Algerian Journal of Environmental Science and Technology
March edition. Vol.9. Nº1. (2023)
ISSN : 2437-1114
www.aljest.org

Adsorption behavior of cadmium and nickel ions from binary systems (isothermal and thermodynamic studies)

A. Boudaoud[1,2,*], M. Djedid[1,3], C. Ad[1,3], M. Guermit[1,2], F. Bensafiddine[1,4], M. Benalia[1,3]

[1]Laboratory of Process Engineering, Faculty of Technology, University of Amar Telidji Laghouat, BP37G, 03000 Laghouat, Algeria
[2]Department of Sciences and Technology, Faculty of Technology, University of Amar Telidji Laghouat, BP37G, 03000 Laghouat, Algeria
[3]Department of Process Engineering, Faculty of Technology, University of Amar Telidji Laghouat, BP37G, 03000 Laghouat, Algeria
[4]Faculty of Sciences and Technology, University of Ghardaia, BP455, 47000 Ghardaia, Algeria

*Corresponding author: asmaboudaoud@gmail.com; Tel.: +213 6 75 56 20 47

ARTICLE INFO

Article History :

Received **: 14/10/2020**
Accepted **: 19/05/2021**

***Key Words*:**

Adsorption; Nickel;
Cadmium;
Binary-metal system;
Isotherm;
Thermodynamic.

ABSTRACT/RESUME

Abstract: *The objective of this research paper is to study the competitive adsorption of cadmium and nickel ions, where the effect of experimental factors such as pH solution, temperature, contact time and initial concentration of metals ions have been studied. The test of isothermal models indicated that the Freundlich model showed more explanation for this competitive adsorption of the ions studied. In addition, the study of thermodynamic parameters has been carried out. The results also showed that the adsorbent have a greater affinity for cadmium ions than nickel ions under optimum experimental conditions.*

I. Introduction

Environmental issues present one of the major challenges of the world today. Human activities are major sources of aquatic pollutions; rapid climate change and the decrease in the proportions of drinking water on the planet are often attributed to this pollution [1, 2].

Therefore the major concern is developing low-polluting processes for treating effluents before they are released into the environment [3, 4]. So it appears urgent to seek reliable, inexpensive solutions using local materials.

Nickel and cadmium ions are among the toxic metals that affect the environment and health; the medical researchers have shown that nickel ions cause a serious allergies and rashes, while cadmium is a major cause of cancer [5-7].

Adsorption is an effective and inexpensive technology to remove heavy metals, especially by using natural adsorbents of plant origin because it has sufficient specific surface area and porosity [8-11].

But the problem posed strongly in many researches is that there is not one type of pollutant in wastewater, there are organic and inorganic pollutants all compete for effective sites located on the adsorbent surface [12, 13].

In this paper, we will study adsorption of cadmium (Cd^{2+}) and nickel (Ni^{2+}) ions form binary aqueous solution system using the local palm fibers powder (PF) as a natural adsorbent.

II. Materials and methods

II.1. Adsorbent

The adsorbent used in this study was collected from Algeria and was prepared by steps carried out by a simple method [14, 15], The PF were washed with distilled water three times and boiled for 30 min in order to remove the impurities and dried in the oven at 105 °C to constant weight; the PF were crushed before use for all the experiments.

II.2. Adsorbats

All the chemicals used were of Sigma-Aldrich reagent. Stock solution of 1000 ppm of Cd^{2+} and Ni^{2+} was prepared by dissolving weighed quantity of quantities of cadmium ($3CdSO_4.8H_2O$) and nickel ($NiSO_4.6H_2O$) hydrated sulfate salts in distilled water, and then the desired concentrations were provided with diluting the stock solution.

II.3. Characterization of PF

The morphology surface of adsorbent was analyzed by scanning electron microscopy (SEM) instrument (model XL-3 CP, Philips). Then the sample of palm fiber powder were metalized and imaged in the size of 20 µm at 10 kV.

II.4. Adsorption experiments

The Adsorption experiments were carried out in a batch system, the agents chemical effects were studied with variation of pH solution (2-8), contact times (0-180 min), initial concentrations (25-100 ppm) and temperatures (298-318 K). Flasks containing 100 mLof the binary solution and the 1g of adsorbent are placed in a reciprocating shaker with a rotating rate of 200 rpm. After adsorption, the samples are filtered to measure the residual concentration of the metals ions using an atomic adsorption spectrometry (ANALYTIK JENA AG GERMANY AAS NOVAA 350.

II.5. Adsorption Data

The percentage *R* (%) and adsorption capacity in equilibrium q_e ($mg.g^{-1}$) of metals ions eliminated by adsorption are calculated from the following equations (1) and (2):

$$R(\%) = \frac{(Ci - C_e)}{Ci} \times 100 \qquad (1)$$

$$qe = \frac{(Ci - Ce)}{m} \times V \qquad (2)$$

Where, *Ci* and *Ce* are the initial and equilibrium concentration of metals in solution ($mg.L^{-1}$), respectively. *V* is the volume of the metal solution (mL) and *m* is the PF mass (g)

III. Results and discussion

III.1. SEM analysis

The figure 1 shows the morphological study of the adsorbent surface, where the surface of PF appears heterogeneously as it consists of many pores and cracks. These characterizations contribute to the diffusion of metal ions in the surface of adsorbent.

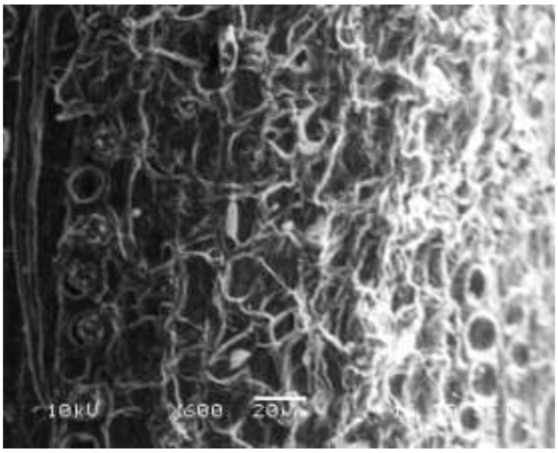

Figure 1. *SEM picture of PF sample*

III.2. Effect of adsorption factors

There are many factors affecting the adsorption process of metals ions, some of which are related to the metals solution and others related to the adsorbent [16]. Among these factors we studied the effect of pH solution, temperatures, contact time and initial concentration of the metals.

Effect of pH solution

The pH of solution is an important factor of adsorption because it affects the nature of solution and the adsorbent surface charge [17], and as it is known that the cations are attracted to negative sites from adsorbent surface and vice versa.

In this part of the work we studied the change of pH from 2 to 8 i.e. the acidity and neutral or alkaline effect of initial solution.

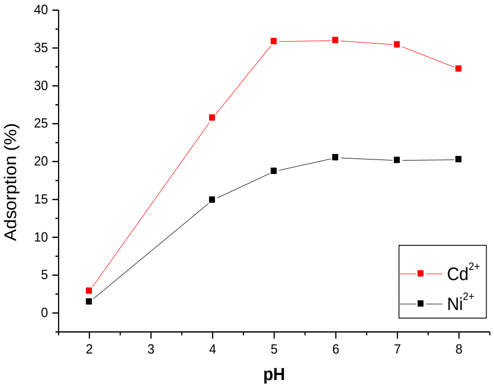

Figure 2. *Effect of pH solution on adsorption of Ni^{2+} and Cd^{2+} from PF*

The results of Figure 2 showed that the adsorption of both metals ions onto PF was weak in the pH < 5 and significantly increased with pH, where the adsorption capacity increased at pH = 6 up to 20% for Ni^{2+} and at pH= 5 it more than 34% for Cd^{2+}, due to the increase of surface negative charge, and then these ratios were stabilized despite the change of initial pH solution, and from that the optimum pH for adsorption of both metals ions is 5.5.

Close results were obtained by the researcher Srivastava et al using bagasse fly ash as an adsorbent to remove Nickel-Cadmium in binary system [18].

Effect of contact time

The contact time between adsorbent and adsorbate is also a very influencing factor on adsorption [19].

After determining the optimum pH of solution for removing the Ni^{2+} and Cd^{2+} ions, we conducted experiments to determine the optimum contact time to remove the largest amount of ions, where we studied the effect of time change as shown in Figure 3, in range from 0 to 180 min at 25°C and initial concentration of 100 ppm.

The results showed that the removal of Ni^{2+} is rapid within the first 60 min, then the removal became very slow and the adsorption rate stabilized within 20%. As for Cd^{2+} the removal went through a longer period to 90 min, but the removal rate reached more than 35%.

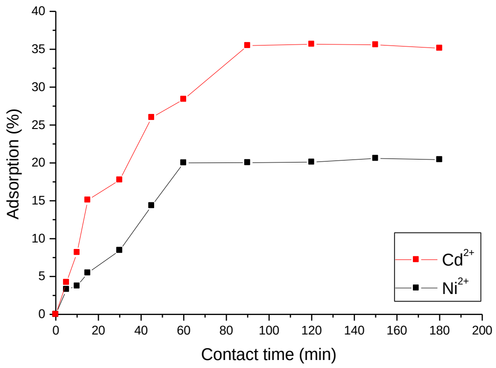

Figure 3. *Effect of Contact time on adsorption of Ni^{2+} and Cd^{2+} from PF*

Effect of Initial ions concentration

To find out the effect of the initial concentration of the metals solution, we changed the concentration from 25 to 100 ppm while fixing the pH solution at 5.5 on 25 °C.

Through the results of Figure 4, it is clear that all concentrations of Ni^{2+} and Cd^{2+} ions have maintained the same equilibrium time, and the results show that the adsorption ratios of both ions increase with increasing initial ion concentration.
Other previous studies of *Zhou et al* have proven similar results in the removal of Ni^{2+} and Cd^{2+} ions from cellulose-based hydrogels adsorbent [20].

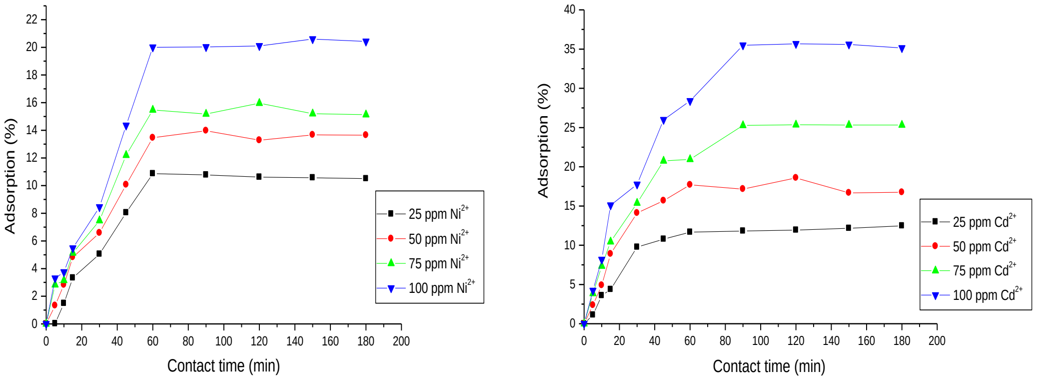

Figure 4. *Effect of initial ion concentration on adsorption of Ni^{2+} and Cd^{2+} from PF*

Effect of solution temperature

The temperature has a major affect on the adsorption process, as it affects the solubility and the diffusion of ions on the one hand, the activity of adsorption sites in the other hand, thus affecting the activity in the solid/liquid interface [21].

To study the effect of temperature on the removal of nickel and cadmium ions in a system, adsorption was studied at 298, 308 and 318 K with an initial ion concentration fixed at 100 ppm and pH=5.5.
The results shown in Figure 5 proved that the removals of both metals ions are decreased with the increase of the temperature, with the highest removal rates recorded at 298 K

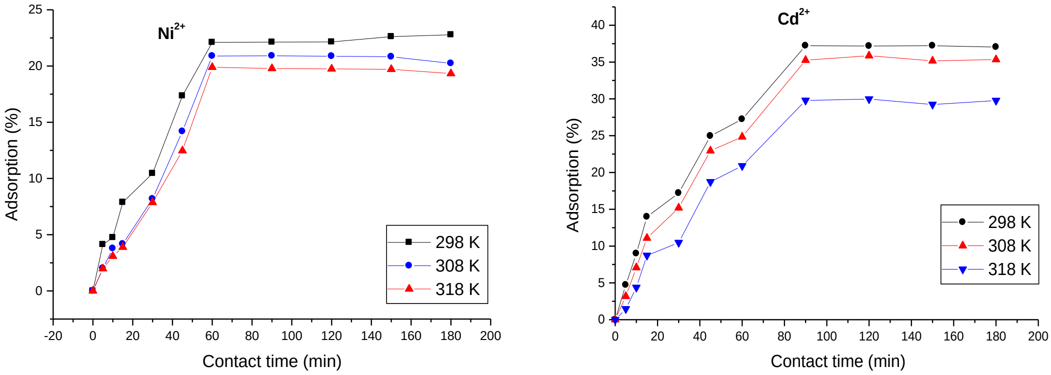

Figure 5. *Effect of temperature on adsorption of Ni^{2+} and Cd^{2+} from PF*

III.2. Adsorption isotherms

The isothermal adsorption study gives supplementary information about the adsorption mechanism of Ni^{2+} and Cd^{2+} ions in binary system from PF. We simulated adsorption of Ni^{2+} and Cd^{2+} using the Langmuir and Freundlich isotherm models because they are the two models most commonly used to explain the phenomenon of adsorption [22].

The constants of the two models were calculated by means of the following linear equations (3) for Langmuir [23] and (4) for Freundlich [24].

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{K_L q_m} \quad (3)$$

Where q_m is the maximum capacity of metals. adsorbed (mg g^{-1}) and K_L is Langmuir constant relating adsorption (L mg^{-1}).

$$\text{Ln } q_e = nLnC_e + LnK_F \quad (4)$$

Where K_F (mg.g^{-1}) (L.g^{-1})$^{1/n}$ and n are Freundlich constant related to the bonding energy and the heterogeneity factor and wich is a measure of the deviation from linearity of adsorption, respectively.

The dimensional parameter (R_L) is indicator of adsorption values calculated by the equation (5):

$$R_L = \frac{1}{1+K_L C_0} \quad (5)$$

Where C_0 is the initial concentration of the metals and K_L is the Langmuir constant relating adsorption

Figures 6 and 7 represent the linear curves of *Ce/qe* versus *Ce* and *Ln qe* versus *Ln Ce*, respectively; and the results of the constants are summarized in Table 1.

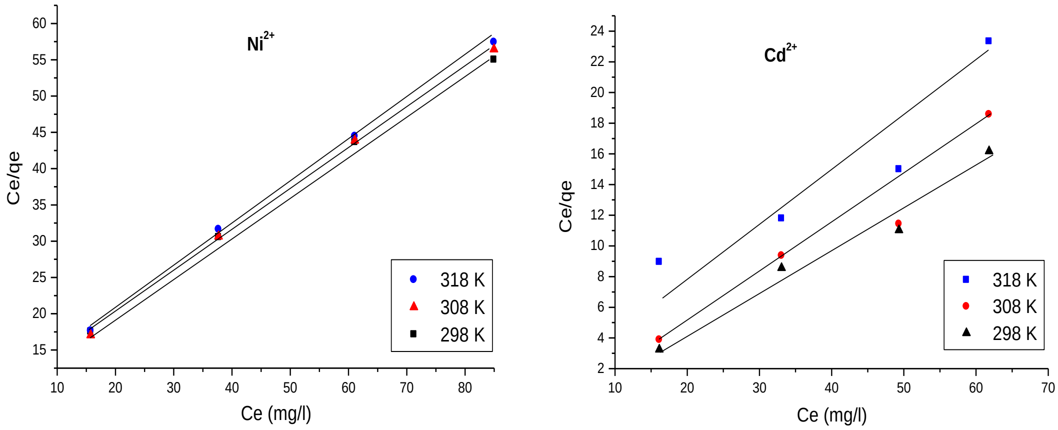

Figure 6. *Linear regression curves of the Langmuir model.*

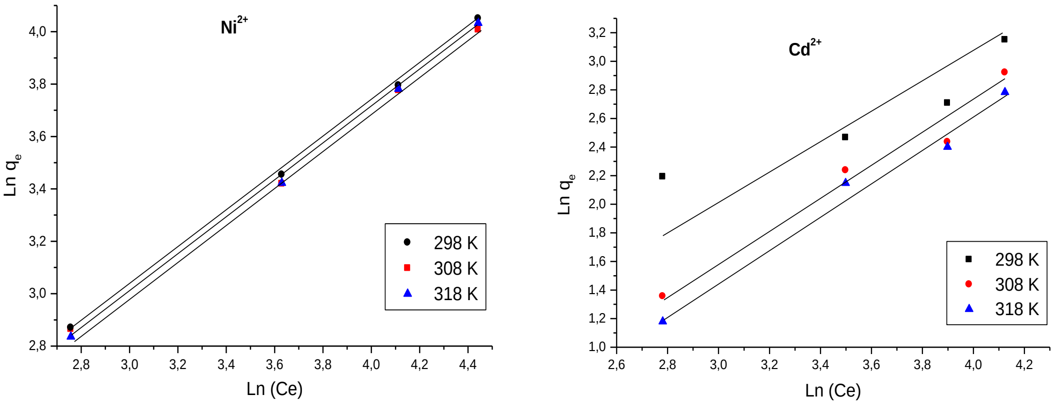

***Figure 7.** Linear regression curves of the Freundlich model.*

Through the results of the table, it was found that the correlation coefficients for both metals ions in different temperatures that Freundlich model is more descriptive of the adsorption process of ions compared to the Langmuir model.

The Freundlich model describes that the adsorption process takes place on monolayer or multilayer and the adsorbent surface is heterogeneous [25]. Also the most of the values of 1/n <1 indicating that adsorption is favorable.

On the other hand, it was observed that the maximum capacity adsorption values q_m calculated by Langmuir model of Cd^{2+} ions (3.44 mg g^{-1}) are greater than Ni^{2+} ions (1.82 mg g^{-1}), which means that the adsorbent prefers adsorption of Cd^{2+} compared to Ni^{2+}. As for the all values of ($0 < R_L < 1$) confirmed that adsorption is favorable [26].

The adsorption amounts obtained in this presented study (1.82 mg g^{-1} for Ni^{2+} and 3.74 mg g^{-1} for Cd^{2+}) are considered significant compared to the results obtained in the previous study of *Jain et al* using a sunflower plant as adsorbent, where the amounts of adsorption are 0.12 mg g^{-1} for Ni^{2+} and 0.10 mg g^{-1} for Cd^{2+}, but it was also found that the sunflower plant was more affinity with nickel [27]. Whereas, the researchers of *Srivastava et al*, found similar results to the presented study [19].

***Table 1.** Parameters of the Langmuir and Freundlich models*

Models	**Parameters**	**Ni^{2+}/ Cd^{2+}**			**Cd^{2+}/ Ni^{2+}**		
	T (K)	**298**	**308**	**318**	**298**	**308**	**318**
Langmuir	q_m (mg g^{-1})	1.8294	1.7476	1.7583	3.7411	3.4494	3.3467
	K_L (L mg^{-1})	0.0577	0.0626	0.0657	0.1672	0.2407	0.2790
	R^2	0.9986	0.9977	0.9987	0.9634	0.9276	0.9104
	R_L	0.1477	0.1377	0.1321	0.0564	0.0398	0.0346
Freundlich	***1/n***	0.6847	0.7088	0.701	1.088	1.1511	0.5629
	K_F (mg g^{-1}) (L g^{-1})$^{1/n}$	2.6077	2.3883	2.5077	0.1706	0.1369	2.0651
	R^2	0.9989	0.9991	0.9992	0.9649	0.9833	0.9211

III.3. Thermodynamic Adsorption

In this part of the work we calculate the thermodynamic parameters to understand more and evaluate the process of removing metals ions from PF adsorbent.

The thermodynamic parameters [28] recorded in Table 2 are calculated by the following equations (6), (7) and (8):

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \qquad (6)$$

$$\Delta G^\circ = -RT \, \mathrm{LnK}_d \qquad (7)$$

$$K_d = C_A / C_e \qquad (8)$$

Where, *ΔG°*, *ΔH°* and *ΔS°* are changes in Gibbs free energy (Kj mol^{-1}), enthalpy (kJ mol^{-1}) and entropy (J $mol^{-1} \cdot K^{-1}$), respectively. *R* is the gas constant (8.314 J $mol^{-1} \cdot K^{-1}$), *T* is the temperature in (K), K_d is the distribution coefficient for the adsorption. C_A and C_e are the equilibrium concentrations of metal on adsorbent and in solution, respectively.

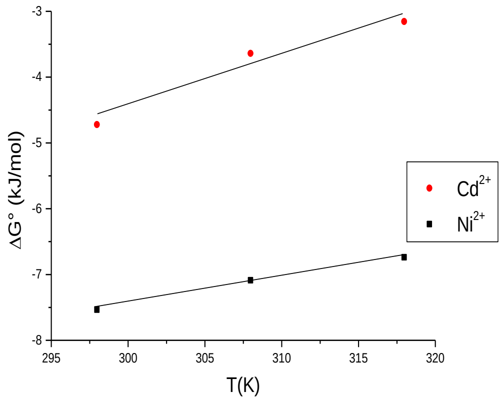

Figure 8. *Linear plots of Gibbs free energy (ΔG°) versus T (K).*

The values of ΔH° and ΔS° were determined from the slopes and intercepts of the plots of ΔG° versus T (K) (Figure 8).

The negative results of ΔG° and ΔS° indicated that the process of adsorption of both metals ions in the binary system was feasible and spontaneous [29].

The negative values of enthalpy also confirmed that the adsorption was exothermic process, where the values of $\Delta H^\circ = -19.38$ kJ mol^{-1} for Ni^{2+} and $\Delta H^\circ = -27.96$ kJ mol^{-1} for Cd^{2+}.
The absolute values of ΔH° were < 50 kJ mol^{-1}, indicate that this competitive adsorption is a physisorption type, which means that metal ions are fixed to the adsorbent surface by weak forces [30, 31].

Table 2. *Thermodynamic parameters of adsorption Ni^{2+} and Cd^{2+} on PF*

	Ni^{2+}/Cd^{2+}	**Cd^{2+}/Ni^{2+}**
ΔG° (kJ mol^{-1})		
***T*=298** K	-4.7287	-7.0957
***T*=308** K	-3.6469	-7.5415
***T*=318** K	-3.1627	-6.7455
ΔH° (kJ mol^{-1})	-19.386	-27.962
ΔS° (J mol^{-1} K^{-1})	-39.800	-78.300
R^2	0.9952	0.9537

IV. Conclusion

In light of the results obtained in this work, we conclude that dry *palm fibers* are a natural adsorbent with high abundance at a low cost, but even though its efficiency is sufficient, it is limited especially in the case of competitive adsorption, where the presence of cadmium ions affects the removal of nickel ions and vice versa, due to the competition of these cations on the same negative sites in the surface of adsorbent.
Where the results of the effect of experimental parameters on competitive adsorption between nickel and cadmium proved that the optimum pH is 5.5 and the adsorption increases with the increasing of the metal ions initial concentration, and that the adsorption increases with the contact time until it reaches the equilibrium time at 90 minutes for cadmium and 60 minutes for nickel.
The isothermal study demonstrated that the Freundlich model was more descriptive of this competitive adsorption, whereas the thermodynamic study indicated that the adsorption process was spontaneous and exothermic and that the ions were fixed with weak forces.

Recommendations

The use of *palm fiber powder* as a locally available and low-cost adsorbent for treatment of contaminated water with cadmium and nickel in binary system is a good gain for the environmental and industrial fields, and the problem of limited efficiency can be addressed in the future by research aimed at increasing the adsorption capacity of palm fiber powder with several chemical modifications.
Studies should also be carried out in order to verify the effectiveness of *palm fiber powder* at removing many organic and inorganic pollutants from single or binary systems.

V. References

1. Owa, F.W. Water pollution: sources, effects, control and management. *International Letters of Natural Sciences* 8 (2014) 1-6.
2. Chaudhry, F.N.; Malik, M.F. Factors Affecting Water Pollution: A Review. *Journal of Ecosystem & Ecography* 7 (2017) 225.
3. Duruibe, J.O.; Ogwuegbu, M.O.C.; Egwurugwu, J.N. Heavy metal pollution and human biotoxic effects. *International Journal of Physical Science* 2 (2007) 112-118.
4. Bharti, C.; Pushpa, M.; Neelam, P. Effect of Heavy Metal Ions in Water on Human Health. *International Journal of Scientific Engineering and Research* 4 (2016) 30-32.
5. Ajmal, M.; Rao, R.A.K.; Ahmad, R.; Ahmad, J. Adsorption studies on Citrus reticulata (fruit peel of orange): removal and recovery of Ni (II) from

6. electroplating wastewater. *Journal of Hazardous Materials* 79 (2000) 117-131.
7. Jadoon, S.; Malik, A. DNA Damage by Heavy Metals in Animals and Human Beings: An Overview. *Biochemistry & Pharmacology* 6 (2017) 235-242.
8. Mehta, V.; Vasanth, V.; Balachandran, C. Nickel contact dermatitis from hypodermic needle. *Indian Journal of Dermatology* 56 (2011) 237-238.
9. Ahmaruzzaman, M. Industrial wastes as low-cost potential adsorbents for the treatment of wastewater laden with heavy metals. *Advances in Colloid and Interface Science* 166 (2011) 36-59.
10. Ince, M.; Ince, O.K. An Overview of Adsorption Technique for Heavy Metal Removal from Water/Wastewater: A Critical Review. *International Journal of Pure and Applied Sciences* 3 (2017) 10-19.
11. Olayebi, O.O.; Olagboye, S.A.; Olatoye R.A.; Olufemi, A.S. Agricultural Waste Adsorbents for Heavy Metals Removal from Wastewater. *Journal of Physical and Chemical Sciences* 5 (2018) 1-5.
12. Hegazi, H.A. Removal of heavy metals from wastewater using agricultural and industrial wastes as adsorbents. *HBRC Journal* 9 (2013) 276-282.
13. Zhang, X.; Hao, Y.; Wang, X.; Chen, Z.; Li, C. Competitive Adsorption of Cadmium (II) and Mercury (II) Ions from Aqueous Solutions by Activated Carbon from Xanthoceras sorbifolia Bunge Hull. *Journal of Chemistry* 2016 (2016) 1-10 Article ID: 4326351.
14. Liu, X.; Xu, X.; Dong, X.; Park, J. Competitive Adsorption of Heavy Metal Ions from Aqueous Solutions onto Activated Carbon and Agricultural Waste Materials. *Polish Journal of Environmental Studies* 29 (2020) 749-761.
15. Ad, C.; Benalia, M.; Laidani, Y.; Elmsellem, H. Adsorptive removal of cadmium from aqueous solution by Luffa Cylindrica: Equilibrium, dynamic and thermodynamic. *Der Pharma Chemica Journal* 7 (2015) 388-397.
16. Boudaoud, A.; Djedid, M.; Benalia, M.; Ad, C.; Bouzar, N.; Elmsellem, H. Removal of nickel (II) and cadmium (II) ions from wastewater by palm fibers. *Scientific Study & Research Chemistry & Chemical Engineering, Biotechnology, Food Industry* 18 (2017) 391-405.
17. Czikkely, M.; Neubauer, E.; Fekete, I.; Ymeri, P.; and Fogarassy, C. Review of Heavy Metal Adsorption Processes by Several Organic Matters from Wastewaters. *Water* 10 (2018) 1377-1391.
18. Meng, K.; Wu, X.; Zhang, X.; Su, S.; Huang, Z.; Min, X.; Liu, Y.; Fang, M. Efficient Adsorption of the Cd(II) and As(V) Using Novel Adsorbent Ferrihydrite / Manganese Dioxide Composites. *ACS Omega* 4 (2019) 18627-18636.
19. Srivastava, V.C.; Mall, I.D.; Mishra, I.M. Equilibrium modelling of single and binary adsorption of cadmium and nickel onto bagasse fly ash. *Chemical Engineering Journal* 117 (2006) 79-91.
20. Iftekhar, S.; Ramasamy, D.L.; Srivastava, V.; Asif, M.B.; Sillanpaa, M. Review Understanding the factors affecting the adsorption of Lanthanum using different adsorbents: A critical review. *Chemosphere* 204 (2018) 413-430.
21. Zhou, Y.; Zhang, L.; Fu, S.; Zheng, L.; Zhan, H. Adsorption behavior of Cd^{2+}, Pb^{2+}, and Ni^{2+} from aqueous solutions on cellulose - based hydrogels. *BioResources* 7 (2012) 2752-2765.
22. Iftekhar, S.; Srivastava, V.; Sillanpaa, M. Enrichment of lanthanides in aqueous system by cellulose based silica nanocomposite. *Chemical Engineering Journal* 320 (2017) 151-159.
23. Khayyun, T.S.; Mseer, A.H. Comparison of the experimental results with the Langmuir and Freundlich models for copper removal on limestone adsorbent. *Applied Water Science* 9 (2019) 170-178.
24. Langmuir, I. Adsorption of gases on plane surfaces of glass, mica and platinum. *Journal of the American Chemical Society* 40 (1918) 1361-1403.
25. Freundlich, H. Adsorption in solution. *Journal of Physical Chemistry* 57 (1926) 384-410.
26. Raganati, F.; Alfe, M.; Gargiulo, V.; Chirone, R.; Ammendola, P. Isotherms and thermodynamics of CO_2 adsorption on a novel carbon-magnetite composite sorbent. *Chemical Engineering Research and Design* 134 (2018) 540-552.
27. Kumar, M.; Singh, K.A.; Sikandar, M. Study of sorption and desorption of Cd (II) from aqueous solution using isolated green algae Chlorella vulgaris. *Applied Water Science* 8 (2018) 225-236.
28. Jain, M.; Garg, V.K.; Kadirvelu, K.; Sillanpaa, M. Adsorption of heavy metals from multi-metal aqueous solution by sunflower plant biomass-based carbons. *International Journal of Environmental Science and Technology* 13 (2016) 493-500.
29. Boparai, H.K.; Joseph, M.; O'Carroll, D.M. Kinetics and thermodynamics of cadmium ion removal by adsorption onto nano zerovalent iron particles. *Journal of Hazardous Materials* 186 (2011) 458-465.
30. Gautam, R.K.; Chattopadhyaya, M.C. Chapter 5- Kinetics and Equilibrium Isotherm Modeling: Graphene-Based Nanomaterials for the Removal of Heavy Metals From Water. *Nanomaterials for Wastewater Remediation Book* (2016) 79-109.
31. Hassan, K.H.; Jarullah, A.A.; Saadi, S.K. Synthesis of Copper Oxide Nanoparticle as an Adsorbent for Removal of Cd (II) and Ni (II) Ions from Binary System. *International Journal of Applied Environmental Sciences* 12 (2017) 1841-1861.
32. Ali, R.M.; Hamad, H.A.; Hussein, M.M.; Gihan, F.; Malash, G.F. Potential of using green adsorbent of heavy metal removal from aqueous solution: Adsorption, Kinetics, isotherm, thermodynamic, mechanism and economic analysis. *Ecological Engineering* 91 (2016) 317-332.

Please cite this Article as:
Boudaoud A., Djedid M., Ad C., Guermit M., Bensafiddine F., Benalia M., Adsorption behavior of cadmium and nickel ions from binary systems (isothermal and thermodynamic studies), ***Algerian J. Env. Sc. Technology*, 9:1 (2023) 2964-2970**