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Removal of Mercury ions (Hg+2) from Aqueous solution by Chemically Modified nano-Cellulose

GOUAMID Messaoud[(1)], KHENBLOUCHE Abdelkader[(1)], BENMEBROUK Lazhar[(2)]

[(1)] Departement of chemisty, Faculty of Mathematics & Materials Science, KM University of Ouargla, 30000, Algeria.

[(2)] LRPPS Laboratory, Faculty of Mathematics & Materials Science, KM University of Ouargla, 30000, Algeria

basp73@gmail.com

***Abstract*—** the removal of Mercury ions (Hg^{+2}) on Chemically Modified nano-Cellulose (CMNC) were investigated using batch adsorption technique. The investigation was carried out by studying the influence of initial solution pH, adsorbent dosage, Time, initial concentration of Mercury ions (Hg^{+2}) and temperature. The equilibrium data was analyzed using Langmuir, Freundlich, Dubinin-Radushkevich and Temkin adsorption isotherms. The results showed that equilibrium was reached within 75 min. The used adsorbent gave the highest adsorption capacity at pH 4.5. The experimental isotherm data were analyzed and modeled. In the studied concentration range (0.5 –1.0 mmol L^{-1}) the maximum adsorption capacity, Langmuir's q_{max}, improved from 173 to 204 mg/g as the temperature increased from 298 to 328 K. The enthalpy ΔH° and entropy ΔS° values were respectively estimated at 2.228 kJ mol^{-1} and 0.010 kJ K^{-1} mol^{-1}. The adsorption of Mercury ions (Hg^{+2}) on (CMNC) is a spontaneous and endothermic process. It was shown that the adsorption of Mercury ions (Hg^{+2}) could be described by the pseudo-second order equation, suggesting that the adsorption process is presumable a chemisorption.

Key-Words— nano-cellulose, Adsorption, Mercury ions, Isotherm, Kinetics

I. INTRODUCTION

One of the most important and useful industrial materials is mercury, at the beginnings and from long time mercury compounds have been used as pigments in ink, as reagent for gold recovery from its ores, in instruments (like barometers or thermometers) and in chemical industries to produce sodium hydroxide or chlorine and so on.

The intensive use of this toxic heavy metal led to serious environmental problems and significant damage to Living organisms, Hg(II) stands on the top of toxicity severity list [1]. Mercury can accumulate in human and animal's bodies once entering to the food chain, when reach large quantity in living organisms it starts causing many adverse effects on their health [2]. To treat contaminated environment and prevent damages related to the toxicity of this metal, several methods and technologies have been proposed for mercury removal from aqueous media, among them we can find: precipitation by sulphide, adsorption, ion exchange, solvent extraction, electrodeposition, membrane filtration [3].

Based on economical feasibility, ease of use and the effectiveness in removing of trace heavy metals from aqueous solutions, we can consider adsorption process as technological alternative available for eliminating of mercury [4-10].

In this work, Date palm residue, an abundant, inexpensive and unexploited material, contains considerable amount of cellulose [11], has been used to extract raw cellulose, later and by acid hydrolysis method, we have transformed extracted cellulose to micro/nano-cellulose (MNC) , obtained (MNC) functionalized by selective and controlled oxidation to produce chemically modified nano-cellulose (CMNC).

II. .MATERIALS AND METHODS

Adsorption experiments were conducted by varying pH, contact time, adsorbent dose, temperature and (Hg^{+2}) 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 analyzed 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 (Hg^{+2}) at maximum absorbance of wavelength (552 nm). A HANNA instrument pH meter was used for pH measurements; A magnetic stirrer was used to agitating the samples.

Adsorbent

The Date palm by-products were collected from Ouargla (Algeria) region palm trees, They were gathered from twigs into clean plastic bags. Washed with triple 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, the hydrolysis process of extracted cellulose followed by oxidation in (4% NaIO4) solution in the dark at (pH =4.5) for three days, finally washed by ionized water, the product obtained is dialdehyde nano-cellulose.

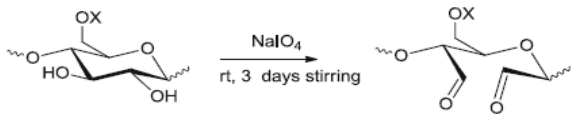

Figure 1: selective oxidation reaction of nano-cellulose

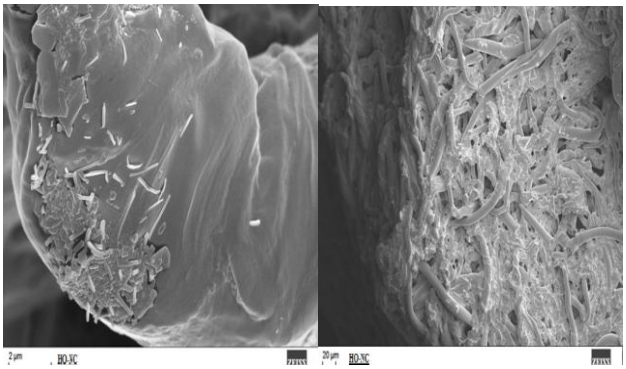

Figure 2: SEM Images of dialdehyde nano-cellulose

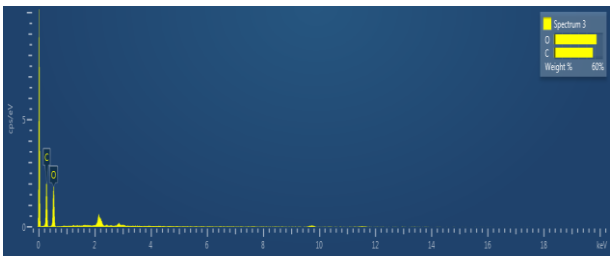

Figure 3. EDS analysis of dialdehtde nano-cellulose

Adsorbate

All the chemicals used were of analytical reagent grade. Distilled water was used throughout the experimental studies. A stock (Hg^{+2}) solution for desired concentration was prepared by dissolving it in distilled water. Working standard was prepared by progressive dilution of stock solutions using distilled water. The pH of solution was maintained at a desired value by adding 0.1M NaOH or HCl.

Biosorption 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 (Hg^{+2}) of desired concentration.

The mixture was agitated at 100 rpm at 20, 30 and 40°C. The contact time was varied from 0 to 120 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 (Hg^{+2}) adsorbed at equilibrium per unit mass of biosorbent 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 (mg/L), Ce is the equilibrium concentration of the adsorbate (mg/L) in solution and qe is quantity adsorbed at equilibrium (mg/g). For the calculation of (Hg^{+2}) rate adsorption (R %), the following expression was used:

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

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 [11].

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

where qe is the adsorption capacity at equilibrium (mg/g), q_{max} is the maximum adsorption capacity (mg/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 (mg/l). 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 (mg/l). The value of R_L indicates whether the type of isotherm is irreversible adsorption (RL=0), favorable adsorption 0< RL < 1 unfavorable adsorption (RL>1), or linear adsorption (RL=1). In this study, R_L for (CMNC) had values less than 1, indicating favorable adsorption. The Freundlich equation is given by [11]:

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

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

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

where qe is the amount of mercury adsorbed onto (CMNC) at equilibrium (mg/g), q!m is the D-R monolayer capacity (mg/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 :

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

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

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

Where K_1 and K_2 are Temkin isotherm constants.

III. RESULTATS AND DISCUSION

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 (mg/g)	K_L	R^2 (%)	K_F	n	R^2 (%)
25	173	1.21	98,99	5,82	2,04	86,11
40	191	1,377	98,96	6,12	2.33	87.12
55	204	1,382	98,97	6.23	2,74	83,32

	Temkin isotherm constants			D-R isotherm constants		
T°©	K1	K2	R^2 (%)	$q_{m,D-R}$	E (KJ/ mol)	R^2 (%)
25	2.10	5,81	88.01	153	6,75	92,5
40	1,93	6,01	85,82	155	6,27	93,7
55	1,805	6,33	85,34	158	6,29	94.0

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 increase in K_d with increase in temperature indicates the endothermic nature of the process. The ΔG°, ΔH°, and ΔS° were calculated using the equations:

$$\Delta G° = -RTLn(K_d)$$

$$\Delta G° = \Delta H° - T\Delta S°$$

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.

Table2-Thermodynamic parameters calculated for the adsorption of CV on DNC

T°C	Ln(K_d)	ΔG° (Kj/mol)	R^2
25	7.38	-17.98	94.31
40	8.12	-20.47	93,9
55	8.81	-22.92	94.26
ΔH° (Kj/mol)		2.228	
ΔS° (Kj/K.mol)		0.010	

I. Conclusion

The equilibrium was reached within 75 min. The used adsorbent gave the highest adsorption capacity at pH 4.5. The enthalpy ΔH° and entropy ΔS° values were respectively estimated at 2.228 kJ mol^{-1} and 0.010 kJ K^{-1} mol^{-1}. The adsorption of Mercury ions (Hg^{+2}) on (CMNC) is a spontaneous and endothermic process. It was shown that the adsorption of Mercury ions (Hg+2) could be described by the pseudo-second order equation, suggesting that the adsorption process is presumable a chemisorption..

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