KINGDOM OF SAUDI ARABIA
AL-IMAM MOHAMMAD IBN SAUD ISLAMIC UNIVERSITY
COLLEGE OF SCIENCE
DEPARTMENT OF CHEMISTRY

المملكة العربية السعودية
جامعة الإمام محمد بن سعود الإسلامية
كلية العلوم
قسم الكيمياء

Efficient and fast removal of cadmium by Nanopowder Material from aqueous solution

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 2016

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ملخص المشروع:

الهدف من هذا المشروع البحثي هو تقييم فعالية الجسيمات نانومترية لاكسيد الزنك، التي صنعت بطريقة السول جال، لازالة ايونات الكدميوم السامة من المحاليل. وقعت دراسة تاثير عوامل مختلفة و اهمها التركيز الاولي والحرارة في نطاق تجارب مخبرية. تم تقدير ثوابت الاتزان، الحركية والثرموحررية لعملية امتزاز ايونات الكدميوم السامة بواسطة المواد النانومترية. حققت عملية الامتزاز القيمة القصوى في اقل مدة زمنية وكانت االنتائج المتحصل عليها في اتفاق جيد مع نموذجي لنجميور وفرندليش في عملية امتزاز أيونات الكادميوم. كما تجانسة حركية عملية الامتزاز مع قانون التسارع من الدرجة الثانية. وقد تبين من خلال معاملات الثرموحررية ان عملية امتزاز الايونات في علاقة طردية مع الحرارة.

Abstract:

The object of this research project was to investigate the performance of zinc oxide nanoparticles for the uptake of toxic cadmium metal ions from aqueous solutions. The prepared ZnO was hexagonal wurtzite and mesopores material with a surface area about $109.7 m^2 g^{-1}$. Batch mode experiments were performed to determine the adsorption equilibrium, kinetics, and thermodynamic parameters of the removal process. The later was found to be highly initial concentration dependent. The adsorption of heavy metal ion reached a maximum value rapidly and the adsorption parameters were in good agreement with the Langmuir and Freundlich models. The kinetics experimental data of the removal process was found to follow the pseudo-second-order rate law. The experimentations of thermodynamic study of adsorption of cadmium metal ions were conducted and the results were collected and analyzed. The removal process of Cd(II) were found to be exothermic.

1. Introduction

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 [1]. Adsorption process in general and in our special study to remove these wastes and heavy metal ions from aqueous solutions occurs when a gas or liquid solute accumulates on the surface of the solid or liquid (adsorbent) forming a molecular or atomic film (adsorbate).Nanomaterial have attracted increasing attention because of their immense potential technological applications [2].

There are various methods for removing heavy metals from wastewater including chemical precipitation, membrane filtration, ion exchange, liquid extraction or electro-dialysis. These methods are not widely used due to their high cost and low feasibility for small-scale industries. In contrast, adsorption technique is by far the most versatile and widely used [3]. Zinc compounds were probably used by early humans, in processed and unprocessed forms, as a paint or medicinal ointment, but their composition is uncertain. Avicenna mentions zinc oxide in The Canon of Medicine (1025 AD), which mentioned it as a preferred treatment for a variety of skin conditions, including skin cancer. Though it is no longer used for treating skin cancer, it is still widely used to treat a variety of other skin conditions, in products such as baby powder and creams against diaper rashes, calamine cream, anti-dandruff shampoos, and antiseptic ointments [4]. Zinc oxide has also been recovered from zinc mines at Zawar in India, dating from the second half of the first millennium BC. This was presumably also made in the same way and used to produce brass. The main usage of zinc oxide (zinc white) was in paints and as an additive to ointments. Zinc white was accepted as a pigment in oil paintings by 1834 but it did not mix well with oil. This problem was solved by optimizing the synthesis of ZnO. In 1845, Le Claire in Paris was producing the oil paint on a large scale, and by 1850, zinc white was being manufactured throughout Europe [5]. Nanoparticulates oxide (ZnO) used as a photo catalyst for mineralization of toxic organic and in organic compounds. Its poor absorbance of photons in the solar light is due to their wide band gap (3.2 ev). Efforts has been focused on the last decade to make these semiconductors active under visible light. Many strategies is applied to increase this activity and make it absorb photons of lower energy. One of these strategies is doping these semiconductors with different elements such as transition metals ZnO was the superior photo catalyst in degrading pesticide carbetamide, herbicide triclopyr, and pulp mill bleaching wastewater. This superiority of ZnO photocatalytic activity is because it has more active sites which makes it higher in reaction rates [6].

In this work, the effects of temperature and initial concentration on Cd(II) removal are particularly investigated. Various mathematical models are also tested: the Langmuir's and Freundlich's models for sorption isotherms, and pseudo-first and pseudo-second order rate equations for the description of kinetics of the removal process. Kinetics parameters such as the rate constants, ultimate adsorption capacities, as well as the thermodynamic functions variations (ΔH°, ΔS°, and ΔG°) are evaluated and discussed.

2. Material and Methods

2.1. Material

Zinc acetate dihydrate ($Zn(CH_3COO)_2.2H_2O$), absolute methanol 99.99%, 2,3.dihydroxysuccinic acid (CHOH-COOH)2 were purchased from Panreac and all chemicals were utilized without further purification. A certain amount of zinc acetate was dissolved in a 75 ml of methanol and stirred at 400 rpm for 30 minutes. The 2.3-dihydroxysuccinic acid catalyst was dissolved in approximately 45ml of distilled water and stirred for 30 minutes. The solution of 2.3-dihydroxysuccinic acid was added dropwise to the mixture. Under vigorous magnetic agitation a white gel was rapidly formed at room temperature and then oven dried at 358 K for 16 hours. The obtained powder was grinded prior to annealing in a tubular furnace at 523 for one hour.

The characteristics of the so-produced nanopowder pores were evaluated from the adsorption-desorption isotherms of 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]. The structure, crystallinity and average particles size of photocatalysts were determined by the powder X-ray diffraction patterns, the XRD pattern of the samples were recorded by a diffractometer (D8 Advance Bruker) using Cu-Kα radiation, $\lambda = 0.15406$ nm, accelerating voltage is 40 kV and 20 -80° as scanning angle. The morphology of the nanopowder samples was examined by a scanning electron microscope. The samples were previously oven dried at 105 °C and coated with a thin film of gold to provide ZnO powder surface with electrical conduction.

A stock solutions (1,000 mg L^{-1}) of Cd(II) were prepared by dissolving cadmium nitrate ($Cd(NO_3)_2$ 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 ± 0.1 mg of adsorbent to 25 ml of a known Cd(II) solution concentration and pH in a 50 ml Erlenmeyer flask. Adsorption studies were conducted at fixed pH values and initial Cd(II) concentrations (20–140 $mg.l^{-1}$) to obtain equilibrium isotherms. Several flasks were placed on a multiposition magnetic stirrer and individually stirred at 500 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 cadmium metal ion 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, *qe*, and the percentage of removal values was calculated by the following relationships:

$$q_e = \frac{\left(\mathrm{C}_0 - C_e\right) * V}{m} \tag{1}$$

where V the volume of the solution in Liter and m is the mass of the nanopowder in gram.

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:

$$\frac{C_e}{q_e} = \frac{1}{q_m} C_e + \frac{1}{q_m . K_L} \qquad \text{linear form of Langmuir equation} \tag{2}$$

$$lnq_e = \frac{1}{n} lnC_e + ln\,K_F \qquad \text{linear form of Freundlich equation} \qquad (3)$$

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 bulk solution (mg·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 $1/q_m. K_L$. The constants k and n of the Freundlich model are respectively obtained from the intercept and the slope of the linear plot of lnq_e versus lnC_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:

$$ln(q_e - q_t) = ln(q_e) - k_1.t \qquad (4)$$

where q_t (in mg.g^{-1}) is solute amounts adsorbed per unit mass of adsorbent at time t (min), and k_1 (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 (Figure 5 a), respectively. According to Ho and McKay [11], sorption kinetics can be represented by a pseudo-second-order model that leads to the following equation:

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

where k_2 is the pseudo-second-order rate constant (g/(mg·min)). An adequate pseudo-second-order kinetic model should show a linear plot of t/q_t versus t (Figure 5 b). The value of qe 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 (ΔH^o), free energy change (ΔG^o) and entropy change (ΔS^o) for the adsorption of Cd(II) by the adsorbent are calculated from the following set of equations:

$$\Delta G^0 = -R.T.lnK \tag{6}$$

$$\Delta S^o = \frac{\Delta H^0 - \Delta G^0}{T} \tag{7}$$

The equilibrium constant of adsorption process is calculated by the equation $Ka = q_m * K_L$. The value of enthalpy change ΔH^o is determined from the slope of the linear curve of ln(Ka) versus the reciprocal temperature (1/*T*) (Figure 6). The free energy change (ΔG^o) and entropy change (ΔS^o) 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.

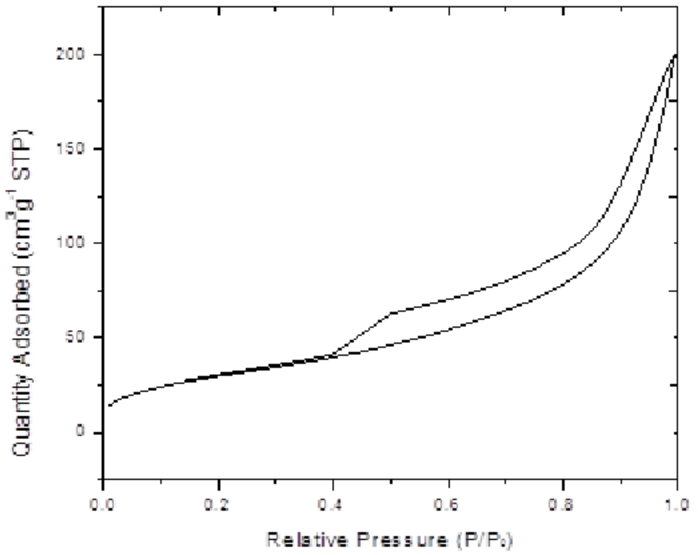

Figure 1. Adsorption-desorption isotherms of N_2 at 77 K of Zinc oxide.

As shown in Fig. 1, the adsorption-desorption isotherm of N_2 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 hysteresis is Type H3 characteristics of a mesoporous material and did not exhibit limiting adsorption at high relative pressure (≈1) suggesting a slit-shaped pores [12]. The specific surface area is $109.7 m^2.g^{-1}$ determined by the conventional BET method, with porous volume of about $0.313 cm^3.g^{-1}$. The mean pore size determined from BET surface area and the pore volume in the approximation of cylindrical pores is about 9.96nm.

3.2. Structure and morphology

Figure 2 (a-b) shows the SEM micrographs obtained for the as prepared ZnO (a) and annealed at (b) 523K. As can be seen from the figure, the shape of the nanoparticles has changed from a plate shape of the as prepared ZnO to spherical shape after annealing. There is a little increase in the agglomeration due the temperature increase leading to a larger particle sizes.

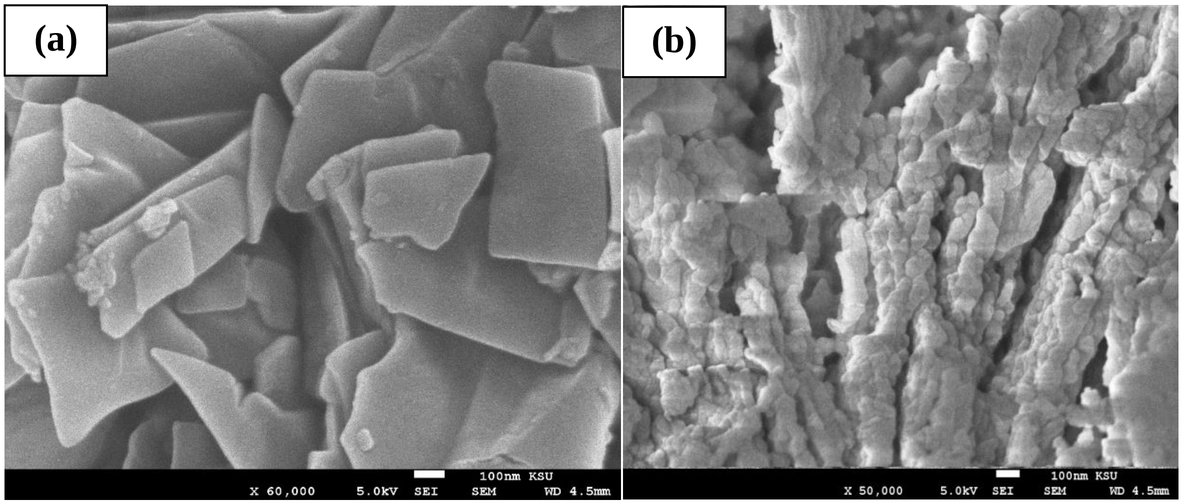

Figure 2: SEM micrographs of (a) xerogel (b) ZnO T523K

The XRD patterns for ZnO nanoparticles are displayed in (Figure.3). The results show broad peaks at position (31.61, 34.39, 36.11, 47.40, 56.52, 62.72, 66.29, 67.91 and 69.08 deg. as 2 tetha). These values are in good agreement with standard card (JCPDS 36-1451) file for ZnO and can be indexed as the hexagonal wurtzite structure. The average crystallite size (D) was calculated using the Scherer's equation 1. [23] and found to be equal to 16.12 nm.

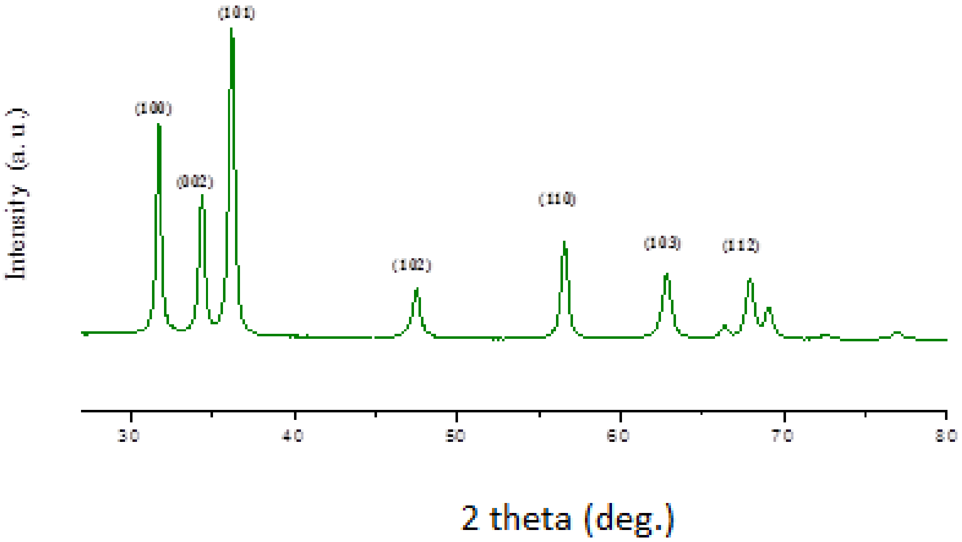

Figure 3: XRD patterns of ZnO at 523K for 1hour.

3.3.Heavy metals ions adsorption study

3.3.1. 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 there is a rapid initial rise of the adsorption capacities q_t up to 10 min and the equilibrium is almost reached within 100min.

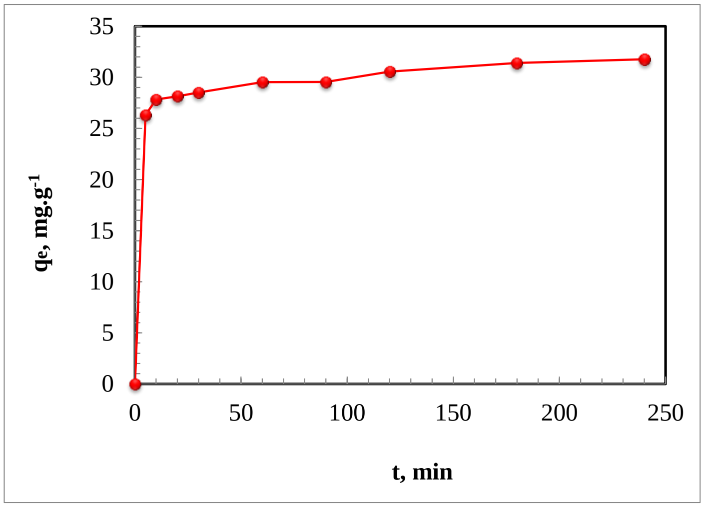

Figure 4: Plot of the adsorption capacity of Cd(II) on ZnO nanopowder as a function of time.

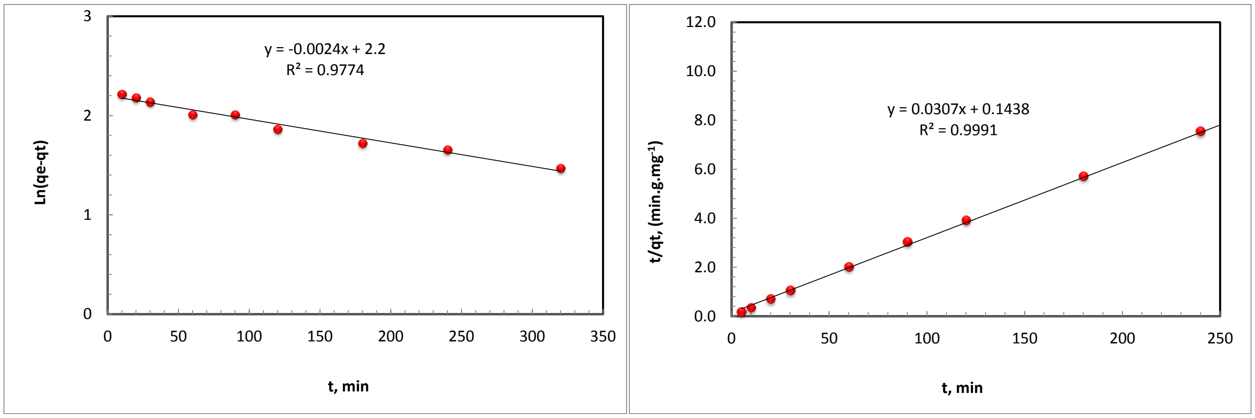

Figure 5: Kinetics of Cd(II) adsorption onto ZnO (a) pseudo first order plot and (b) pseudo-second-order plot. Conditions: 298 K, pH = 7, 0.12 g ZnO in 0.2 L of solution 27mg/L.

The estimated pseudo-first order and pseudo-second order model respective parameters ($q_{m(cal)}$, K_1 and K_2) with correlation coefficient (r^2) are gathered in Table 1. The validity of the kinetic models is tested by the magnitude of the regression coefficient r^2, given in table 1. It is important to note that for a pseudo-first order model, the correlation coefficient is about 0.977. 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 1: rate adsorption constants for the adsorption of Cd(II) by the adsorbent

$q_{m\ (exp)}^{a}$ (mg/g)	First-order			Second-order		
	k_1x 10^3 (1/min)	$q_{m(cal)}^{b}$ (mg/g)	r^2	k_2 x 10^3 (g/(mg.min))	$q_{m(cal)}^{b}$ (mg/g)	r^2
35.33	**2.4**	**9.03**	**0.9774**	**6.55**	**32.57**	**0.9991**

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 0.9991. Furthermore, the experimental and calculated values of q_m are very close, as indicated in table 1, thus, the pseudo-second order kinetic model is well suitable to describe the experimental adsorption data of Cd (II) onto the nanopowder material.

3.3.2. Equilibrium study

The removal of Cd(II) as a toxic heavy metal ion from aqueous solutions is investigated at room temperature and a pH value fixed to 7.0 ± 0.2. 10 mg of zinc oxide (ZnO) are mixed with 25 ml of different initial concentration solution varying from 20 to 140 mg.L^{-1} and stirred at 500 rpm for 12 hs in 50 ml Erlenmeyer flask.

Figure 6 illustrates the experimental data of adsorption capacities of the cadmium heavy metal ions by ZnO nanopowder. The linearized Langmuir and Freundlich isotherms of Cd(II) (figure 6a and 6b) in solutions are drawn and the estimated model respective parameters (q_m, K_L, K_F and n) with correlation coefficient (r^2) are gathered in Table 2.

Table 2: Equilibrium constants for the removal of heavy metal ions.

T(K)	**Langmuir constants**			**Freundlich constants**		
	q_m(mg.g^{-1})	K_L(l.mg^{-1})	r^2	n	k_f	r^2
298	106.4	0.00635	0.9972	1.687	4.11	0.9813
318	112.4	0.00389	0.9988	1.963	7.35	0.9873
338	121.9	0.00256	0.9927	2.128	10.46	0.9739

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. It is obvious from this table that the adsorption of ZnO for Cd(II) directly proportional to the temperature, i.e. the adsorption capacity of Cd(II) is about 121.9 mg g^{-1}, which was significantly higher than the values 106.4 and 112.4 mg g^{-1} observed for the two other operational temperatures. The n values greater than 1 are indicative of a Langmuir process and of very weak interactions between molecules of solute. Moreover, the values of Freundlich constants increase proportionally to the temperature.

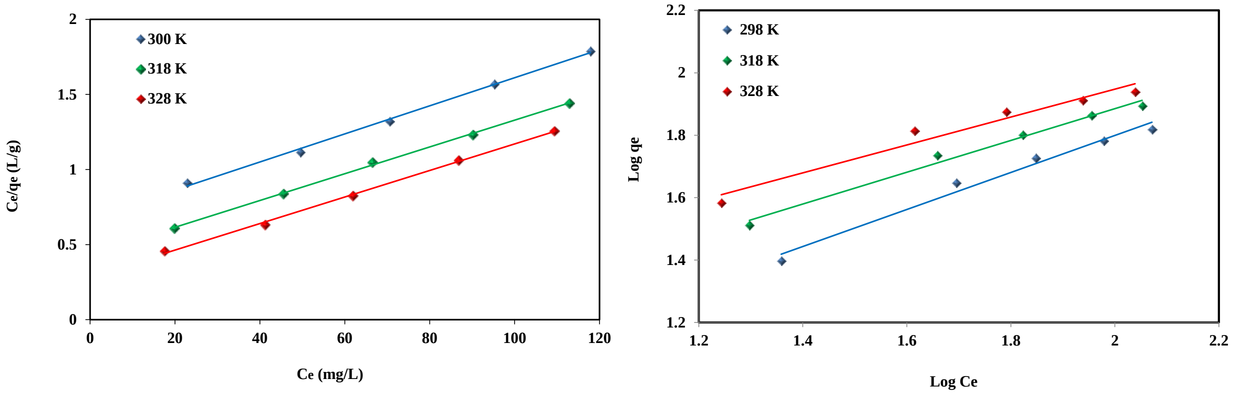

Figure 6. Linearized adsorption equilibrium isotherms of Cd(II) at different temperatures by adsorbent nanopowder (a) Langmuir linear equation, (b) Freundlich linear equation.

3.3.3. Thermodynamic study

The effect of temperature is investigated from adsorption tests carried out at three constant temperatures: 298, 318 and 338 K. The amount of Cd(II) removed by the adsorbents rises with temperature as shown in the equilibrium isotherm plots of Figure 7.

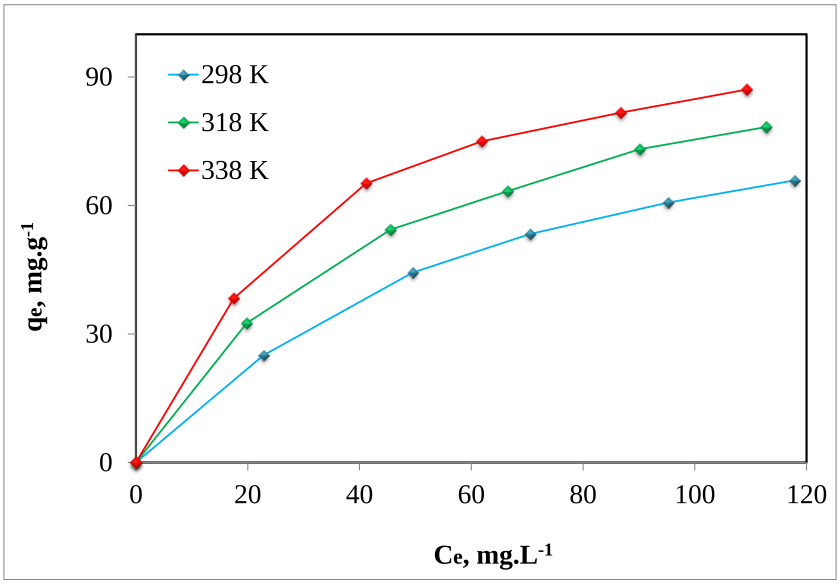

Figure 7: Equilibrium isotherms for adsorption of Cd (II) onto ZnO nanopowder at different temperatures.

The value of enthalpy change ΔH^o is determined from the slope of the linear curve of ln(Ka) versus the reciprocal temperature (1/T) (Figure 8). The free energy change (ΔG^o) and entropy change (ΔS^o) values are calculated from Eq. 6 and Eq. 7. Thermodynamic parameters are gathered in table 3. Negative values of ΔH^0 indicate the exothermic nature of the adsorption process meanwhile negative values of ΔS^0 suggest the decreased randomness at the solid-solution interface. Table 3 summarizes the values of these thermodynamic properties.

Table 3: Thermodynamic parameters for Cd(II) adsorption

Temperature (K)	K	ΔG^0 (kJ.mol^{-1})	ΔS^0 (J.mol^{-1}.K^{-1})	ΔH^0 (kJ.mol^{-1})	r^2
298	0.676	0.971	-57.7	-16.218	0.9986
318	0.437	2.189	-57.9		
338	0.312	3.275	-57.7		

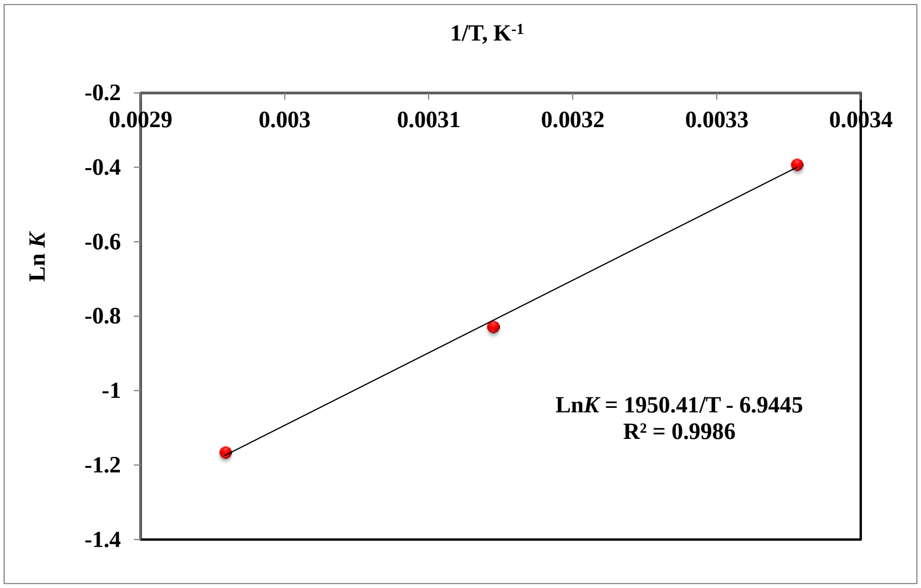

Figure 8: Plot of ln(Ka) versus the reciprocal temperature of cadmium ion adsorption

The positive values of the free energy change ΔG^0 suggest the non-spontaneous nature of adsorption. This phenomena could be explained by the release of Zn(II) ions in solution confirmed by the measurements realized by ICP after the adsorption of Cd(II) ions. Such behaviour could be a result of a possible exchange of ions at the surface of the nanomaterial due to the non-stability of the later. The change of the standard free energy increases with increasing temperatures. This indicates that a better adsorption is actually obtained at low temperatures.

4. Conclusion

A suitable nanomaterial elaborated by flash sol-gel method has been identified as an effective adsorbent for the removal of cadmium metal ion from aqueous solutions. The equilibrium data of adsorption are in good agreement with the Langmuir and Freundlich models, and the adsorbent was found to be more effective for the uptake of Cd(II) at height temperature (i.e. 122 mg.L^{-1} for Cd(II) at 338 K). 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. The negative values of the free energy with low enthalpy value at different temperatures suggest a spontaneous physical adsorption process.

References

[1] 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.

[2] S. Babel, T.A. Kurniawan, Cd(II) Removal from synthetic wastewater using coconut shell charcoal and commercial activated carbon modified with oxidizing agents and/or chitosan chemosphere 54, 7(2004), pp. 951-967.

[3] J.W. Patterson, Industrial wastewater treatment technology, 2nd Ed, 1985, Butterworth-Heinemann, London.

[4] Harding, Fred John (2007). Breast Cancer: Cause – Prevention – Cure. Tekline Publishing. pp. 83.

[5] Sanchez-Pescador, R; Brown, JT; Roberts, M; Urdea, MS "The nucleotide sequence of the tetracycline resistance determinant tet M from Urea plasma urea lyticum ". Nucleic Acids Research 16 (2014).

[6] Rao AN, Sivasankar B, Sadasivam V: Kinetic study on the photocatalytic degradation of salicylic acid using ZnO catalyst. J Haz. Mat. 166 (2009), pp. 1357–1361.

[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-thechnol. 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-thechnol. 71 (1998) 180-186.

[11] Ho, Y.S., Mckay, G., Sorption of dye from queous solution by peat, Chemical Engineering Journal, 70(1998), 115-124