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Removal of Cd Ions from Aqueous Solution onto functionalized nano-fibers derived from *Phragmites communis* Trin.

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ABSTRACT

In this work, a series of batch laboratory experiments were conducted in order to investigate the feasibility of functionalized nano-fibres derived from Phragmites communis Trin (FNF-PCT) for the removal of Cadmium ions from aqueous solution by the adsorption process. Investigation was carried out by studying the influence of initial solution pH, adsorbent dosage and initial concentration of Cd ions and temperature. The single component equilibrium data was analysed using Langmuir, Freundlich, Dubinin-Radushkevich and Temkin adsorption isotherms. The results showed that equilibrium was reached within 15 min. The highest adsorption capacity was at pH 4.5. The experimental isotherm data were analysed and modelled. The maximum adsorption capacity, Langmuir's q_{max}*, was 2,51 mmol/g at room temperature from (30°C). The enthalpy* $\Delta H°$ *and entropy* $\Delta S°$ *values were respectively estimated at -51.57 kJ* mol^{-1} *and -157.89 J* K^{-1} mol^{-1} *for the process, the negative value of* $\Delta G°$ *indicates that the adsorption of Cd(II) ions on (FNF-PCT) is a spontaneous process. Three simplified kinetic models including a pseudo-first-order equation, pseudo-second-order equation and intraparticle diffusion equation were selected to follow the adsorption process. Kinetic parameters, rate constants, equilibrium sorption capacities and related correlation coefficients, for each kinetic model were calculated and discussed. It was shown that the adsorption of Cd(II) could be described by the pseudo-second order equation, suggesting that the adsorption process is presumable a physisorption.*

Keywords: functionalized nano-fibres, *Phragmites communis* Trin , Adsorption, Isotherm, Kinetics.

INTRODUCTION

Contamination of the environment with hazardous and toxic compounds such as heavy metals is one of the serious public problems today [1]. Heavy metals are essentially non-biodegradable and hence are accumulated in living organisms [2]. Cadmium is one of the heavy metals with a greatest potential hazard to humans and environment [3]. Cadmium may come from various industrial sources such as metal plating, metallurgical alloying, mining, ceramics and other industrial activities [4]. Its toxic effects are well documented. Diseases such as renal dysfunction (Fanconi syndrome), bone degradation (itai–itai syndrome), cancer, hypertension, liver damage, and blood damage [5-6-7]. Development of technically simple and economically attractive methods of industrial waste purification is one of the most important priorities of the 21st century [8]. There are several methods for treating Cadmium contaminated effluents such as ion exchange, chemical precipitation, oxidation, reduction, and reverse osmosis [9-10-11-12]. However, many of these approaches can be less cost effective or difficult for practical use. Also, most of these are ineffective or excessively expensive when the metal concentrations are less than 100 mg L^{-1} [13]. Since then, search is going on for low-cost and easily available adsorbent and this has led to the investigation of materials from agricultural and biological origin along with industrial by-products that can be used as adsorbents. The Biosorption has distinct advantages over the conventional methods as it is non-polluting and can be highly selective, more efficient, easy to operate, and hence cost effective for treatment of large volumes of wastewater containing low metal concentration [14]. Several plant derived materials such as orange peel [15], wheat based materials [16], brown seaweed [17], brown algae [18] eucalyptus bark [19], sugar beet pulp [20] coconut copra meal [21], olive stone [22] Hydrilla verticillata biomass [23], and papaya Seed [24] have been studied for their biosorptive capacity in the removal of cadmium and other heavy metals from aqueous solutions.

In this work, functionalized nano-fibres derived from *Phragmites communis* Trin (FNF-PCT), an abundant, inexpensive and unexploited plant material, has been used as adsorbent for removing Cd(II) from aqueous solution by batch. The influences of various operating parameters such as initial metal concentration, contact time, adsorbent dose, and initial pH of solution on the Cd(II) Biosorption were investigated. The adsorption capacity of (FNF-PCT) toward cadmium was investigated and adsorption isotherms were determined.

MATERIALS AND METHODS

2.1. Materials

Adsorption experiments were conducted by varying pH, contact time, adsorbent dose and Cadmium concentration. The experiments were carried out in 250 ml Erlenmeyer flasks and the total volume of the reaction mixture was kept at 100 ml. The equilibrium concentrations of the solution samples were analysed using UV-Vis spectrophotometer (Model SHIMADZU 1800) using 1,2-dihydroxyanthraquinone-3-sulphonic acid sodium salt as a spectrophotometer reagent, Standard calibration curve was prepared by recording the absorbance values of various concentration of Cadmium at maximum absorbance of wavelength (422 nm). A HANNA instrument pH meter was used for pH measurements, a magnetic stirrer was used to agitating the samples.

2.2. Adsorbent

The *Phragmites communis* Trin leaflets were collected from Ouargla (Algeria), They were gathered into clean plastic bags. Washed with double distilled water and laid flat on clean table to dry. Dry fibers were grounded with grinder. After grounded, the cellulose was extracted by using (50/50 v/v) of ethanol/acetone to remove extractive, later treated with (7.5% NaOH) solution, the residue washed several times by ionized water, obtained cellulose hydrolyzed using H_2SO_4 (64%), finally, nano-cellulose produced oxidized by (4% NaIO4) solution in the dark at (pH =4) for three days, finally washed by ionized water, the product obtained is dialdehyde nano-cellulose.

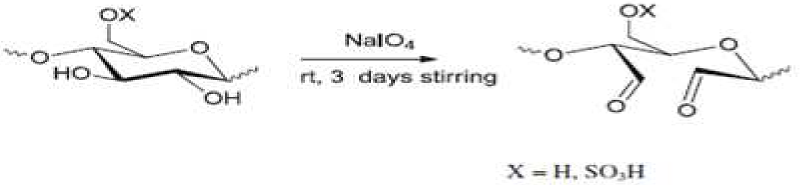


Figure 1: Reaction of nano-cellulose oxidation

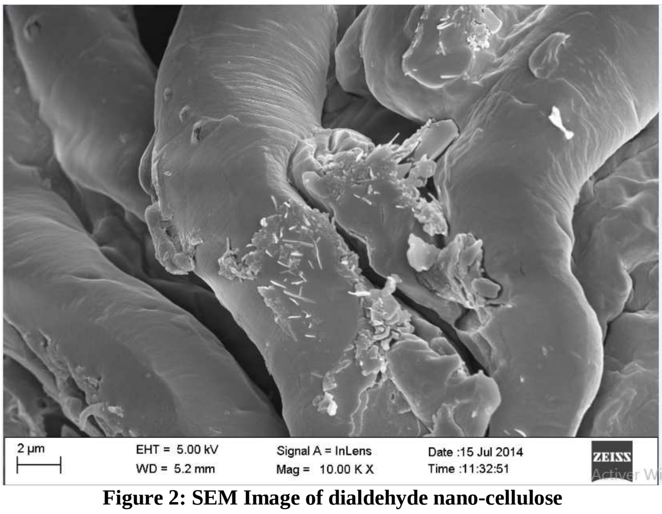
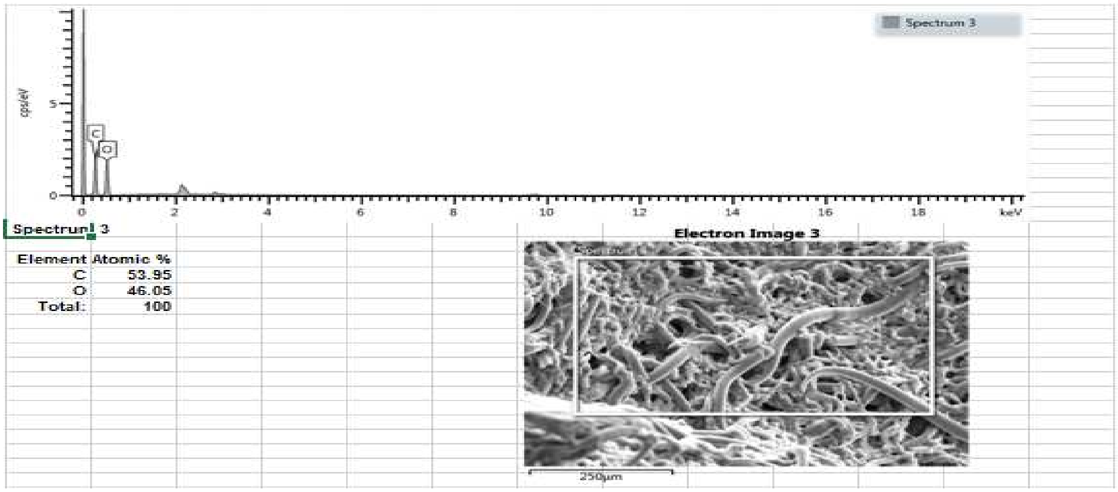


Figure 2: SEM Image of dialdehyde nano-cellulose



Element	Atomic %
C	53.95
O	46.05
Total:	100

Figure 3: EDS analysis of dialdehyde nano-cellulose

2.3. Adsorbate

All the chemicals used were of analytical reagent grade. Distilled water was used throughout the experimental studies. A stock cadmium solution for desired concentration was prepared by dissolving cadmium nitrate $Cd(NO_3).4H_2O$ in distilled water. Working standard was prepared by progressive dilution of stock cadmium solutions using distilled water. The pH of solution was maintained at a desired value by adding 0.1M NaOH or HCl.

2.4. Adsorption studies

The adsorption experiments were carried out by batch process, 1.00 g of adsorbent was placed in Erlenmeyer flasks with 100 mL solution of metal ions of desired concentration.

The mixture was agitated at 100 rpm, temperature was 30°C and pH=4.5 . The contact time was varied from 0 to 60 minutes. At predetermined time, the flasks were withdrawn from the agitator and the reaction mixtures were filtered through Whitman filter paper No. 40. All the experiments were performed in duplicates. The amount of metal ions adsorbed at equilibrium per unit mass of adsorbent was determined according to the following equation:

$$qe = \frac{(C_0 - Ce)*V}{m}$$

Where, m is the mass of adsorbent (g), V is the volume of the solution (L), C_0 is the initial concentration of metal ions (mmol/L), Ce is the equilibrium concentration of the adsorbate (mmol/L) in solution and qe is the metal quantity adsorbed at equilibrium (mmol/g). For the calculation of cadmium rate adsorption (R %), the following expression was used:

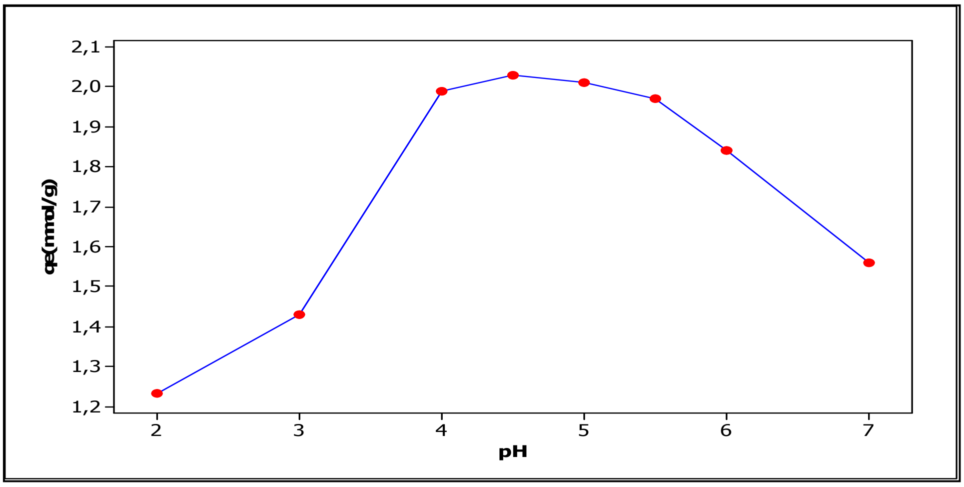
$$R(\%) = \frac{(C_0 - Ce)*100}{C_0}$$

2.5. effect of contact time

Results show that the adsorption of Cadmium ions onto functionalized nano-fibres derived from *Phragmites communis* Trin (FNF-PCT) reached equilibrium in 15 min. Adsorption first followed linear rising in which instantaneous, extremely fast uptake takes place, and then a stationary state was observed. The fast initial uptake was due to accumulation of metal ions on surfaces of (FNF-PCT) adsorbents which is a rapid step. It was concluded that 15 min was sufficient for adsorption to attain equilibrium.

2.6. effect of pH

The acidity of solution (pH) is one of the most important parameters controlling the uptake of heavy metals from wastewater and aqueous solutions. The uptake and percentage removal of Cadmium from the aqueous solution are strongly affected by the pH of the solution .The uptake of Cadmium increases from 1.23 mmol/g to 1.82 mg/g when the pH increases from pH 2 to pH 7. Cadmium adsorption is noted to increase significantly at pH 4 with 2.01 mmol/g and 1.89 mmol/g adsorption capacity at pH 6 respectively. After that the capacity of adsorption decreases slightly in pH range of 6 to 7.



Figure,4 effect of solution pH on adsorption of Cadmium ions onto (FNF-PCT) at 30°C

2.7. Adsorption Isotherm

The four most common adsorption isotherm models, Langmuir, Freundlich, Temkin and Dubinin-Radushkevich (D-R), were applied to understand the adsorbate–adsorbent interaction. The Langmuir equation can be described by the linearized form [25] (Langmuir 1918):

$$\frac{Ce}{qe}=\frac{1}{K_L*q_{\max}}+\frac{Ce}{q_{\max}}$$

where qe is the adsorption capacity at equilibrium (mg/g), qmax is the maximum adsorption capacity (mmol/g), K_L is the Langmuir equilibrium constant related to the affinity of binding sites and energy of adsorption, and Ce is the equilibrium solution concentration (mmol/l). According to (Vasanth and Kumara 2005), the essential features of the Langmuir isotherm can be expressed in terms of separation factor or equilibrium parameter R_L that can be calculated from the relationship :

$$R_L=\frac{1}{1+K_L C_0}$$

Where C_0 is the highest initial concentration (mmol/l). The value of R_L indicates whether the type of isotherm is irreversible adsorption ($R_L=0$), favorable adsorption $0< R_L < 1$ unfavorable adsorption ($R_L>1$), or linear adsorption ($R_L=1$). In this study, R_L for (FNF-PCT) had values less than 1, indicating favorable adsorption.

The Freundlich equation is given by (Freundlich 1906):

$$Log(qe)=Log(K_F)+\frac{1}{n}Log(Ce)$$

Where K_F is the Freundlich constant (mg/g) and 1/n is the adsorption intensity. Log(qe) was plotted against log(Ce) and a straight line was fitted in the data.

The D-R equation is given by [25] (Dubinin et al. 1947)

$$Ln(qe)=Ln(q_m)-\beta\varepsilon^2$$

where qe is the amount of heavy metal adsorbed onto clay at equilibrium (mmol/g), qm is the D-R monolayer capacity (mmol/g), β is a constant related to sorption energy (mol^2kJ^{-2}), and ε is the Polanyi potential which is related to the equilibrium concentration as follows:

$$\varepsilon=RTLn\left[1+\frac{1}{Ce}\right]$$

where R is the gas constant (8.3145 J $K^{-1}mol^{-1}$), T is the temperature in K. The mean energy of adsorption (E) is calculated by using the following formula [25] (Krishna et al. 2000):

$$E = (2\beta)^{-0.5}$$

The Temkin isotherm also used in this study to fit with the experimental data, it can be represented as:

$$qe = K_1 Ln(Ce) + K_2$$

Where K_1 and K_2 are Temkin isotherm constants. Temkin isotherm contains a factor that explicitly takes into the account adsorbing species-adsorbent interactions. This isotherm assumes that (i) the heat of adsorption of all the molecules in the layer decreases linearly with coverage due to adsorbent-adsorbate interactions, and that (ii) the adsorption is characterized by a uniform distribution of binding energies, up to some maximum binding energy. All of the constants are presented in Table 1.

Table 1. The Value of Parameters for Each Isotherm Model Used in The Studies

	Langmiur isotherm constants				Freundlich isotherm constants		
T°C	qmax (mmol/g)	K_L	R_L	R^2 (%)	K_F	n	R^2 (%)
10	2,098	24,19	0,0019	99,99	65,37	3,34	62,90
30	2,513	2,71	0,017	99,00	24,05	2,00	71,50
50	2,798	1,65	0,028	82,10	19,49	1,91	52,8
	Temkin isotherm constants				D-R isotherm constants		
T°C		K1	K2	R^2 (%)	$q_{m,D-R}$	E (KJ/mol)	R^2 (%)
10		38,10	59,70	74,20	1,73	0,562	92,70
30		62,00	61,60	81,20	1,78	0,154	93,50
50		68,50	99,00	67,20	2,41	0,084	90,10

2.8 Thermodynamic Parameters

The mechanism of adsorption may be determined through thermodynamic quantities such as change in Gibbs free energy (ΔG°), change in enthalpy of adsorption (ΔH°), and change in entropy (ΔS°). The thermodynamic equilibrium constant Kd for adsorption was determined by (Gunay et al. 2007) by plotting ln(qe/Ce) versus qe and extrapolating to zero qe. The increase in Kd with increase in temperature indicates the endothermic nature of the process. The ΔG°, ΔH°, and ΔS° were calculated using the equations:

$$\Delta G^\circ = -RTLn(K_d)$$
$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

A plot of $Ln(K_d)$ versus 1/T was found to be linear, ΔH° and ΔS° were determined from the slope and intercept of the plot, respectively.

Table 2. Thermodynamic parameters calculated for Cd(II) adsorption on (FNF-PCT)

T°C	**Ln(K_d)**	**ΔG°(Kj/mol)**	**ΔH° (Kj/mol)**	**ΔS°(j/mol.K)**	**R^2 (%)**
10	3,186	-7,492	-51,57	-157,89	82,1
30	0,996	-2,507			80,9
50	0,504	-1,449			80,6

2.9. Kinetic studies

A quantitative understanding of the adsorption is possible with the help of kinetic models. The pseudo-first-order kinetic model, as expressed by [25] (Lagergren 1898), can be written as:

$$Log(qe - q_t) = Log(qe) - K_1.t / 2.303$$

Where qe and q_t are the amounts of metal adsorbed (mmol/g) at equilibrium and at time t, respectively, and K_1 is the pseudo-first-order equilibrium rate constant (1/min). A plot of log(qe - q_t) vs t gives curved line confirming the unapplicability of the pseudo-first-order rate equation (R^2 = 55,80 %).

Pseudo-second-order sorption rate equation [25] (Ho et al.1996) may be expressed as follows :

$$\frac{t}{q_t} = \frac{1}{K_2 qe^2} + \frac{1}{qe}.t$$

Where h = K_2qe^2 (mmol/g.min) can be regarded as the initial adsorption rate as t→0 and K_2 (g/mmol.min) is the rate constant of pseudo-second-order adsorption (g/mmol.min). The plot t/qt versus t should give a straight line if pseudo-second-order kinetics is applicable and the qe, K_2 and h can be determined from the slope and intercept of the straight lines in plot of t/qt versus t.

The intraparticle diffusion model (Weber Jr Wj et al. 1963), was also tested. The initial rate of the intraparticle diffusion is given by the following equation [25]:

$$q_t = K_P t^{1/2}$$

Where K_p is the intraparticle diffusion rate constant, (mmol/g.min$^{1/2}$). Such plots may present a multilinearity indicating that two or more steps take place.

Table 3. Comparison between the Adsorption Rate Constants, qe, Estimated and Correlation Coefficients Associated with Pseudo-order-order and the Pseudo-second-order Equation and Intraparticle Diffusion

Pseudo-order-order constants			**Second-order-order constants**			
K_1 (min^{-1})	Qe (mmol/g)	R^2 (%)	K_2	qe	h (mmol/g.min)	R^2 (%)
0,069	0,096	55,80	4,05 E-5	2,05	1,7E-4	99,90

Intraparticle diffusion constant	
Kp (g/mmol,min$^{1/2}$)	R^2 (%)
0,062	55,00

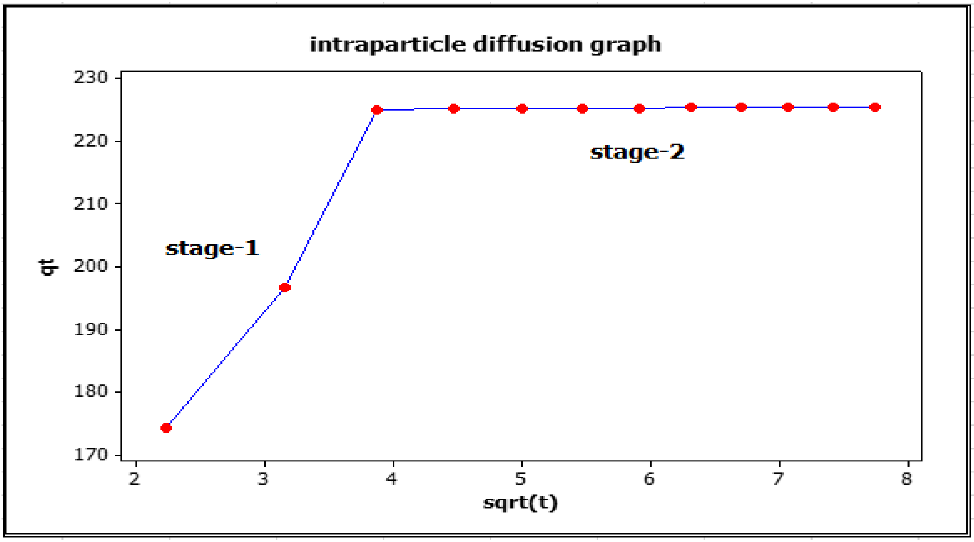


Fig. 5. Intraparticle Diffusion Model for Cd(II) Adsorbed onto (FNF-PCT) at pH =4,5 and T= 30°C

The first, sharper portion is the external surface adsorption or instantaneous adsorption stage. The second stage indicate the surface saturation (constant with time), practically, there is no intraparticle diffusion because of smooth polite surface of oxidized nano-fibers, (R^2 = 55,00 %) that's confirmed by the SEM image on fig.2 is rate-controlled. As shown in Fig. 4., the external surface adsorption (stage 1) is completed within 15 min, and then the surface saturation is attained (stage 2).

CONCLUSION

Equilibrium, kinetic and thermodynamic studies were made for the adsorption of Cd(II) from aqueous solution onto (FNF-PCT) at pH 4,5 . The equilibrium data have been analysed using Langmuir, Freundlich, Temkin and Dubinin-

Radushkevich isotherms. The characteristic parameters for each isotherm and related correlation coefficients have been determined. The Langmuir isotherm was demonstrated to provide the best correlation for the sorption of Cd(II) onto (FNF-PCT). The suitability of the pseudo first-order equations kinetic model for the adsorption of Cd(II) onto (FNF-PCT) is also discussed and related parameters calculated. There is no intraparticle diffusion adsorption because of sooth polite of oxidized nano-cellulose. The pseudo second-order kinetic model agrees very well with the dynamical behaviour for the adsorption of Cd(II) onto (FNF-PCT) for different initial Cd(II) concentrations over the whole range studied. The adsorption of Cd(II) on (FNF-PCT) is a spontaneous, exothermal and physio-sorption process. It may be concluded that (FNF-PCT) may be used as an efficient adsorbent for the removal of Cd(II) from the wastewater.

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