximum value of adsorption at neutral pH (pH 7). Similar results were reported by Mohapatra et al. [14] when studying the removal of Pb(II), Cd (II), Cu(II), and Co(II) ions by additive assisted nanostructural goethite. They observed decrease of uptake capacity was explained by the existence of a large competition between hydronium ions and cadmium cations over the adsorption sites, thereby maintaining the surface of the adsorbent rich with protonated sites. Accordingly, the amount of the removed Cd(II) ions decreases at low pH values. On the other hand, the uptake of cadmium decreases significantly at pH value of 8 which could be explained by the precipitation of Cd(II) as hydroxides in alkaline medium rich by hydroxide anions (i.e. $Cd^{2+} + 2OH^{-}$ $Cd(OH)_2$) at pH ranging from 8 to 11.

3.2.3. Kinetic study

In this paper, only the equilibrium time of Cd(II) ions adsorption and pseudo-second-order model data as function of time are illustrated by Fig. 6(a) and (b), respectively. It appears from Fig. 6(a) that after a rapid initial rise of the adsorption q_t (about 6 min), the equilibrium is almost reached within 40 min. The validity of the kinetic models is dependent upon the magnitude of the regression coefficient r^2, given in Table 1. The low value of correlation coefficient (about 0.75) reveals that the pseudo-first-order model is inadequate to model the kinetic experimental data. In contrast, the application of a pseudo-second-order model leads to a regression coefficient value close to unity. Furthermore, the experimental and calculated values of q_e are in close agreement, thus, the pseudo-second-order kinetic model is appropriate to describe the adsorption rate process of Cd(II) onto milled goethite. Many studies dealing with the adsorption rate process of heavy metal uptake by adsorbent materials have been reported in the literature. Mohapatra et al. [14,15] reported that a pseudo-second-order model describes better the sorption kinetics of Cd(II) onto iron oxide/hydroxide adsorbents surface. Similarly, Fifi et al. [16] in a study devoted to the reactivity of Pb(II), Cu(II), and Cd(II) during their transfer in a calcareous soil, found a good fit of their experimental data with pseudo-second-order kinetic model.

3.2.4. Effect of temperature on the adsorption process

The effect of temperature is investigated by performing tests at 25, 40, and 55˚C. In general, raising the temperature is known to decrease the viscosity of

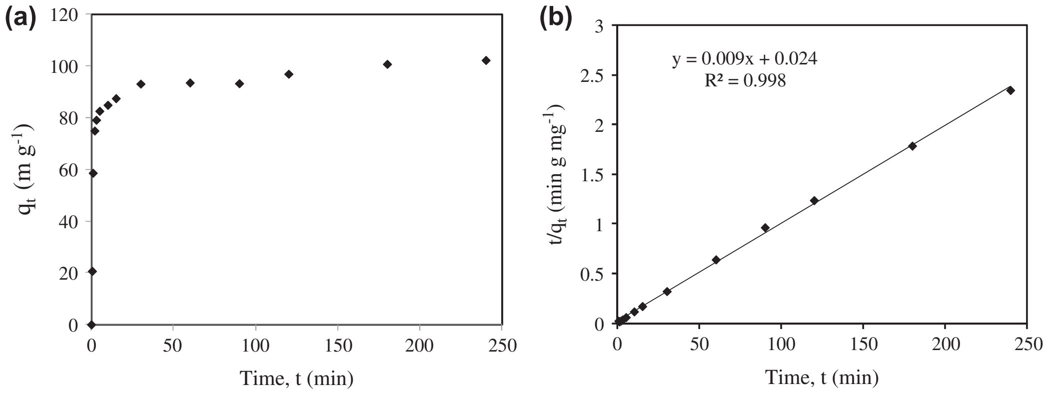

Fig. 6. (a) Equilibrium time and (b) second-order kinetic equations for the adsorption of Cd(II) onto milled goethite nanocrystallines at 298 K, pH 7 ± 0.2, and $C_0 = 50$ mg L^{-1}.

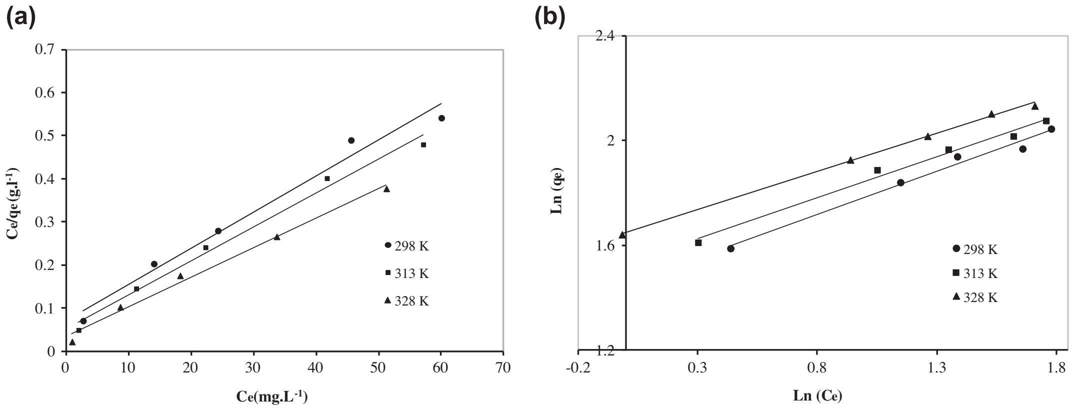

Fig. 7. Equilibrium adsorption isotherms for Cd(II) onto milled goethite at different temperatures, pH 7 ± 0.2. (a) Langmuir linear model and (b) Freundlich linear model.

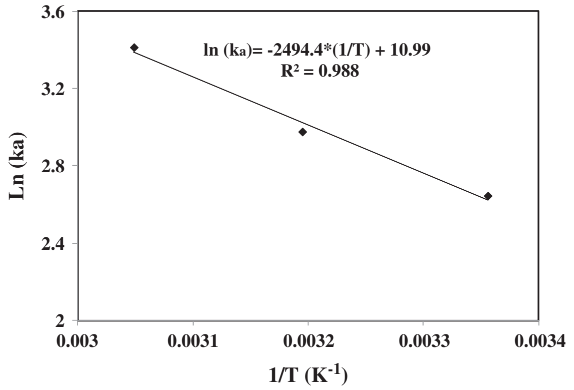

Fig. 8. Plot of ln ka vs. the reciprocal temperature (1/*T*) for the adsorption of Cd(II) ontomilled goethite at pH 7 ± 0.2.

the solution that could increase the diffusion rate of the adsorbate molecules across the external boundary layer and in the internal pores of adsorbent particles. Furthermore, varying the temperature will modify the equilibrium capacity of adsorbent for a particular adsorbate. The uptake of Cd(II) by milled goethite at different temperatures, is illustrated in the Langmuir and Freundlich linear plots in Fig. 7(a) and (b), respectively. The Langmuir Q_0 and *b*, R_L coefficients, the Freundlich *k* and *n* coefficients, and the regression coefficients r^2 are reported in Table 2. In regard of the high values of r^2, both Freundlich or Langmuir models fit well to the equilibrium adsorption data at the three chosen temperatures. Considering the values of Q_0 and *k*, the efficiency of milled goethite for the removal of Cd(II) increases with the increase of temperature. From Table 2, it can also be noticed that the value of the Freundlich parameter *n* is usually greater than the unit which corresponds to an *L*-type Langmuir isotherm. Mohapatra and Anand [17] studied the adsorption of cadmium by a commercial activated carbon, and reported that the larger is the difference between *n* and 1, the wider is the distribution of surface bond energies. Therefore, milled goethite shows wider Cd (II)-surface bond energies distribution with the temperature increase (Fig. 7).

Table 3 summarizes the results of the thermodynamic parameters. The positive value of ΔH° indicates the endothermic nature of the adsorption process of Cd(II) ions. In addition, the positive value of ΔS° suggests that the randomness increased at the milled goethite–solution interface during the adsorption. These results agree with those reported in the literature [14,15]. They found positive values of ΔH° and

Table 2
Effect of temperature on the values of Langmuir and Freundlich isotherm constants

	Langmuir constants				Freundlich constants		
Temperature (K)	Q_0 (mg g^{-1})	*b* (l mg^{-1})	r^2	R_L	*n*	*k*	r^2
298	125.00	0.1127	0.979	0.0815	3.039	28.38	0.984
313	142.86	0.1372	0.987	0.0679	3.205	34.04	0.987
328	166.67	0.1818	0.989	0.0521	3.460	44.57	0.998

Table 3
Thermodynamic parameters for Cd(II) adsorption at pH 7

Temperature (K)	K_a	ΔG° (kJ mol^{-1})	ΔS° (J mol^{-1} K^{-1})	ΔH° (kJ mol^{-1})	r^2
298	14.087	−6.555	91.6	20.738	0.988
313	19.619	−7.747	91.0		
328	30.361	−9.309	91.6		

ΔS° for the adsorption of Cd(II) on goethite [15] and additive assisted-nanostructured geothie [14]. The negative values of the free energy change ΔG° affirm the spontaneous nature of adsorption, which is confirmed by the separation factor (R_L) value, found to be less than unity. The value of ΔG° decreases when the temperature increases from 25 to 55℃, which indicates that a better adsorption is actually obtained at higher temperatures.

4. Conclusion

This study has identified milled goethite as an effective and fast nanomaterial for the removal of Cd (II) ions from aqueous solutions. Equilibrium data are well fitted by both Freundlich and Langmuir's models. The adsorption capacity of cadmium ions of about 167 mg g^{-1} is obtained for a pH value of 7 at 328 K. Both pH and temperature are critical parameters for the extend of Cd(II) uptake. Furthermore, results from the kinetics measurement of adsorption process are found to follow a pseudo-second-order rate law. The evaluated thermodynamic parameters indicated that the adsorption process of Cd(II) ions on milled goethite is spontaneous and endothermic.

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