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## Removal of Heavy Metals Ions from Waste water by Nanopowder Material

A graduation research project

submitted to the Department of Chemistry in partial fulfillment of the requirements for the completion of the degree of Bachelor of Science in Chemistry

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Second Semester, May 2015

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## ملخص المشروع:

الهدف من هذا المشروع البحثي هو تقييم فعالية جسيمات نانوية، صنعت عن طريق طحن مسحوق الهيماتايت واكسيد الزنك، في ازالة المعادن الثقيلة من المحاليل. وقعت دراسة تأثير عوامل مختلفة و اهمها التركيز الاولي والحرارة في نطاق تجارب مخبرية. تم تقدير ثوابت الاتزان، الحركية والثرموحرارية لعملية امتزاز ايونات المعادن الثقيلة السامة بواسطة المواد النانومترية. حققت عملية الامتزاز القيمة القصوى في اقل مدة زمنية وكانت النتائج المتحصل عليها في اتفاق جيد مع نموذج لنجميور في حالة أيونات الكاديوم. في حين وصف نموذجي لفرنديش ولنجمير بكيفية ممتازة نتائج امتزاز ايونات النيكل. كما تجانسة حركية عملية الامتزاز مع قانون التسارع من الدرجة الثانية. كما تبين من خلال معاملات الثرموحرارية ان عملية امتزاز الايونات في علاقة طردية مع الحرارة وهي من النوع الماص للحرارة.

**Abstract:**

The purpose of this research project was to evaluate the performance of milled commercially powders of hematite ( $\alpha\text{-Fe}_2\text{O}_3$ ) and zinc oxide (ZnO) as an effective nanomaterial for the removal of Cd(II) and Ni(II) ions from aqueous solutions. Batch mode experiments were performed to determine the adsorption equilibrium, kinetics, and thermodynamic parameters of toxic heavy metals ions by milled nanocrystalline. The adsorption process was found to be highly concentration dependent. The adsorption of heavy metal ions reached a maximum value rapidly and the adsorption parameters were in good agreement with the Langmuir isotherm in the case cadmium ions. However, the adsorption data fits both the Langmuir or Freundlich models well in the case nickel metal ions. 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.

## 1. Introduction

The presence of heavy metals in industrial waste waters is particularly problematic because these metals are very soluble in the aquatic environments, and they can be absorbed by living organisms. These heavy metals enter the food chain, and accumulate in the human body on large concentrations. If they are ingested beyond the permitted concentration, they can cause serious health disorders. Therefore, it is necessary to treat metal-contaminated wastewater prior to its discharge to the environment [1]. Cadmium is a toxic heavy metal of significant environmental and occupational concern. It has been released to the environment through the combustion of fossil fuels, metal production, and application of phosphate fertilizers, electroplating, and the manufacturing of batteries, pigments, and screens. This heavy metal has resulted in serious contamination of both soil and water. Cadmium (Cd) has been classified as a human carcinogen and teratogenesis impacting lungs, kidneys, liver, and reproductive organs [2]. Nickel is generally considered to be one of the most toxic metal found in environment, once it enters in the food chain progressively larger accumulation of nickel compounds takes place in humans and animals. Ni (II) is present in the effluents of silver refineries, electroplating, zinc base casting and storage battery industries [3].

There are various methods for removing heavy metals from waste water including chemical precipitation, membrane filtration, ion exchange, liquid extraction, or electro dialysis [4, 5]. However, these methods are not widely used due to their high cost and low feasibility for small-scale industries [6]. In contrast, adsorption technique is by far the most versatile and widely used.

Recently, Adsorption is operative in most natural physical, biological, and chemical systems, and is widely used in industrial applications such as activated charcoal, synthetic resins and water purification. Adsorption is a process that occurs when a gas or liquid solute accumulates on the surface of a Solid or a liquid (adsorbent), forming a molecular or atomic film (adsorbate). Recently, many research groups have explored several nanoparticles for removal because of the ease of modifying their surface functionality and their high surface area to volume ratio for increased adsorption capacity and efficiency.

In this work, the effects of temperature and initial concentration on Cd(II) and Ni(II) are particularly investigated. Various mathematical models are also tested: the Langmuir's and Freundlich's models for sorption isotherms, and first and second-order rate equations for description of kinetic. Kinetic parameters such as the rate constants calculated ultimate adsorption capacities, as well as the thermodynamic functions variations ( $\Delta H^\circ$ ,  $\Delta S^\circ$ , and  $\Delta G^\circ$ ) are evaluated and discussed.

## 2. Material and Methods

### 2.1. Material

Commercially powders of hematite ( $\alpha\text{-Fe}_2\text{O}_3$ ) and zinc oxide (ZnO) with equal molar (1:1) were introduced into a planetary milling “PULVERISETTE”. The powder was milled for 10hs with rotation speed and mass ratio of ball to powder of 400 rpm and 10:1 respectively. The characteristics of the so-produced nanopowder pores were evaluated from the adsorption-desorption isotherms of  $\text{N}_2$  at 77 K, through an apparatus ASAP 2020 (Micromeritics). The surface area of pores was calculated from the BET equation (Brunauer, Emmett and Teller). The volume of micropores and the surface area attributes to mesopores were calculated from the t-plot method of Lippens and de Boer [7].

A stock solutions ( $1,000 \text{ mg L}^{-1}$ ) of Ni(II) and Cd(II) were prepared by dissolving nickel nitrate ( $\text{Ni}(\text{NO}_3)_2$ ), cadmium nitrate ( $\text{Cd}(\text{NO}_3)_2$ ) 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.

Experiments were carried out in batch mode by adding  $10 \pm 0.1 \text{ mg}$  of adsorbent to 25 ml of a known Ni(II) and Cd(II) solution concentration and pH in a 50 ml Erlenmeyer flask. Adsorption studies were conducted at fixed pH values and initial Ni(II) and Cd(II) concentrations ( $20\text{--}150 \text{ mg.l}^{-1}$ ) to obtain equilibrium isotherms. Several flasks were placed on a multiposition magnetic stirrer and individually stirred at 600 rpm. After 12 h of contact, 15 ml of suspension was sampled from each flask, centrifuged (centrifuge, Hettich Zentrifugen EBA 20), and then passed through filter paper filters. Residual nickel and cadmium ions concentration in filtrate was measured with an inductively coupled plasma apparatus (Genius, ICP-EOS, Germany).

The amount of adsorbed metal ion per gram of adsorbent,  $q_e$ , and the percentage of removal values was calculated by the following relationships:

$$q_e = \frac{(C_0 - C_e) * V}{m} \quad (1)$$

## 2.2. Methods

The equilibrium established between adsorbed component on the adsorbent and unadsorbed component in solution can be represented by adsorption isotherms. The most widely used isotherm equations for equilibrium data modeling are the Langmuir and the empirical Freundlich models:

$$\frac{C_e}{q_e} = \frac{1}{q_m} C_e + \frac{1}{q_m \cdot K_L} \quad \text{linear form of Langmuir equation} \quad (2)$$

$$\log q_e = \frac{1}{n} \log C_e + \log K_F \quad \text{linear form of Freundlich equation} \quad (3)$$

where  $q_e$  is the amount of metal ions adsorbed per unit mass of adsorbent ( $\text{mg}\cdot\text{g}^{-1}$ ),  $C_e$  is the equilibrium concentration of solute in bulk solution ( $\text{mg}\cdot\text{l}^{-1}$ ),  $q_m$  is the solid-phase concentration corresponding to the complete monolayer coverage of adsorption sites [8], and  $K_L$  is the constant related to the free energy of adsorption. Values of  $q_m$  and  $K_L$  can be graphically determined from the linear form of the Langmuir model (Eq. 2): the slope is  $1/q_m$  and the intercept  $1/q_m \cdot K_L$ . The constants  $k$  and  $n$  of the Freundlich model are respectively obtained from the intercept and the slope of the linear plot of  $\log q_e$  versus  $\log C_e$  (Eq. 3). The constants  $K_F$  and  $n$  of the Freundlich model can be related to the strength of adsorptive bond and the bond distribution, respectively [9].

In fact, the kinetic study is generally done using various models. In this research project only two kinetic models were tested to predict the adsorption data of Cd(II) as a function of time using a pseudo-first- and pseudo-second-order kinetic models. According to Gupta et al. [10], the first-order model can be expressed as follows:

$$\ln(q_e - q_t) = \ln(q_e) - k_1 \cdot t \quad (4)$$

where  $q_t$  (in  $\text{mg}\cdot\text{g}^{-1}$ ) is solute amounts adsorbed per unit mass of adsorbent at time  $t$  (min), and  $k_1$  ( $\text{min}^{-1}$ ) is the adsorption rate constant.  $k_1$  and  $q_e$  were determined from the slope and intercept of



plots of  $\ln(q_e - q_t)$  versus  $t$ , respectively. According to Ho and McKay [11], sorption kinetics can be represented by a pseudo-second-order model that leads to the following equation:

$$\frac{t}{q_t} = \frac{1}{k_2 \cdot q_e^2} + \frac{t}{q_e} \quad (5)$$

where  $k_2$  is the pseudo-second-order rate constant ( $\text{g}/(\text{mg} \cdot \text{min})$ ). An adequate pseudo-second-order kinetic model should show a linear plot of  $t/q_t$  versus  $t$ . The value of  $q_e$  can be easily deduced from the slope of the plot of  $t/q_t$  versus  $t$ . Once  $q_e$  is identified, the value of  $k_2$  can be obtained either from the intercept. Values of first- and second-order model parameters, are reported in Table 1.

The thermodynamic properties: enthalpy change ( $\Delta H^\circ$ ), free energy change ( $\Delta G^\circ$ ) and entropy change ( $\Delta S^\circ$ ) for the adsorption of Cd(II) and Ni(II) by the adsorbent are calculated from the following set of equations:

$$\Delta G^\circ = -R.T.\ln K_a \quad (6)$$

$$\Delta S^\circ = \frac{\Delta H^\circ - \Delta G^\circ}{T} \quad (7)$$

The equilibrium constant of adsorption process is calculated by the equation  $K_a = q_m^* K_L$ . The value of enthalpy change  $\Delta H^\circ$  is determined from the slope of the linear curve of  $\ln(K_a)$  versus the reciprocal temperature ( $1/T$ ) (Figure 6). The free energy change ( $\Delta G^\circ$ ) and entropy change ( $\Delta S^\circ$ ) values are calculated from Eq. 6 and Eq. 7.

### 3. Result and discussion

#### 3.1. Nitrogen Isotherm

Isotherm shape provides information on pore size, which is usually categorized as micropore, mesopore, or macropore.

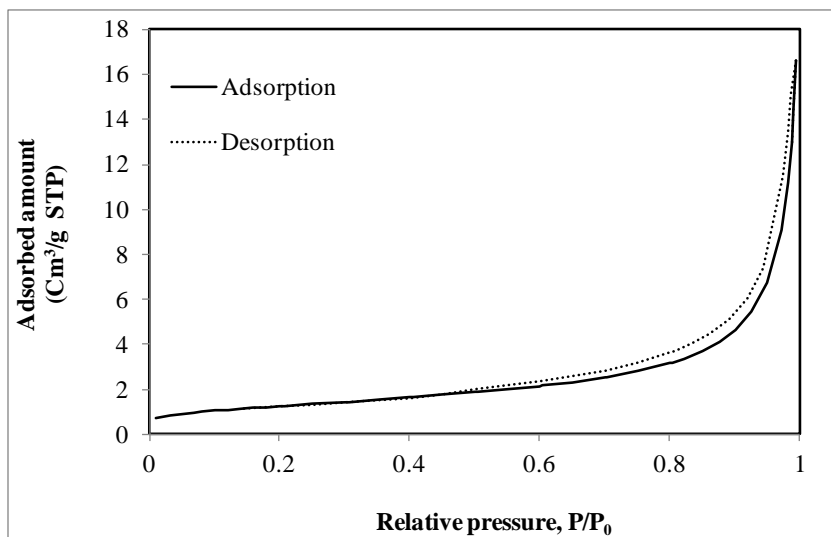


Figure 1. Adsorption-desorption isotherms of N<sub>2</sub> at 77 K of adsorbent nanopowders.

As shown in Fig. 1, the adsorption-desorption isotherm of N<sub>2</sub> at 77 K for adsorbent is clearly of type II, according to the IUPAC classification of sorption isotherms [12], formerly designated as Brunauer's classification. The isotherm is a type H4 hysteresis loop, characteristic of aggregated particles with nonporous or macroporous adsorbents and unrestricted monolayer-multilayer adsorption [12]. The specific surface area is 4.5 m<sup>2</sup>.g<sup>-1</sup> determined by the conventional BET method, with porous volume of about 0.0201 cm<sup>3</sup>.g<sup>-1</sup>. The mean pore size determined from BET surface area and the pore volume in the approximation of cylindrical pores is higher than to 20 nm.

#### 3.2. Heavy metals ions adsorption study

##### 3.2.1. Equilibrium study

The selective removal of two toxic heavy metal ions (Cd(II) and Ni(II)) from aqueous solutions were investigated at room temperature and a pH value fixed to 7.0 ± 0.2. 10 mg of milled hematite (α-Fe<sub>2</sub>O<sub>3</sub>) and zinc oxide (ZnO) are mixed with 25 ml of different initial concentration solution of each metal ion and stirred for 12 h in 50 ml Erlenmeyer flask. Figure 2 illustrates the

experimental data of adsorption capacities of the two heavy metals ions by milled nanopowder. The curves of adsorption isotherms present a plateau for large metallic ion concentrations, and their shape is characteristic of type L classic Langmuir isotherm.

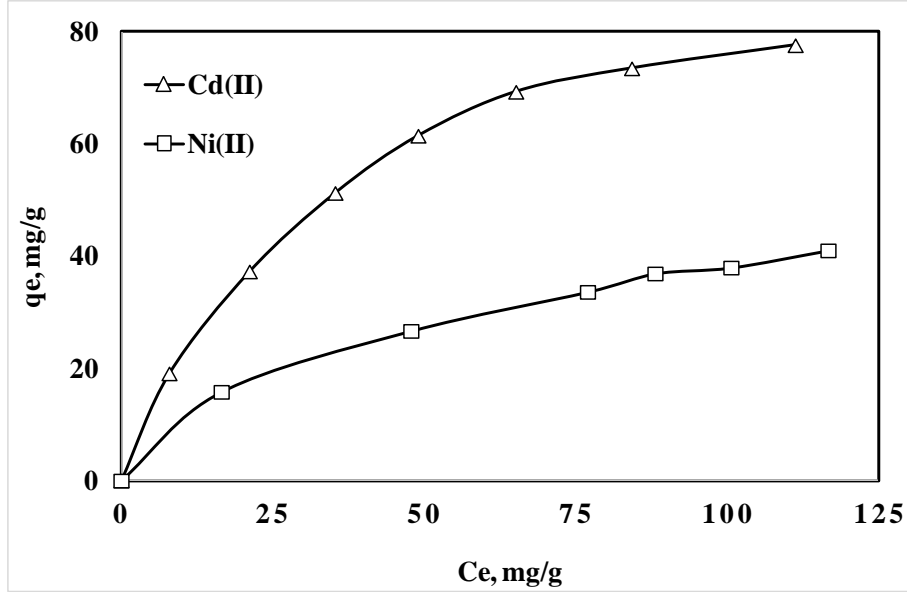


Figure 2. Adsorption equilibrium isotherms of Cd(II) and Ni(II) at 25 oC by adsorbent nanopowder.

The linearized Langmuir and Freundlich isotherms of Ni(II) and Pb(II) (figure 3a and 3b) in solutions are drawn and the estimated model respective parameters ( $q_m$ ,  $K_L$ ,  $K_F$  and  $n$ ) with correlation coefficient ( $r^2$ ) are shown in Table 1.

Table 1: Equilibrium constants for the removal of heavy metal ions.

Metal ion	T(K)	Langmuir constants			Freundlich constants		
		$q_m(\text{mg}\cdot\text{g}^{-1})$	$K_L(\text{l}\cdot\text{mg}^{-1})$	$r^2$	$n$	$k_f$	$r^2$
Ni (II)	298	57.14	0.0204	0.9906	2.099	4.21	0.9947
	298	104.17	0.0264	0.9960	1.837	6.799	0.9706
Cd (II)	313	111.12	0.0281	0.9885	-	-	-
	328	128.21	0.0294	0.9961	-	-	-

Considering the high values of the regression coefficient  $r^2$  near unity in this table, it is clear that the adsorption data fits both the Langmuir or Freundlich models well in the case nickel metal ion. Nevertheless, Langmuir models fits better the adsorption equilibrium data in the case of cadmium metal ions. It is obvious from this table that the adsorption of the adsorbent for Cd(II) is higher than that for Ni(II), i.e. the adsorption capacity of Cd(II) is about  $104.17 \text{ mg g}^{-1}$ , which was significantly higher than the values  $57.14 \text{ mg g}^{-1}$  observed for Ni metal ion.

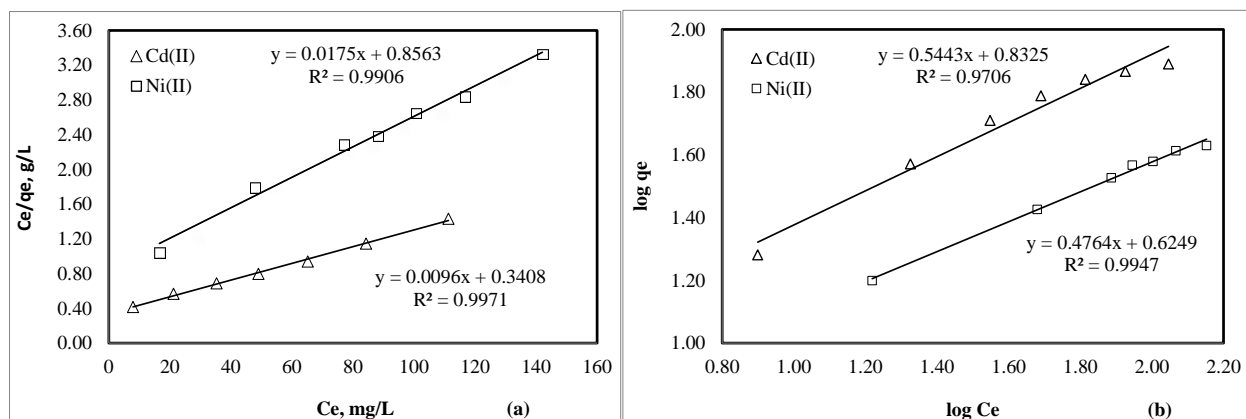


Figure 3. Linearized adsorption equilibrium isotherms of Cd(II) and Ni(II) at 25 °C by adsorbent nanopowder (a) Langmuir linear equation, (b) Freundlich linear equation.

Subsequently, owing to the reason that the milled goethite is highly efficient for 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. Kinetic study

The evolution of the sorption data of Cd(II) as function of time are illustrated by Figure 4 for the nanopowder at 298 K. It appears from Figure 4 that for all the experiments a rapid initial rise of the adsorption capacities  $q_t$  and the equilibrium is almost reached within 150 min.

The validity of the kinetic models is tested by the magnitude of the regression coefficient  $r^2$ , given in table 2.

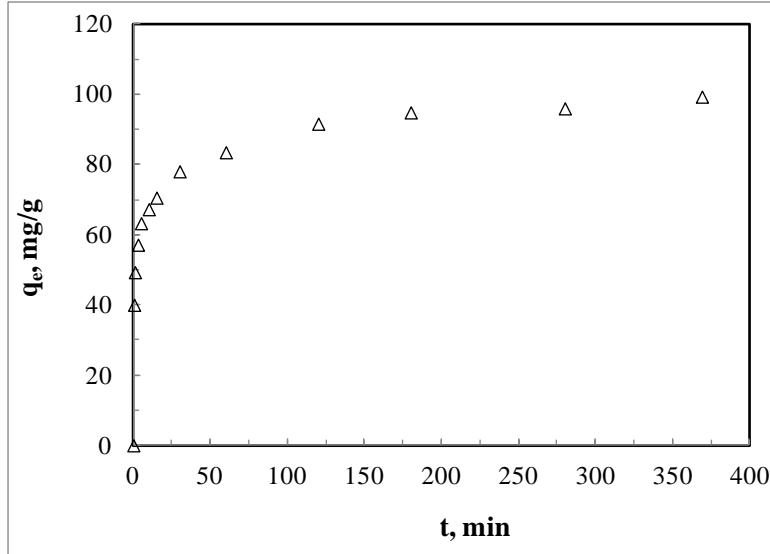


Figure 4: Langmuir isotherm for the adsorption of Cd(II) on nanopowder.

It is important to note that for a pseudo-first order model, the correlation coefficient is about 0.94, which is indicative of a bad correlation. Moreover, from same table, it can be seen that the experimental value of  $q_m$  are not in good agreement with the theoretical values calculated from the equation (4).

Table 2: rate adsorption constants for the adsorption of Cd(II) by the adsorbent

$q_m (exp)^a$ (mg/g)	First-order			Second-order		
	$k_1 \times 10^3$ (1/min)	$q_{m(cal)}^b$ (mg/g)	$r^2$	$k_2 \times 10^3$ (g/(mg.min))	$q_{m(cal)}^b$ (mg/g)	$r^2$
104.16	5.7	40.96	0.9424	1.95	99.01	0.9988

Therefore, the pseudo-first order model is not suitable for modeling the adsorption of Cd(II) onto the used adsorbent. In contrast, the application of a pseudo-second order model leads to much better regression coefficients, near to the unit 0.9988. Furthermore, the experimental and calculated values of  $q_m$  are very close, as indicated in table 2, thus, the pseudo-second order kinetic model is well suitable to model the sorption curves of Cd(II) onto the nanopowder adsorbent.

### 3.2.3. Thermodynamic study

The effect of temperature is investigated from adsorption tests carried out at three constant temperatures: 298, 313 and 328 K. The amount of Cd(II) removed by the adsorbents rises with temperature as shown in the Langmuir isotherm plots of Figure 5.

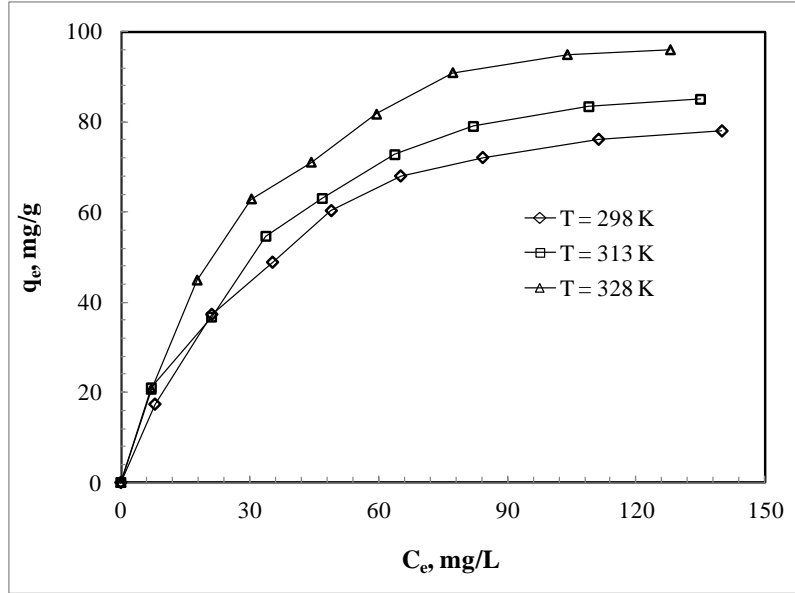


Figure 5: Langmuir isotherms for adsorption of Cd (II) onto nanopowder material at different temperatures.

Considering the results obtained in the section 4.2.1 concerning equilibrium study only Langmuir model is applied to the experimental adsorption data. Langmuir equation constants are listed in table 1.

The value of enthalpy change  $\Delta H^0$  is determined from the slope of the linear curve of  $\ln(K_a)$  versus the reciprocal temperature ( $1/T$ ) (Figure 6). The free energy change ( $\Delta G^0$ ) and entropy change ( $\Delta S^0$ ) values are calculated from Eq. 6 and Eq. 7. thermodynamic parameters are gathered in table 3.

Positive values of  $\Delta H^0$  indicate the endothermic nature of the adsorption process meanwhile positive values of  $\Delta S^0$  suggest the increased randomness at the solid-solution interface.

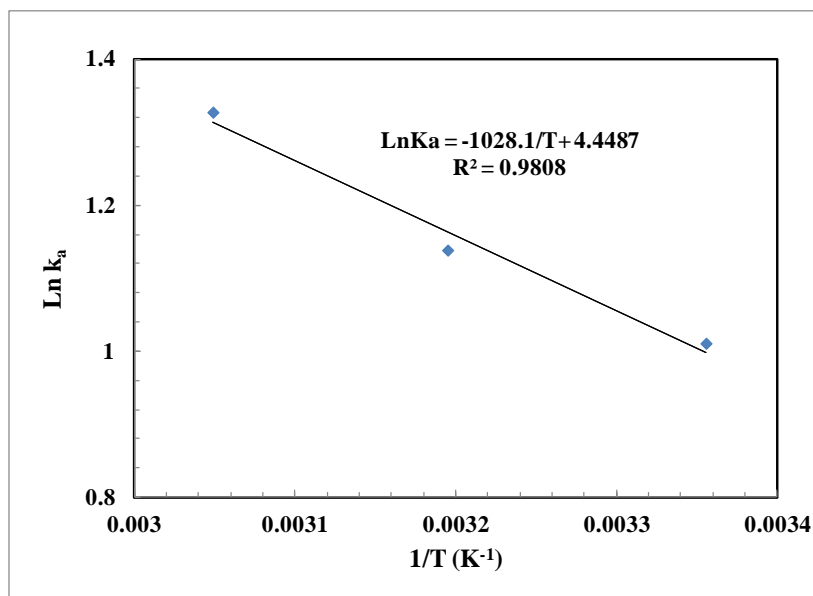


Figure 6: Plot of  $\ln(K_a)$  versus the reciprocal temperature of cadmium ion adsorption

Table 3: Thermodynamic parameters for Cd(II) adsorption

Temperature (K)	$K_a$	$\Delta G^0$ (kJ.mol <sup>-1</sup> )	$\Delta S^0$ (kJ.mol <sup>-1</sup> .K <sup>-1</sup> )	$\Delta H^0$ (kJ.mol <sup>-1</sup> )	$r^2$
298	2.748	-2.505	0.0371		
306	3.122	-2.963	0.0368	8.55	0.9808
313	3.772	-3.621	0.0371		

The negative values of the free energy change  $\Delta G^0$  confirm the spontaneous nature of adsorption. Table 3 summarizes the values of these thermodynamic properties. The change of the standard free energy decreases with increasing temperatures regardless of the nature of adsorbent. This indicates that a better adsorption is actually obtained at higher temperatures.

## 4. Conclusion

A suitable indigenous milled nanomaterial has been identified as an effective adsorbent to remove Cd(II) and Ni(II) metal ions from aqueous solutions. The equilibrium data of adsorption are in good agreement with the Langmuir's model, and the adsorbent was found to be more effective for the uptake of Cd(II) than Nickel (i.e.  $104 \text{ mg.L}^{-1}$  for Cd(II) to  $57 \text{ mg.L}^{-1}$  for Ni(II)). Furthermore, it was found that a second-order rate model well mimics the kinetic data for the removal cadmium ions. Temperature is besides determinant factor for the removal of Cd(II). Increasing temperature not only enhances the rate of adsorption, but also its extent, this finding can be explained by the positive value found for the enthalpy change of the adsorption reaction. Besides, the positive values of the entropy suggest an increase of randomness at the solid–solution interface during the heavy metal ions adsorption.



## References

- [1] S. Babel, T.A. Kurniawan, Cr(VI) removal from synthetic wastewater using coconut shell charcoal and commercial activated carbon modified with oxidizing agents and/or chitosan, *Chemosphere* 54(7) (2004) 951–967.
- [2] K.H. Boparai, M. Joseph, D.M. O’Carroll, Kinetics and thermodynamics of cadmium ion removal by adsorption onto nano zerovalent iron particles, *J. Hazard. Mater.* 186 (2011) 458–465.
- [3] Mishra G.K. Meena A. K., Rai, P.K, Chitra R.G, Nagar, P.N. 2005. Removal of heavy metal ions from aqueous solutions using carbon aerogel as an adsorbent. Elsevier B.V. All rights reserved. doi:10.1016/j.jhazmat. 03.02
- [4] M. Sittig, *Handbook of Toxic and Hazardous Chemicals*, Noyes Publications, Park Ridge, NJ, 1981.
- [5] J.W. Patterson, *Industrial Wastewater Treatment Technology*, 2nd ed., Butterworth-Heinemann, London, 1985.
- [6] A. Sohail, S.I. Ali, N.A. Khan, R.A.K. Rao, Removal of chromium from wastewater by adsorption, *Environ. Pollut. Control* 2 (1999) 27–31.
- [7] Lippens, B.C. and De Boer, J.H., Pore systems in catalysts .V. the t-method, *J. Catalysis*, 4 (1965), 319-323.
- [8] C.P. Huang, E.H. Smith, *Chemistry in water reuse*, Ann Arbor Science Publishers, Ann Arbor, Michigan, 2 (1981).
- [9] V.K. Gupta, S. Sharma, I.S. Yadau, M. Dinesh, Utilisation of bagasses fly ash generated in the sugar industry for the removal of phenol and p-nitrophenol from wastewater. *Journal Chemical Technology and Bio-technol.* 71 (1998) 180-186.
- [10] V.K. Gupta, S. Sharma, I.S. Yadau, M. Dinesh, Utilisation of bagasses fly ash generated in the sugar industry for the removal of phenol and p-nitrophenol from wastewater. *Journal Chemical Technology and Bio-technol.* 71 (1998) 180-186.
- [11] Ho, Y.S., McKay, G., Sorption of dye from aqueous solution by peat, *Chemical Engineering Journal*, 70(1998), 115-124.
- [12] F. Rouquerol, J. Rouquerol, K. Sing, *Adsorption by Powder and Porous Solids: Principles, Methodology and Applications*, Academic Press, 1999.