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ORIGINAL RESEARCH PAPER

REMOVAL OF NICKEL (II) AND CADMIUM (II) IONS FROM WASTEWATER BY PALM FIBERS

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Abstract: The palm fibers powder (PFP) was evaluated for the selective removal of nickel (Ni) and cadmium (Cd) from wastewater. The adsorbent was characterized by means of Fourier transform infrared spectrophotometer (FT-IR), X-ray diffraction (XRD) and polarized light microscopy (POM) measurements. The adsorption process was found to be highly *p*H dependent, facilitating selective adsorption of metals tested. The best Ni (II) and Cd (II) adsorption occurred at an initial concentration of 100 mg·L^{-1}, 1 g doses of PFP, a temperature of 20 °C, and *p*H = 5, 6.5 respectively. The maximum sorption capacities obtained with PFP for the studied metal ions were 6.81 mg·g^{-1} for Cd (II) at 60 min and 4.42 mg·g^{-1} for Ni (II) at 45 min. The adsorption is best fitted in Freundlich isotherm. A comparison of kinetic models (pseudo first-order and the pseudo second-order) at different conditions showed that the pseudo second-order kinetic model correlate the experimental data well. Van't Hoff equation was used to evaluate the thermodynamic parameters (ΔH°, ΔS°, and ΔG°), which indicate that adsorption process is exothermic in nature, with the absolute values of ΔH° in range of 20-50 kJ·mol^{-1} for the two metal ions and the values of ΔS° are found to be -0.142 and -0.062 kJ·mol^{-1} for Cd (II) and Ni (II) ions respectively.

Keywords: *adsorption, cadmium, isotherms, kinetics, nickel, palm fibers, thermodynamics*

INTRODUCTION

Heavy metals are natural constituents of the environment, which is an important constituent of the requirements of the ecological system. But the accumulation of heavy metals is among the pollutants that enter the waters create serious problems causing extensive damage to the life and activities of human and the living aquatic organisms [1 – 4].

The most heavy metal have devastating effects on the ecological balance and the long term effects of which might not be yet known. Such as cadmium, nickel, mercury, lead, arsenic, and copper etc. and are extensively available in the form of oxides or sulfides or as a salt of iron, sodium, calcium, copper etc. [5]. Humans may encounter heavy metal by natural means, industrial source, or from unintended sources. Drinking water may get contaminated by use of pesticides, natural mineral deposits or inappropriate disposal of metals chemicals [6, 7].

The general purpose of heavy metals removal is to treat metal-contaminated wastewater. The excess heavy metals is removal using various physical and chemical processes such as chemical precipitation [8, 9], ion exchange [10, 11], biosorption, adsorption [12, 13], membrane filtration [14, 15], coagulation and flocculation [16, 17], electrochemical treatments etc. [18, 19].

In recent years, several agriculture wastes were explored as adsorbents in the treatment of wastewater [20 – 23]. An optimal adsorbent for the removal of organic and inorganic compounds in wastewater should have the following properties: low cost, ease of handing, environmental neutrality, high affinity and high capacity. In this context, several plants adsorbents like Sugarcane bagasse were proposed by Rao et al. (2002) [24]; Ibrahim et al. (2006) [25] as a novel adsorbent for the removal of nickel and cadmium ions from solutions. Shukla et al. (2005) [26] studied adsorption of Nickel using Maple sawdust, the nickel removing capacity of a biosorbent Pine bark [27]. A batch adsorption study of cadmium ions from aqueous solution by Luffa cylindrica has also been reported [28]. Therefore, the current study examined the adsorption capacity of palm fibers on cadmium and nickel ions removal from the aqueous solution.

The palm fibers are the fibers cellulosic consisting mostly of polysaccharides, have a general formula of $C_x(H_2O)_y$. These refer to a wide variety of polymers, initially called carbohydrates, the main ones, according to their abundance in nature, cellulose, hemicellulose, lignin etc. [29]. Palm fibers has drawn particular attention as effective biosorbent due to its low cost compared with activated carbon and its high contents of hydroxyl functional groups, the carbon content and surface area showing high adsorption potential for removal of pollutant in wastewater [30, 31].

No studies have been reported the removal of inorganic pollutants such as cadmium (Cd), nickel (Ni) in an aqueous solutions by the Algerian palm fibers powder. The objective of the present paper was to explore the possibility of using the palm fibers powder for the removal of cadmium (Cd), nickel (Ni) ions. The effects of adsorbent concentration, *p*H, contact time and initial metal ion concentration on the adsorption capacity were investigated. The rate kinetics parameters were determined. Adsorption isotherm models and thermodynamic parameters were also investigated. This research was performed in Laghouat University of Algeria.

MATERIALS AND METHODS

Preparation of adsorbent

The palm fibers (PF) were collected from Laghouat region, Algeria. The PF were washed many times with distilled water to make the PF surface free of all the dust particles adhered to it. The PF was boiled in distilled water at 100 °C, filtered then again boiled at same temperature. This boiling procedure was repeatedly performed till colorless clear solution was obtained. The boiled biosorbent was oven dried at 80 °C for 24 h, sieved for desired particle size and stored to use in biosorption study.

Preparation of adsorbate

For Ni (II) ions, a stock solution of 1000 $mg \cdot L^{-1}$ was prepared by dissolving 4.479 g of ultra-pure nickel sulfate ($NiSO_4 \cdot 6H_2O$) in distilled water. Moreover, a stock solution of Cd (II) was prepared by dissolving 2.282 g of $3CdSO_4 \cdot 8H_2O$ in distilled water (1000 $mg \cdot L^{-1}$). Different concentrations of Ni (II) and Cd (II) were prepared by appropriate dilutions of the stock standards with suitable volumes of distilled water. The *p*H of the solution was adjusted with 0.1 M NaOH or 0.1 M H_2SO_4.

Characterization experiments

Chemical characterization

In this work, the chemical characterization of the FP was determined by:
The methods outlined by Ramadevi et al. (2012) [32] were adopted to estimate the cellulose, hemicellulose and lignin content (gravimetric method) [33]. The hemicellulose content was calculated by subtracting the hollocelulose from the cellulose content [34] and the ash, % extractives contents were determined by the ASTM standard methods [35, 36].

FT-IR analysis

FT-IR spectroscopy (4200-FTIR JASCO, Japan) was used to identify the chemical functional groups and absorption bands of the studied biosorbent. About 0.1-0.2 g of plant biosorbent were ground to fine powder and mixed with potassium bromide (KBr) powder in order to form samples that were transparent to FT-IR. Solid samples were examined as translucent KBr pellets. The samples were then inserted into FT-IR spectroscopy, and spectra were recorded over the range of 400-4000 cm^{-1}.

X-ray diffraction

The elemental composition of the biosorbent was determined by using a X-Ray (Philips PW3373) diffractometer with Ni-filtered Cu Kα radiation (λ=1.54 Å), and scan from 5° to 70°.

Microscopic analysis

The surface structure of biosorbent before and after adsorption was analyzed by polarized light microscopy POM was performed using a microscope (Axioscope, Zeiss,

Oberkochen, Germany) equipped with a heating stage (THMS600 Linkam, Guilford, UK) and controller (T93 Linkam).

Adsorption experiments

The adsorption experiments were conducted under shaking conditions (300 rpm) in Erlenmeyer flasks containing 100 mL of nickel (Ni) or cadmium (Cd) solutions. All the chemicals used in the present study were of analytical grade and purchased from Sigma-Aldrich. The working solutions were prepared by diluting the stock solutions (1000 $mg \cdot L^{-1}$: $NiSO_4 \cdot 6H_2O$; $CdSO_4 \cdot 8H_2O$) to appropriate concentrations.
In the present study, five parameters as: *p*H (2–12), biosorbent dosage (B: 0.1–5 $g \cdot L^{-1}$), initial metal concentration (C: 10-150 $mg \cdot L^{-1}$), contact time (t: 1-180 min) and temperature (T: 10-60 °C) were varied. Samples were collected at regular time intervals, filtered and analyzed for the residual metal concentrations by an atomic adsorption spectrophotometer (Analytik Jena Ag Germany AAS NOVAA350).
The Ni (II) and Cd (II) uptake capacities were calculated using the mass balance equation (1) as shown below:

$$q_e = (C_0 - C_e) \times V / m \quad (1)$$

where q_e is the metal quantity adsorbed at equilibrium ($mg \cdot g^{-1}$); C_0 and C_e ($mg \cdot L^{-1}$) are the initial and equilibrium concentrations of metal in the solutions respectively; V is the volume of the aqueous phase (L); and m is the mass of adsorbent (g).
The removal of the metal (R %) was calculated using the following eqn. (2) :

$$R(\%) = (C_0 - C_e) \times 100 / C_0 \quad (2)$$

RESULTS AND DISCUSSION

Adsorbent characterizations

Chemical characterization

The chemical characterization of the palm fibers based on the three main components namely cellulose, hemicellulose and lignin are presented in Table 1. These analyses show that the palm fibers have the higher content in cellulose (56.73%) and a lesser content in lignin (17.93%). This set of data, integrated with FT-IR measurements enables a correlation between the surface composition of palm fibers and the structure. On the other hand, palm fibers showed lower fractions of ashes (1.62%) and extractives (1.5%) content.

Table 1. *Chemical composition of palm fibers (PF)*

Constituent	Weight [%]
Cellulose	56.73
Hemicellulose	17.67
Lignin	17.93
Extractives	1.5
Ashes	1.62
Other	4.55

FT-IR analysis

FT-IR is used to discover the chemical functional groups in a material as different chemical bonds have different energy adsorption bands and can give a quick and qualitative indication about the change in the chemical structure [37]. Figure 1 shows the FT-IR spectra of PFP. The adsorption bands ranging from 3450 to 3200 cm^{-1} represents –OH stretching vibrations of cellulose, hemicellulose and lignin [38]. The peaks at 2930 cm^{-1} and 2845 cm^{-1} are in conformity with C-H groups. The unique peak at 1621 cm^{-1} conforms C=O stretching from ester groups or carboxylic groups. The peak at 1264 cm^{-1} and 1035 cm^{-1} which indicates the stretching vibration of C-O. These chemical groups observed in PFP could help to attract and sequester Ni (II) and Cd (II) onto the biosorbent.

By comparing the FT-IR spectra of PFP before and after adsorption using IR correlation Table 2 there were remarkable shifts in some bands (Table 2). These shifts may be attributed to the changes in counter ions associated with carboxylate and hydroxylate anions, suggesting that acidic groups, carboxyl and hydroxyl, are predominant contributors in metal ion uptake. Moreover, decreases in intensity of peaks were observed in all the PFP loaded with Cd (II), Ni (II) IR spectrums. The reason of this is between ionized functional groups with protons or metal ions may be interact [39].

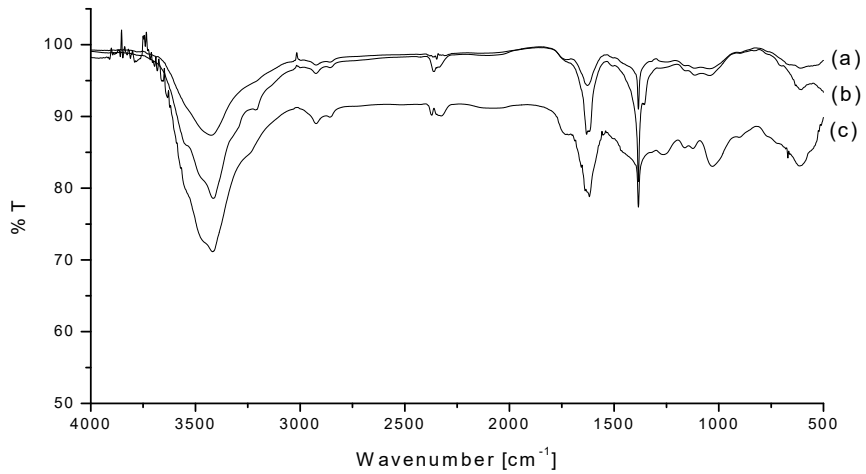

Figure 1. *FT-IR spectral characteristics of PFP (a) before and (b, c) after biosorption of Ni (II) and Cd (II)*

Table 2. *FT-IR characteristics of PFP before and after biosorption of Ni(II) and Cd(II)*

Transmission band [cm^{-1}]			Assignments
Peak before adsorption	**Peak after adsorption of Ni(II)**	**Peak after adsorption of Cd(II)**	
3440.27	3416.27	3417.24	-OH stretching
2930.3	2917.77	2919.69	C-H stretching
2845.11	2831.95	2844.48	C-H stretching
1621.87	1615.87	1617.05	C=O stretching
1387.53	1381.14	1381.74	C-O Stretching
1241.93	1251.57	1241.28	C-O Stretching
1042.33	1020.72	1031.15	C-C stretching

X-ray diffraction

The resulting X-ray (Fig. 2) was similar for the PFP before and after the adsorption of metals ions, the peaks observed are attributed to the cellulose family crystal planes [40, 41]. The values found for two more intense peaks at 16.03° and 22.06°. These planes indicate the presence of native cellulose, the main component of all the samples under study, can be found in the crystalline or amorphous form.

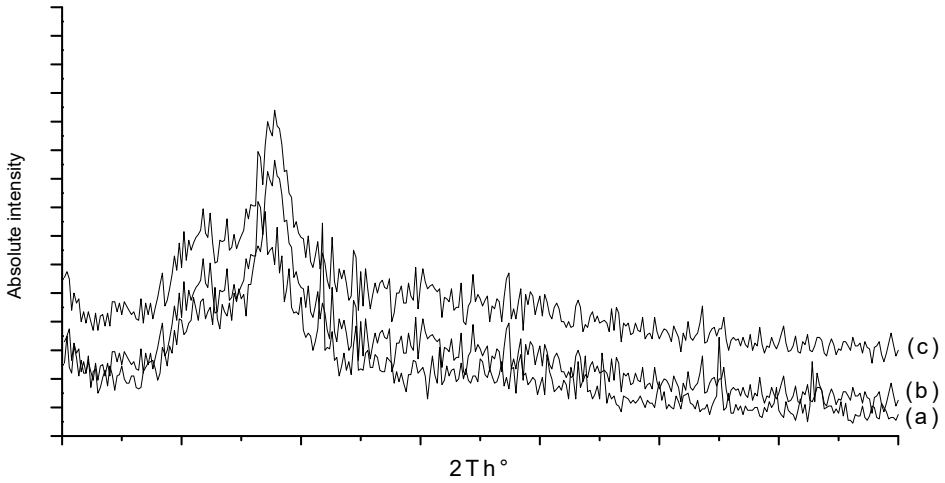

Figure 2. *X-ray diffraction patterns of PFP (a) before and (b, c) after biosorption of Ni (II) and Cd (II)*

The crystallinity index (CI) and the percentage crystallinity (X_C %), calculated according to eqn. (3), eqn. (4) [42] and presented in Table 3, collaborated with this observation: raw PFP have the higher CI (0.406), X_C % (62.73), and PFP loaded ions the less CI (0.404 for Ni and 0.389 for Cd) and X_C % (62.65 for Ni and 62.10 for Cd). This smaller CI in the PFP loaded ions is due to the higher presence of non-crystalline extractive free components.

$$Xc\% = 100 \times I_C/(I_C + I_A) \quad (3)$$

$$CI = (I_C - I_A)/I_C \quad (4)$$

where, I_C is peak intensity of crystalline phase, I_A is peak intensity of amorphous phase. The intense main peak shows the presence of highly organized crystalline structure of raw PFP, after the adsorption of Ni (II) and Cd (II) ions, the intensity of the highly organized peaks is increases slightly. This has attributed to the adsorption of Ni (II) and Cd (II) ions on the crystalline structure of the PFP surface by means of chemisorption rather than physisorption [43].

Table 3. *X-ray diffraction of PFP before and after biosorption of Ni (II) and Cd (II)*

Sample	2θ [°]		Intensity			
	Crystalline peak	Amorphous peak	I_C	I_A	X_C [%]	C.I
PFP before adsorption	22.06°	16.03°	165	98	62.73	0.406
PFP loaded with Ni (II)	22.67°	16.32°	156	93	62.65	0.404
PFP loaded with Cd (II)	22.76°	16.64°	159	97	62.10	0.389

Microscopic analysis

In order to get an idea of the microscopic structure of the biosorbent surface and to estimate the biosorption mechanisms the surface of PF before and after adsorption was determined by magnification. Figures 3 (a-c) show a photo of PF before and after adsorption respectively, indicating that all adsorbent surfaces are very rough with the presence of cracks and cavities which play a major role in the biosorption and intraparticle diffusion.

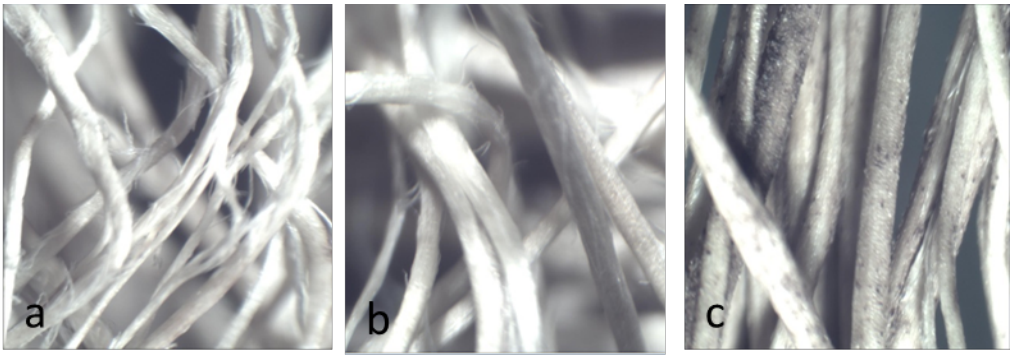

Figure 3. *Microscopic structure of PFP before (a) and after biosorption of Ni (II) (b) and Cd (II) (c)*

Adsorption studies

Effect of pH

The *p*H of the solution has a significant impact on the uptake of heavy metals, since it determines the surface charge of the adsorbent, the degree of ionization and speciation of the adsorbate, The biosorption of Ni (II) and Cd (II) ions by PFP at different *p*H values were carried out in the range of 2-12 is presented in Figure 4. In the present investigation, the rate of removal of Ni (II) and Cd (II) ions in synthetic wastewater is mainly controlled by *p*H of the solution. The optimal *p*H for Ni (II) and Cd (II) removal was 6 and 5, respectively.

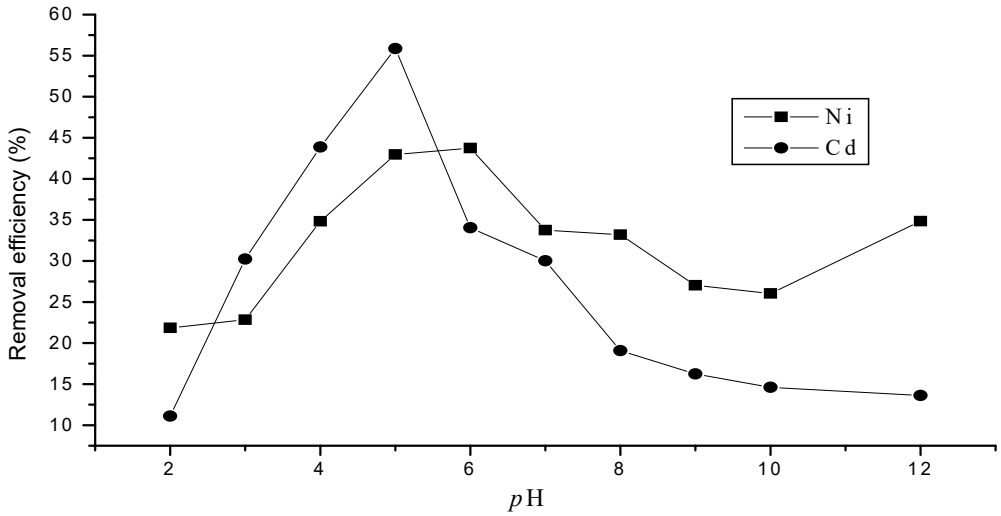

Figure 4. *Effect of pH value on the biosorption of Ni (II) and Cd (II) by PFP at 20 ºC and initial metal ions concentration of 100 mg·L^{-1}; at equilibrium time*

At *p*H higher than 7 both metals were precipitated due to the formation of hydroxides and removal due to sorption was very low. At low *p*H the concentration of protons was high and metal binding sites became positively charged repelling the Ni (II) and Cd (II) cations. With an increase in *p*H, the negative charge density on the PFP increases due to deprotonation of the metal binding sites, thus increasing metal biosorption.

Effect of contact time

After optimization of the *p*H value for the two heavy metals, the effect of contact time for the efficient removal of metal ions was studied. The removal of Ni (II) and Cd (II) ions by PFP was a very rapid process with in the first 30 min, and the Ni (II) and Cd (II) ions uptake gradually decreased after 45 min for Ni (II) and 60 min for Cd (II). The adsorption capacity was almost unchanged to 180 min. Therefore, after initial reaction, the adsorption of Ni (II) and Cd (II) ions reached equilibrium.

During the first 30 min, the most readily available.

Adsorption site and high concentration gradient might lead to the rapid metals adsorption, while the adsorption equilibrium time due to a quick exhaustion of the adsorption sites. The rate of metal removal is higher in the beginning due to a larger surface area of the adsorbent being available for the adsorption of the metals [43]. In these studies, 38 % removal of Ni (II) and 63 % removal of Cd (II) were achieved at equilibrium time (Figure 5). That equilibrium of Cd (II) removal was attained after approximately 1 h stirring in the work of Bulut and Tez. (2007) [44], and A similar equilibrium contact time was observed for the adsorption of Ni (II) on pigeon pea pod in the study of Aravind et al. (2015) [45].

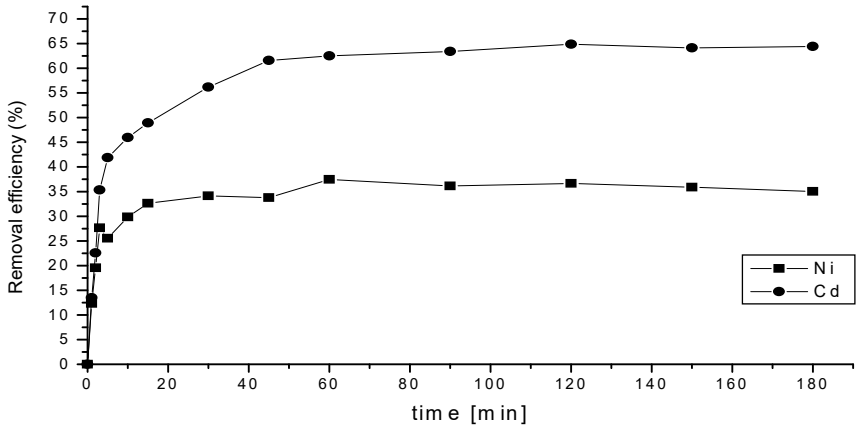

Figure 5. *Effect of contact time on the biosorption of Ni (II) and Cd (II) by PFP at 20 ºC and initial metal ions concentration of 100 mg·L^{-1}*

Effect of adsorbent dosage

The results investigating the effect of adsorbent dosage on Ni (II) and Cd (II) ions removal with an initial Ni (II) and Cd (II) ions concentrations of 100 mg·L^{-1} are shown in Figure 6 and revealed that the adsorption capacity of Ni (II) and Cd (II) ions by the PFP adsorbent increased with an increase in adsorbent dosage. It was obvious that the available exchange sites. were enlarged with increasing the adsorbent dosage; thus, the adsorption amount of Ni (II) and Cd (II) ions was increased, and the removal efficiency

was improved. The adsorption capacity was almost unchanged with the increase of adsorbent dosages ranging from 2 $g \cdot L^{-1}$ to 5 $g \cdot L^{-1}$; however, the removal efficiency increased from 5 % to 15 % for Cd (II) ions.

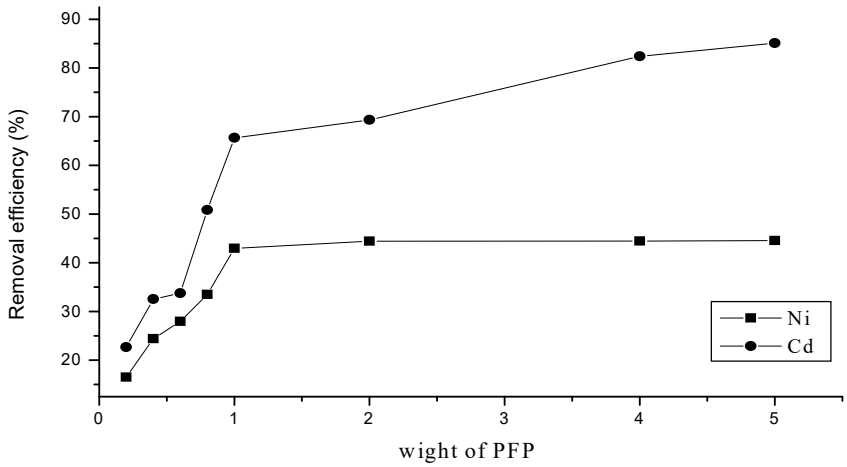

***Figure 6**. Effect of initial dose of PFP on the biosorption of Ni (II) and Cd (II) at 20 ºC and initial metal ion concentration of 100 $mg \cdot L^{-1}$ at equilibrium time*

Effect of metal ion concentration

The metal uptake mechanism is particularly dependent on the initial heavy metal concentration, Initial concentrations of 10-150 $mg \cdot L^{-1}$ of metal ions were selected for the comparative study for the removal of Ni (II) and Cd (II): at low concentrations, metals are adsorbed by specific sites, while with increasing metal concentrations the specific sites are saturated and the exchange sites are filled [46].

Figure 7 shows the effect of metal concentration on the percent removal of Ni (II) and Cd (II) ions respectively. It is clear that with increasing initial concentrations, the percent metal removal increases.

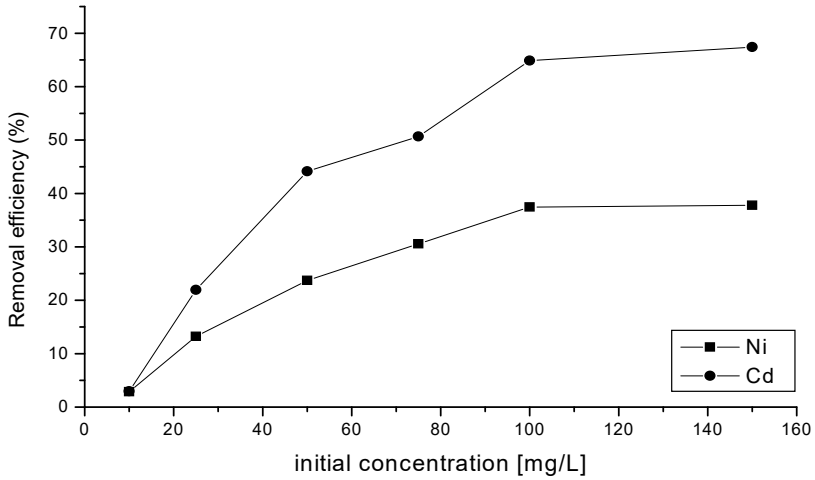

***Figure** 7. Effect of initial concentration on the Biosorption of Ni (II) and Cd (II) by PFP at 20 ºC at equilibrium time*

Adsorption isotherms

Biosorption isotherms describe how adsorbate interacts with biosorbent and equilibrium is established between adsorbed metal ions on the biosorbent and the residual metal ions in the solution during the surface biosorption. Equilibrium isotherms are measured to determine the capacity of the biosorbent for metal ions.
The equilibrium data was analyzed using two parameter isotherms: Langmuir and Freundlich.
The Langmuir model is expressed by the linearized eqn. (5) [47]:

$$1/q_e = 1/q_{max} + 1/(bC_e \times q_{max}) \quad (5)$$

where q_{max} is the maximum amount of metal sorbed (mg·g^{-1}), b is a constant related to the energy of sorption.
The Freundlich model is represented by the linearized equation as follows [48]:

$$Ln(q_e) = Ln(K_f) + 1/nLn(C_e) \quad (6)$$

where K_f is the biosorption equilibrium constant, representative of the sorption capacity, and n is a constant indicative of biosorption intensity. It has been suggested that n is the heterogeneity factor.
The estimated adsorption parameters by the different models Langmuir, Freundlich isotherms are shown in Table 4. The *1/n* values are between 0 and 1 (n>1), indicating that the adsorption of both metal ions onto PFP is a physical process [48] and the values of correlation coefficient (R^2) are regarded as a measure of the goodness-of-fit of experimental data on the isotherm's models. The applicability of the two isotherm's models for the present data approximately follows the order: Freundlich > Langmuir, in case of Ni (II) and Cd (II) ions. The adsorption results obtained are best described by the Freundlich isotherm model.

Table 4. *The conform parameters of Langmuir and Freundlich equation for biosorption of Ni (II) and Cd (II) ions on PFP*

Metal ions	Langmuir model			Freundlich model		
	q_{max} [mg·g^{-1}]	K_L [L·mg^{-1}]	R^2	K_f [mg·g^{-1}]	1/n	R^2
Cd (II)	6.81	0.015	0.960	0.870	0.54	0.990
Ni (II)	4.42	0.294	0.916	5.058	0.1	0.937

As shown in the Table 4, the maximum sorption capacities obtained with PFP for the studied metals were 6.81 mg·g^{-1} for Cd (II) and 4.42 mg·g^{-1} for Ni (II); It can be observed that the nickel uptake is less than cadmium uptake, Similarly, Fawzy et al., 2016 [49] revealed that the affinity order of Cd (II) was higher than Ni (II) when studying the adsorption of heavy metals on sugar beet pulp.
Table 5 presents the comparison of adsorption potential of cadmium and nickel removal from aqueous solution on similar materials. It can be observed the obtained values are within the range of other materials that have been previously reported in literature as: Maple sawdust [26], Zea maize leaves [23], Raw corn stalk [13], Luffa cylindrical [28], Coconut shell [50], Sugarcane bagasse [24, 26], Pine bark [27], Maize bran [51] and Teak tree bark powder [52]. The adsorption by PFP is found to be higher than most of

the other agricultural adsorbents. It shows that PFP is a potent for the effective removal of Cd (II) and Ni (II) from aqueous solutions through biosorption.

Table 5. *Comparison of different agricultural biosorbents for Cd (II) and Ni (II) removal*

Adsorbent	q_m [mg·g^{-1}]		References
	Ni (II)	Cd (II)	
Maple sawdust	0.29	--	[26]
Zea maize leaves	--	0.44	[23]
Raw corn stalk	--	3.39	[13]
Luffa cylindrica	--	5.46	[28]
Coconut shell	1.56	--	[50]
Sugarcane bagasse	2.0	6.79	[24,26]
Palm fibers powder	4.42	6.81	This study
Pine bark	6.28	--	[27]
Maize bran	--	7.4	[51]
Teak tree bark powder	9.6	--	[52]

Adsorption kinetics

Kinetic experiments were conducted under optimized conditions and samples were withdrawn at regular intervals for analysis. Pseudo-first order, Pseudo-second order model have been used for modeling the kinetic data of Ni (II) and Cd (II) biosorption.
The pseudo-first-order rate expression is given by the linearized equation as follows [53]:

$$\mathrm{Ln(qe-qt)} = Ln(q_e) - k_1 t \quad (7)$$

The pseudo-second-order equation is given by the following linearized form and assuming a rate of site occupation proportional to the square of the number of unoccupied sites [53]:

$$\mathrm{t/q_t} = 1/k_2 q_e^2 + t/q_e \quad (8)$$

where, *qt* is the solid phase concentration at time (*t*) in (mg·g^{-1}); k_1 is the rate constant of Lagergren first-order adsorption (min^{-1}) and k_2 is the rate constant of second order adsorption (g·mg^{-1}·min^{-1}).
The pseudo-second-order rate expression suggests that the adsorption is probably controlled by the chemical process, involving valency forces through the sharing or exchange of electrons between the adsorbent and adsorbate as covalent forces [53].
During the present study, the three different kinetic models were applied for Ni (II) and Cd (II) respectively. The estimated model and the related statistic parameters are reported in Table 6. Based on linear regression ($R^2 > 0.99$) values, the kinetics of Ni (II) and Cd (II) adsorption on to the adsorbent can be described well by second-order equation.
The pseudo-second order model was selected for all further studies. This is rather as a compared with the results obtained with other adsorbents referred to literature (Table 5).

***Table 6**. Kinetic parameters for biosorption of Ni (II) and Cd (II) ions on PFP at 20 °C*

Metal ions	qe (exp.) [mg·g^{-1}]	Pseudo-first-order			Pseudo-second-order		
		qe (cal.) [mg·g^{-1}]	k_1 [min^{-1}]	R^2	qe (cal.) [mg·g^{-1}]	k_2 [g·mg^{-1}· min^{-1}]	R^2
Cd (II)	6.486	5.09	0.082	0.950	6.430	0.120	0.998
Ni (II)	3.746	2.423	0.117	0.886	3.736	0.041	0.996

Adsorption thermodynamics

Thermodynamic parameters such as the free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) changes during adsorption can be evaluated from the Equations (9) and (10) below as in [54]:

$$\Delta G^\circ = -RTLnK_C \quad (9)$$

$$LnK_C = -(\Delta H^\circ / RT) + (\Delta S^\circ / R) \quad (10)$$

where K_C is the equilibrium constant, ΔG°, ΔH° and ΔS° are changes in Gibbs free energy (kJ·mol^{-1}), enthalpy (kJ·mol^{-1}) and entropy (J·mol^{-1}·K^{-1}), respectively. *R* is the gas constant (8.314 J·mol^{-1}·K^{-1}) and *T* is the temperature in (K)
Equilibrium constant (Kc) was calculated from the following relationship [54]:

$$K_C = C_{Ae}/C_e \quad (11)$$

where, C_{Ae} and C_e are the equilibrium concentrations of metal (mg·L^{-1}) on adsorbent and in solution, respectively.

***Table 7**. Thermodynamic parameters for adsorption of Ni (II) and Cd (II) on PFP*

Metal ions	ΔH° [kJ·mol^{-1}]	ΔS° [kJ·mol^{-1}]	ΔG° [kJ·mol^{-1}]			R^2
			283 K	293 K	333 K	
Cd (II)	- 45.760	-0.142	-0.720	-3.550	-5.670	0.945
Ni (II)	-20.845	-0.062	-0.702	-1.889	-4.174	0.900

A plot of Ln K_C versus 1/T was found to be linear; ΔH° and ΔS° were determined from the slope and intercept of the plot, respectively. The negative values of ΔG° indicate the process to be feasible and adsorption to be spontaneous. The negative values of ΔH° indicate that the adsorption interaction of metals ions and PFP is exothermic and the negative values of ΔS° indicate that the adsorbed species are more ordered on the surface during the adsorption (Table 7). This is consistent with the results of other literature as Erdem et al. (2005) [55], Singh et al. (2006) for the adsorption of Cd (II) and Satish et al. (2012) [56], similarly reported that the adsorption of Ni (II) is spontaneous and exothermic.

CONCLUSIONS

In this work, we conducted a comprehensive study of the adsorption of cadmium and Nickel ions on Palm Fibers Powder.

The adsorption kinetics of both metal ions on PFP is fast; the equilibrium is reached after a contact time of about 45 min for Ni (II) and 60 min for Cd (II) for the initial concentration 100 $mg \cdot L^{-1}$. The results showed that the change in *p*H has influence on the adsorption of metals ions on the PFP and therefore the variation of the concentration selected is important (the initial *p*H varies). The retained concentration increases with the initial concentration for both metal ions.
The study of the variation of the retention concentration of metal ions in terms of the temperature indicates that this adsorption is slightly exothermic.
The maximum adsorption capacity of metal ions adsorbed per 1 g of the PFP was about 6.81 $mg \cdot g^{-1}$ for Cd (II) and 4.42 $mg \cdot g^{-1}$ for Ni (II).
The values of all the isotherm model constants indicate a favorable adsorption of metal ions on PFP and an adsorption process involved both chemisorption and physisorption.
Thermodynamic parameters ($\Delta G°$, $\Delta H°$ and $\Delta S°$) showed that the adsorption process is spontaneous and exothermic in nature.
We can therefore conclude that PFP has great potential adsorbent to metal ions.
In the view of these results, it can be concluded that the PFP can be utilized as a low cost and effective adsorbent in removal of Cd (II) and Ni (II) ions from aqueous solutions.
Further future work will be comparative study to test the modified PFP at a wastes in adsorption of the inorganic pollutants from water.

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REFERENCES

1. Baby, J., Raj, J.S., Biby, E.T., Sankarganesh, P., Jeevitha, M.V., Ajisha, S.U., Rajan, S.S.: Toxic effect of heavy metals on aquatic environment, *International Journal of Biological and Chemical Sciences*, **2010**, **4**, 939-952;
2. Islam, M.S., Tanaka, M.: Impacts of pollution on coastal and marine ecosystems including coastal and marine fisheries and approach for management: a review and synthesis, *Marine Pollution Bulletin*, **2004**, **48**, 624-649;
3. Duruibe, J.O., Ogwuegbu, M.O.C., Egwurugwu, J.N.: Heavy metal pollution and human biotoxic effects, *International Journal of Physical Sciences*, **2007**, **2**, 112-118;
4. Sardar, K., Ali, S., Hameed, S., Afzal, S., Fatima, S., Shakoor, M.B., Bharwana, S.A., Tauqeer, H.M.: Heavy Metals Contamination and what are the Impacts on Living Organisms, *Greener Journal of Environmental Management and Public Safety*, **2013**, **2**, 172-179;
5. Singh, S., Kumar, M.: Heavy metal load of soil. Water and vegetables in periurban Delhi, *Environmental Monitoring and Assessment*, **2006**, **120**, 79-91;
6. Matta, G., Gjyli, L.: Mercury, lead and arsenic: impact on environment and human health, *Journal of Chemical and Pharmaceutical Sciences*, **2016**, **9**, 718-725;
7. Bradl, H.B., Heavy Metals in the Environment: Origin, Interaction and Remediation, *Elsevier Academic Press, Amsterdam/Boston*, 1St Ed, **2005**, 282;
8. Gonzalez-Munoz, M.J., Rodriguez, M.A., Luquea, S., Alvareza, J.R.: Recovery of heavy metals from metal industry waste waters by chemical precipitation and nanofiltration, *Desalination*, **2006**, **200**, 742-744;

9. Mahmood, M.B., Balasim, A.A., Najah, M.A.: Removal of Heavy Metals Using Chemicals Precipitation, *Engineering & Technology Journal*, **2011**, **29**, 595-612;
10. Budak. T.B.: Removal of Heavy Metals from Wastewater Using Synthetic Ion Exchange Resin, *Asian Journal of Chemistry*, **2013**, **25**, 4207-4210;
11. Bai, Y., Bartkiewicz, B.: Removal of Cadmium from Wastewater Using Ion Exchange Resin Amberjet 1200H Columns, *Polish Journal of Environmental Studies*, **2009**, **18**, 1191-1195.
12. Reddad, Z.: Adsorption of several metal ions onto low-cost biosorbent: kinetic and equilibrium studies, *Environmental science & technology*, **2002**, **36**, 2067-2073;
13. Zheng, L., Dang, L., Yi, X., Zhang, H.: Equilibrium and kinetic studies of adsorption of Cd (II) from aqueous solution using modified corn stalk, *Journal of hazardous materials*, **2010**, **176**, 650-656;
14. Juang, R.S., Shiau, R.C.: Metal removal from aqueous solutions using chitosan-enhanced membrane filtration, *Journal of Membrane Science*, **2000**, **165**, 159-167;
15. Maximous, N., Nakhla, G., Wan, W., Wong, K.: Preparation, characterization and performance of Al_2O_3/PES membrane for wastewater filtration, *Journal of Membrane Science*, **2009**, **341**, 67-75;
16. Lopez-Maldonado, E.A., Oropeza-Guzman, M.T., Jurado-Baizaval, J.L., Ochoa-Terán, A.: Coagulation – flocculation mechanisms in wastewater treatment plants through zeta potential measurements, *Journal of hazardous materials*, **2014**, **279**, 1-10;
17. Amuda, O., Amoo, I., Ipinmoroti, K., Ajayi, O.: Coagulation / flocculation process in the removal of trace metals present in industrial wastewater, *Journal of Applied Sciences and Environmental Management*, **2006**, **10**, 159- 162;
18. Sousa, F.W., Oliveira, A.G., Moreira, S.A., Cavalcante, R.M., Rosa, M.F., Nascimento, R.F.: Use of green coconut shells as adsorbent in the removal of heavy metals, *Química Nova Journal*, **2008**, **30**, 1153-1157;
19. Chen, G.: Electrochemical Technologies in Wastewater Treatment, *Separation and Purification Technology*, **2004**, **38**, 11-41;
20. Marshall, W.E., Johns, M.M.: Agricultural By-products as Metal Adsorbents: Sorption Properties and Resistance to Mechanical Abrasion, *Journal of Chemical Technology and Biotechnology*, **1996**, **66**, 192- 198;
21. Hegazi, H.A.: Removal of heavy metals from wastewater using agricultural and industrial wastes as adsorbents, *HBRC Journal*, **2013**, **9**, 276-282;
22. Khan, N.A., Ibrahim, S., Subramaniam, P.: Elimination of Heavy Metals from Wastewater Using Agricultural Wastes as Adsorbents, *Malaysian Journal of Science*, **2004**, **23**, 43-51;
23. Uzma, N.: Bioremediation of cadmium (II) from aqueous solution using agricultural waste: zea maize leaves, *European Chemical Bulletin*, **2013**, **2**, 993-998;
24. Rao, M., Parwate, A.V., Bhole, A.G.: Removal of Cr^{6+} and Ni^{2+} from aqueous solution using bagasse and fly, *waste management journal*, **2002**, **22**, 821-830;
25. Ibrahim, S.C., Hanafiah, M.A.K.M., Yahya, M.Z.A.: Removal of Cadmium form aqueous solutions by adsorption on sugarcane bagasse, *American-Eurasian Journal of Agricultural & Environmental Sciences*, **2006**, **1**, 179-184;
26. Shukla, S.S., Yu, L.J., Dorris, K.L., Shukla, A.: Removal of nickel from aqueous solutions by sawdust, *Journal of Hazardous Materials*, **2005**, **121**, 243-246;
27. Reddad, Z.: Adsorption of several metal ions onto low-cost biosorbent: kinetic and equilibrium studies, *Environmental science & technology*, **2002**, **36**, 2067-2073;
28. 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*, **2015**, **7**, 388-397;
29. Al-Khanbashi, A., Al-Kaabi, K., Hammami, A.: Date palm fibers as polymeric matrix reinforcement: fiber characterization, *Polymer Composites*, **2005**, **26**, 486-497;
30. Riahi, K., Thayer, B.B., Mammou, A.B., Ammar, A.B., Jaafoura, M.H.: Biosorption characteristics of phosphates from aqueous solution onto *Phoenix dactylifera* L. date palm fibers, *Journal of hazardous materials*, **2009**, **170**, 511-519;
31. Mahmoud, M.A., El-Halwany, M.M.: Kinetics and Thermodynamics of Date Palm Fibers (DPF) as Agricultural Waste Materials, *Journal of Chromatography & Separation Techniques*, **2013**, **4**, 2157-7064;
32. Ramadevi, P., Dhanalakshmi, S., Srinivasa, C.V., Basavaraju, B.: Effect of Alkali Treatment on Water Absorption of Single Cellulosic Abaca Fiber, *Bioresource Technology*, **2012**, **7**, 3515-3524;

33. Oladele, I.O., Omokafe, M.S., Olusegun, S.J.: Influence of Chemical Treatment on the Constituents and Tensile Properties of Selected Agro-Fibres, *The West Indian Journal of Engineering*, **2016**, **38**, 4-12;
34. Kalia, S., Kaith, B.S., Kaur, I.: Pretreatments of natural fibers and their application as reinforcing material in polymer composites - A review, *Polymer Engineering & Science*, **2009**, **49**, 1253-1272;
35. ASTM. Standard D-1102-84, 1984, Stander test method for ash in wood, *West Conshohocken, PA: ASTM International*, **2001**;
36. NREL CAT Task Laboratory Analytical procedure # 010, *Standard method for the determination of extractives in biomass*, **1994**;
37. Romera, E., Gonzalez, F., Ballester, A., Blazquez, M., Munoz, J.: Comparative study of biosorption of heavy metals using different types of alga, *Bioresource Technology*, **2007**, **98**, 3344-3353;
38. Jonoobi, M., Niska, K.O., Harun, J., Misra, M., Shakeri, A., Misra, M., Oksman, K.: Chemical composition, crystallinity, and thermal degradation of bleached and unbleached kenaf bast (*Hibiscus cannabinus*) pulp and nanofibers, *Bioresource Technology*, **2009**, **4**, 626-639;
39. Cheraghi, E., Ameri, E., Moheb, A.: Adsorption of cadmium ions from aqueous solutions using sesame as a low-cost biosorbent: kinetics and equilibrium studies, *International Journal of Environmental Science and Technology*, **2015**, **12**, 2579-2592;
40. Chauhan, A., Kaith, B.: XRD and Physicochemical Evaluation of Hibiscus sabdariffa Cellulose-Butyl Acrylate-co-vinyl Monomer Graft, *American Journal of Biochemistry and Molecular Biology*, **2013**, **3**, 61-70;
41. Park, S., Baker, J.O., Himmel, M.E., Parilla, P.A., Johnson, D.K.: Research Cellulose crystallinity index: measurement techniques and their impact on interpreting cellulase performance, *Biotechnology for Biofuels*, **2010**, **3**, 1-10;
42. Kaith, B.S., Singha, A.S., Sharma, K.S.: Synthesis of graft co-polymers of binary vinyl monomer mixtures and flax fiber using FAS-KPS Redox system, *International Journal of Chemical*, **2004**, **2**, 37-43;
43. Abdel-Ghani, N.T., El-Chaghaby, G. A.: Sorption for metal ions removal from aqueous solutions: a review of recent studies, *International Journal of Latest Research in Science and Technology*, **2014**, **3**, 24-42;
44. Bulut, Y., Tez, Z.: Removal of heavy metals from aqueous solution by sawdust adsorption, *Journal of Environmental Sciences*, **2007**, **19**, 160-166;
45. Aravind, J., Lenin, C., Nancyflavia, C., Rashika, P., Saravanan, S.: Response surface methodology optimization of nickel (II) removal using pigeon pea pod biosorbent, *International Journal of Environmental Science and Technology*, **2015**, **12**, 105-114;
46. Nurdin, S., Roslan, A., Seddiq M.,Syafiqah, A.A., Khairuddin, A., Athirah, H.: Activated Carbon (RMAC) for Removal of Cd (II), Ni (II) and Cu(II) from Wastewater: Kinetics and Adsorption Equilibrium, *International Journal of Chemical Engineering and Applications*, **2015**, **6**, 105-110;
47. Langmuir, I.: The constitution and fundamental properties of solids and liquids, *American Chemical Society*, **1916**, **38**, 2221-2295;
48. Freundlish, H.: Over the adsorption in solution, *Journal of Physical Chemistry*, **1906**, **57**, 385-470;
49. Fawzy, M., Nasr, M., Adel, S., Nagy, H., Helmi, S. : Environmental approach and artificial intelligence for Ni (II) and Cd (II) biosorption from aqueous solution using *Typha domingensis* biomass, *Ecological Engineering*, **2016**, **95**,743-752;
50. Sousa, F.W., Oliveira, A.G., Moreira, S.A., Cavalcante, R.M., Rosa, M.F., Nascimento, R.F. :Use of green coconut shells as adsorbent in the removal of heavy metals, *Química Nova Journal*, **2008**, **30**, 1153-115;
51. Singh, K.K., Rupainwar, D.C., Hasan, S.H.: Low cost bio-sorbent 'maize bran' for the removal of cadmium from wastewater, *Journal Indian Chemical Society*, **2005**, **82**, 342-346;
52. Satish, P., Renukdas, S., Patel, N.: Kinetic and thermodynamic study of removal of Ni (II) ions from aqueous solution using low cost adsorbents, *International Journal of Environmental Science*, **2012**, **3**, 322-340;
53. Ho, Y.S., McKay, G.: A comparison of chemisorption kinetic models applied to pollutant removal on various sorbents, *Process Safety and Environmental Protection* (Trans. I chem. E., Part B), **1998**, **76**, 332-340;
54. Sujana, M.G., Pradhan, H.K., Anand, S.: Studies on sorption of some geometrical for fluoride removal from aqueous solutions, *Journal of Hazardous Materials*, **2009**, **161**, 120-125;

55. Erdem, M., Duran, H., Şahin, M., Ozdemir, I.: Kinetics, thermodynamics, and isotherms studies of Cd(II) adsorption onto grape stalk, *Journal of Desalination and Water Treatment*, **2015**, **54**, 3348-3357;
56. Singh, K.K., Singh, A.K., Hasan, S.H.: Low cost bio-sorbent 'wheat bran' for the removal of cadmium from wastewater: Kinetic and equilibrium studies, *Bioresource Technology*, **2006**, **97**, 994-1001.