

Thermodynamic Study And Competition Effects Of Cadmium Ions Biosorption From Synthetic Wastewater Using A Dairy Sludge

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Abstract—Local dairy sludge as a biosorbent has been used in this study for cadmium ion biosorption from aqueous solution. Batch experiments were carried out as a function of temperature, initial concentration and ionic strength. Cadmium uptake was significantly enhanced from 67.7 to 84.7 mg.g⁻¹ of dairy sludge by temperature increase at pH 5. Equilibrium data for metal ion biosorption were analyzed using model equations namely Langmuir and Freundlich isotherms and the best fit to the experimental data was provided by the first isotherm model. BET and FT-IR were also performed to characterize the biosorbent. Ionic strength using NaCl, NaNO₃ and Ca(NO₃)₂ doesn't affect Cd(II) sorption while there was 20 per cent decrease using CaCl₂. A significant effect of Pb(II) ions present in the binary system on cadmium sorption was observed specially in strong concentration (100 and 500 mg.L⁻¹). This study shows that this local dairy sludge can be an alternative to the commercially available adsorbents for heavy metals removal from liquid effluents.

Keywords—Heavy Metals; Biosorption; Dairy Sludge; Isotherms; Competition Effects.

I. INTRODUCTION

Manufacturing (plating, metallurgy, etc...) and mining industries are producing waste water streams contaminated with hazardous metal ions [1]. International regulations are becoming more and more drastic concerning the level of metal discharge in the environment. Cadmium may have a cumulative effect in the organism and may result in adverse effects such as cancer, lung insufficiency, renal dysfunction, bone degradation disturbances in

The characterization of the dairy sludge as a biosorbent was carried out by Fourier Transform Infra Red (FTIR) spectrum and Scanning Electron Microscopy (SEM-EDX) analysis.

cardiovascular system, liver and kidney damage [2]. accumulating throughout the food chain. For these reasons a great attention has been attached to cadmium recovery from industrial wastewater in order to reduce the global impact of this metal on the environment [3]. Different processes can be used for the removal of cadmium from aqueous streams, including precipitation [4], solvent extraction [5], solvent impregnated resins, ion exchange resins, or membrane processes [6]. However, these processes generally face economical (expensive treatments for low-concentration effluents), technical (difficulty to raise the regulation levels) or environmental (sludge production, loss of solvent) constraints that limit their application [7]. Biosorption that consists in using materials of biological origin for the sorption of target solutes has been proposed as an alternative to conventional ion exchange and chelating resins or activated carbon.

Different materials can be used such as bacterial [8], algal [9] or fungal biomass [10, 11], but also Biopolymers [12, 13, 14] or by-products of agriculture [15, 16, 17]. Dairy sludge constitutes one of these sub-products of agriculture and farming which can produce significant amounts of waste material that can be only valorized as energy source [18], or fertilizer in agriculture [19]. Recently, dairy sludge was tested for the sorption of Cd(II) and Pb(II) [20]. This preliminary study required complementary investigations to evaluate the thermodynamic parameters of Cd(II) sorption, and the competitor effects. The present study investigates (a) the effect of temperature on sorption isotherms (to determine the sorption enthalpy (ΔH°), entropy (ΔS°) and the Gibbs energy (ΔG°)) and (b) the sorption of Cd(II) in binary solutions (in the presence of increasing concentrations of Pb(II), and other salts).

II. MATERIAL AND METHODS

A. Materials

Dairy sludge was collected at the drying beds of the Dairy Unit Sidi-Khaled, close to Tiaret (Algeria). The sludge was first dried at 105 °C overnight. The biomass was grinded and sieved. Biosorbent was stored in desiccators. Pre-treatments of the

biosorbents were tested using either NaOH or HCl. A suspension was prepared incorporating 10 g of biomass into 100 mL of solution (either 0.2 M NaOH or 0.1 M HCl). The suspension was maintained in agitation for 12 h at 30 °C. The solid fraction was then recovered by centrifugation at 3000 rpm for 5 min. The centrifuged fraction was dried at 55 °C before being grinded and sieved.

Cadmium chloride (Fluka AG, Switzerland) was used as the metal salt for the preparation of solutions. Other reagents (NaCl, NaNO₃, Ca(NO₃)₂, CaCl₂) were also analytical grade. KBr (Carlo Erba, Italy) was an IR spectrometry grade reagent.

B. Characterization of Materials

The organic fraction was determined by sludge calcinations to constant weight while the microbiological observation allowed identifying bacteria, fungi and algae. FT-IR spectrometry was performed on KBr discs (approximate weight fraction: 0.1 %) using a Perkin Elmer Spectrum One spectrometer on the biomass before and after Cd(II) sorption. The dry sorbent was analyzed using an Environmental Scanning Electron Microscopy (ESEM) Quanta FEG 200, equipped with an OXFORD Inca 350 Energy Dispersive X-ray microanalysis (EDX) system. The topography of the samples was observed using secondary electron flux, while the backscattered electrons were used for the identification and localization of heavy metals at the surface of the materials (by phase contrast). SEM-EDX facilities were used for the analysis of specific zones at the surface of sorbent particles.

C. Sorption Experiments

Sorption experiments were performed at pH 5, based on previous results using the same biosorbent for the sorption of Pb(II) and Cd(II) [20]. Sorption isotherms were tested at 20 °C, 30 °C, 40 °C and 50 °C by contact of 25 mL (volume, V) of metal solution (C₀, concentration ranging between 10 and 500 mg Cd L⁻¹) with 20 mg of biosorbent for 48 h (under 200 rpm agitation). After filtration (through a 1.2 µm pore size filter membrane) residual metal concentration was determined by ICP-AES (Jobin-Yvon Activa M, Jobin-Yvon, Longjumeau, France). The mass

balance equation ($q = \frac{V(C_0 - C_{eq})}{m}$) served to determine the sorption capacity (q, mg Cd g⁻¹). Based on the limit of detection for Cd(II) for proprietary equipment and taking into account the experimental inaccuracies the limit of quantification was evaluated to 0.05 mg L⁻¹. The effect of Cd(II) competition was carried out testing the sorption isotherms (same experimental procedure as cited above) in the presence of Pb(II) at concentrations of 50, 100 and 500 mg Pb L⁻¹. The impact of ionic strength was determined by comparing the sorption capacities for Cd(II) in the presence of 0.1 M, 0.5 M and 0.8 M of NaCl, NaNO₃, CaCl₂ and Ca(NO₃)₂.

III. RESULTS AND DISCUSSION

A. Biomass Characterization and Interpretation of Sorption Mechanism

The microbiological observations showed that aerobic microorganisms including coliforms, staphylococcus, lactic spectrococcus, yeats, protozoae and algae are present together with bacterial spores. This constitutes about 65 % of the total mass of the biosorbent (organic matter determined by weight loss at 500 °C). SEM-EDX analysis was used for evaluating the chemical composition of the sludge (Table 1). Apart organic materials (evidenced by the percentage of carbon, oxygen compounds), the material is characterized by a high level of calcium (i.e., about 20 % w/w, and 8.3 % in atomic fraction).

The presence of a consortium of microorganisms induces the presence of a wide variety of functional groups that are constitutive of the cell wall of these microorganisms such as hydroxyl, carboxyl, sulfonic, amine groups [21].

Previous investigations have shown (using B.E.T. analysis) that the specific surface area of the biosorbent is quite low (close to 1 m² g⁻¹) [20]: the post-treatment using either NaOH or HCl solutions did not significantly change the specific surface that remained below 2 m² g⁻¹.

TABLE I: Chemical composition of the dairy sludge (SEM-EDX analysis)

Element	C	O	Mg	Al	Si	P	S	K	Ca	Fe	Sn	Total
% Mass	32.19	40.72	0.42	0.64	2.22	1.57	0.45	0.42	19.76	0.67	0.94	100%
% Atomic	45.17	42.89	0.29	0.4	1.33	0.85	0.24	0.18	8.31	0.20	0.13	

SEM-EDX analysis is presented on Figure 1 before (Figure 1a) and after Cd(II) sorption (Figure 1b). The microscope observation shows the presence of small

grains/aggregates at the surface of the biosorbent after Cd(II) sorption, their analysis (using EDX facilities) confirms that they contain Cd element.

Their respective contributions may depend on several parameters such as the density of sorption sites, their

accessibility, their chemical state, and their affinity for metal ions (which depends on their speciation).

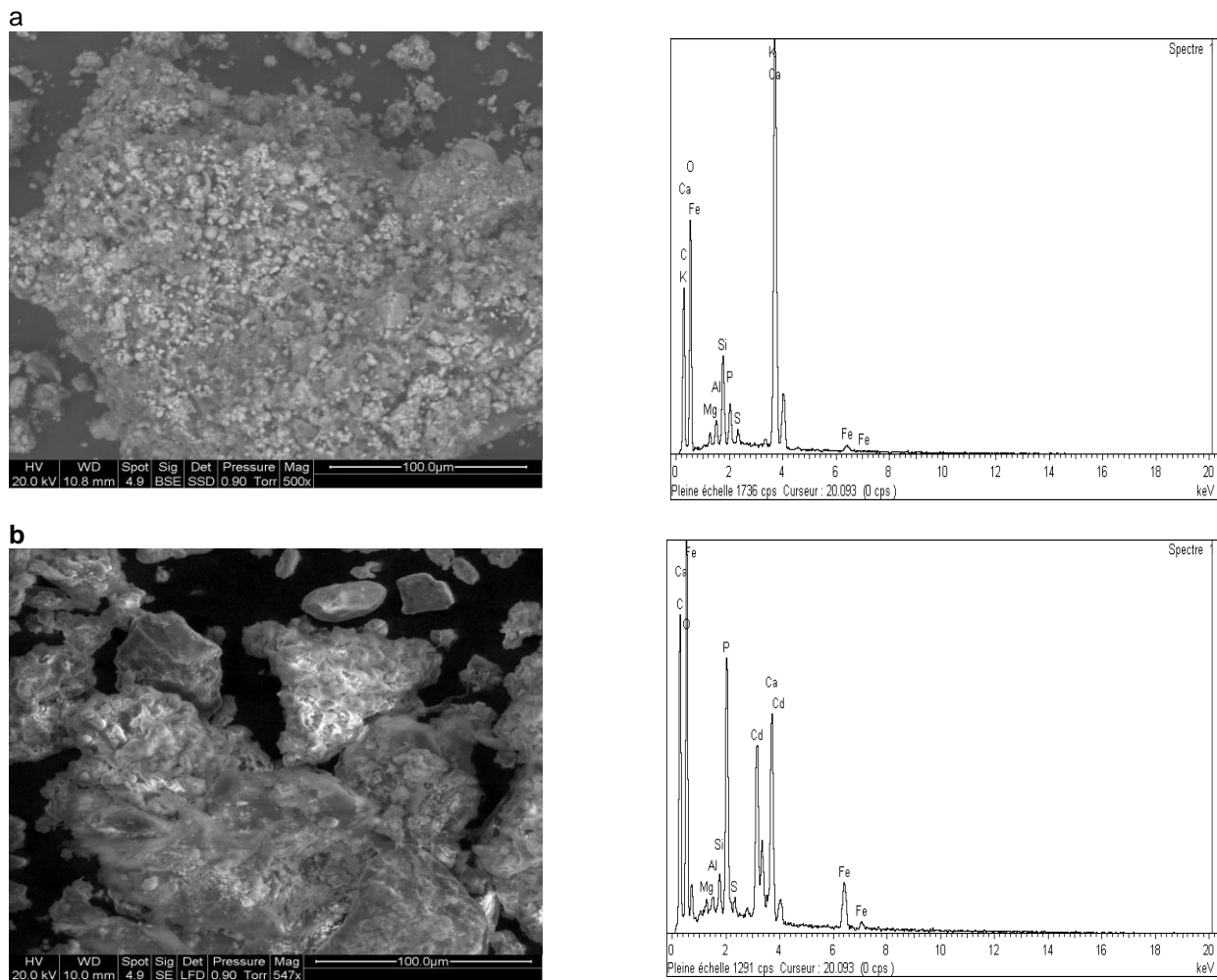


Fig.1: SEM-EDX analysis of dairy biosorbent before (a) and after (b) Cd(II) biosorption.

FT-IR spectroscopy is frequently used for characterizing the interactions of metal ions with biosorbents [22]. Though the spectrum for the biomass after metal sorption is less resolved than the spectrum of the raw biomass it is possible to identify some differences in the wavenumbers and relative intensities of specific bands. The FT-IR spectrum of the biomass, shown in "Fig. 2", is characterized by bands at 1651 cm^{-1} (carbonyl function of Amide I: C=O stretching combined with N-H deformation), 1424 cm^{-1} (C-H deformation and possible contribution of amino-acid groups), 1036 cm^{-1} (carbohydrate ring), 874 cm^{-1} and 713 cm^{-1} (amine). Some other bands in the range $2800\text{-}2950\text{ cm}^{-1}$ are representative of C-H stretching in CH/CH₂/CH₃ groups, while the large

band in the range $3200\text{-}3600\text{ cm}^{-1}$ corresponds to the superimposition of O-H and N-H bands. After metal sorption there is a decrease in the intensity and a shift of the band at 1651 cm^{-1} (moved to 1635 cm^{-1}): this means that the Amide I band environment was affected by metal sorption, the band at 1036 cm^{-1} was replaced by a band around 1050 cm^{-1} with possible contributions of other groups (alcohol groups). These changes on various bands (which are not fully assigned due to the poor resolution of the spectra and the co-existence of many functional groups) demonstrate that metal binding occurs through chemical interactions with the material and not only by local precipitation.

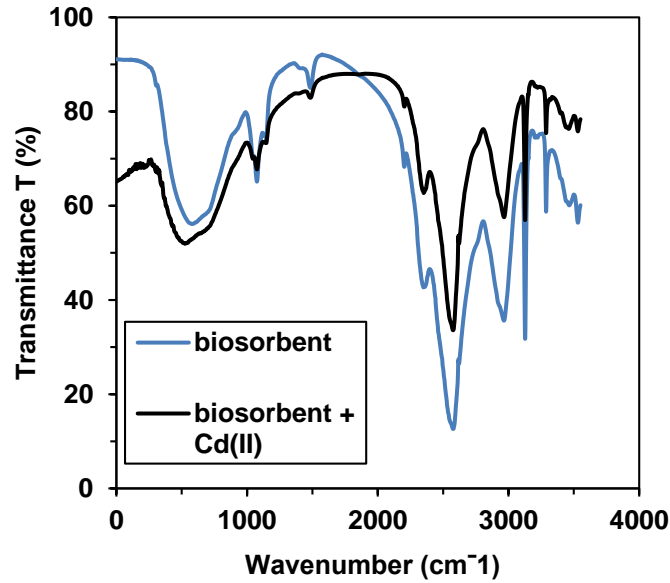


Fig. 2: FT-IR spectroscopy of the biosorbent before and after Cd(II) sorption.

B. Temperature Effect On Sorption Isotherms And Thermodynamic Study

Preliminary study on Cd(II) sorption using the same biomass have shown that the sorption capacity tended to increase with temperature. “Fig. 3” confirms that increasing the temperature improves the sorption capacity of the biosorbent for Cd(II) recovery at pH 5. It is noteworthy that the affinity constant (which is

$$q = \frac{q_m b c_{eq}}{1 + b c_{eq}} \quad (1)$$

Where q_m is the maximum sorption capacity (mg Cd g^{-1}), b is the affinity coefficient (L mg^{-1}). Though the trends are generally respected in the modeling of experimental data with the Langmuir model some discrepancies were observed at the level of

proportional to the initial slope of the curve) decreased with increasing the temperature.

The isotherms that plot the sorption capacity ($q \text{ mg Cd g}^{-1}$) vs. C_{eq} (equilibrium concentration, mg Cd L^{-1}) were modeled using the Langmuir equation (Table 2):

maximum curvature of the different series. The maximum sorption capacity roughly increased with temperature; this means that the sorption process is endothermic. On the other hand, the affinity coefficient tended to decrease: this is consistent with the shape of the sorption isotherms (Figure 3).

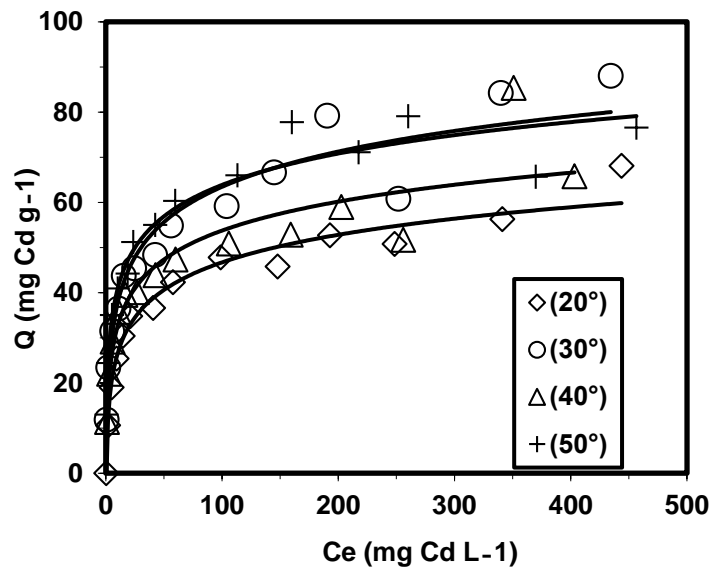


Fig. 3 : Effect of temperature on Cd(II) sorption isotherms at pH 5.

TABLE. II: Effect of temperature on sorption isotherms for Cd(II) binding on dairy sludge - Langmuir parameters

T (°C)	q _m (mg Cd g ⁻¹)	b (L mg ⁻¹)	q _m × b (L g ⁻¹)	R ²
20	66.7	0.049	3.27	0.979
30	69.9	0.046	3.73	0.963
40	76.6	0.043	3.29	0.944
50	84.7	0.118	9.04	0.989

The thermodynamic parameters can be deduced from the variations of the equilibrium constant with temperature according to the equations [23]—:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

$$\ln K_d = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT}$$

and ΔG°) (table 3). These values should be taken as indicative since a significant dispersion was observed in the distribution of the values. The positive values of Gibbs energy with increasing the temperature indicate that the reaction is not spontaneous and that the biosorbent has not a great affinity for Cd(II) [24]. On the other side, The enthalpy of biosorption (ΔH°) was found to be -21,4 kJ/mol. The negative (ΔH°) is indicator of exothermic nature of the biosorption. The

K_d values have been evaluated for a given equilibrium concentration (C_{eq}) of 200 mg Cd L⁻¹.

"Fig. 4" shows the variation of $\ln K_d$ as a function of the reciprocal of absolute temperature. From the slope and the ordinate intercept (2) it is possible to calculate the thermodynamic parameters (ΔH° , ΔS°) (3)

value of the biosorption heat of Cd(II) ions confirm that the physical adsorption play a greater role in the biosorption process [25]—. The ΔS° parameter was found to be - 45,8 J/mol K. The negative value of the entropy suggests a decrease in the randomness at the solid/solution interface during the biosorption process [26]—. These values are of the same order of magnitude than the values cited for cadmium and lead biosorption using dried activated sludge [27]—.

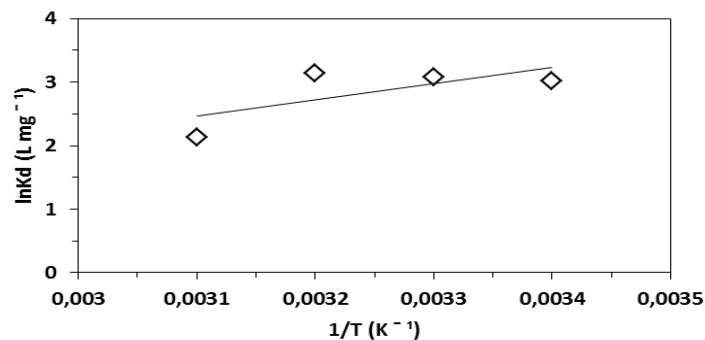


Fig. 4: Thermodynamic analysis of sorption isotherms at different temperatures

TABLE III: Thermodynamic data for the sorption of Cadmium using dairy sludge (pH 5).

T (K)	ΔG° (KJ/mol)	ΔH° (kJ/mol)	ΔS° (J/K.mol)
293	7,9	- 21,4	- 45,8
303	7,5		
313	7,1		
323	6,6		

C. Competition Effects and Selectivity

The efficiency of a sorbent for the recovery of a given metal is generally controlled by the composition of the solution and more specifically by the presence of competitor ions. In order to verify the sensitivity of the biosorbent to the presence of competitor ions in the sorption of Cd(II), a series of isotherms have been obtained in the presence of increasing concentrations of Pb(II) at pH 5 (Figure 5). The figure clearly shows that the addition of Pb(II) ions significantly affect the sorption of Cd(II): the uptake capacity of Cd is inhibited by 25 % when Pb is present at 100 mg/L and 85 % at 500 mg/L.

This means that the dairy sludge is relatively selective to Pb(II), at least over Cd(II). Alaa and

Mulligan [28]— investigated the effect of the presence of lead on the biosorption of copper, cadmium and nickel by anaerobic biomass: they observed competition effects in metal sorption from bi-component solutions, though the sorbent had a marked preference for Pb(II).

The salinity of the solution may affect the sorption efficiency since ionic strength may induce a screening effect that can significantly decrease, and even, suppress metal uptake when metal ions are recovered by electrostatic or covalent bonding [29]—. Metal anions can also contribute to complex formation with target metal changing their affinity for metal ions and even changing the mechanism of metal sorption [30, 31]—. In addition, the presence of other cations may compete with target metal for

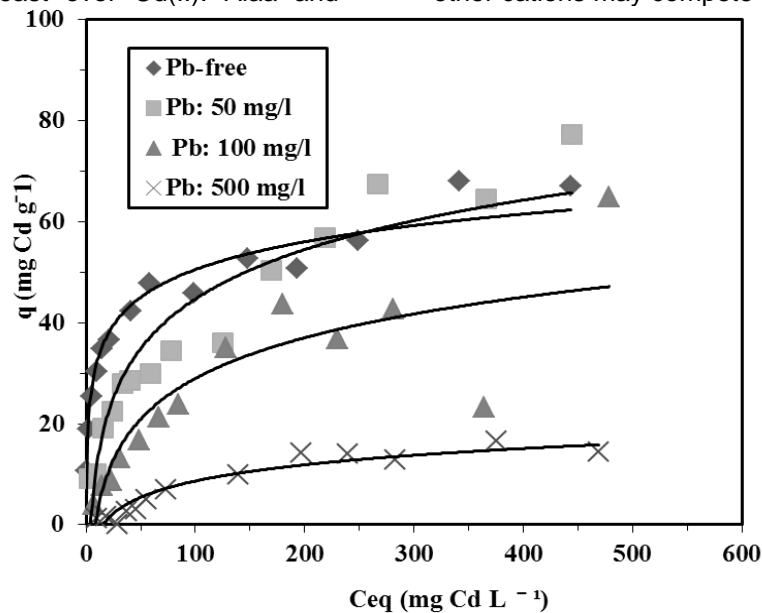


Fig. 5: Influence of increasing amounts of Pb(II) on Cd(II) sorption isotherm at pH 5 for dairy biosorbent.

binding on reactive groups. In order to verify the impact of ionic strength (presence of salts) Cd(II) sorption efficiency was compared, under similar experimental conditions, adding to cadmium solution (salt-free): NaCl, NaNO₃, CaCl₂ or Ca(NO₃)₂ (to reach a final concentration of 0.1 M). Figure 6 shows that in the presence of sodium salt, Cd(II) sorption efficiency remained constant (and close to 80 %). In the case of calcium salts a small decrease was observed with CaCl₂, while with Ca(NO₃)₂ the decrease in sorption

efficiency was weak but significant (down to 72 %) compared to the other systems. Lodeiro, Barriada, Herrero, and Sastre [32]— compared the sorption of Pb(II) and Cd(II) by a marine algae (*Cystoseira baccata*) in the presence of calcium and sodium nitrate (at increasing concentrations). The ionic strength had a lesser impact on Pb(II) than on Cd(II) probably due to the fact that covalent bonding is more relevant for Pb(II) sorption than for Cd(II) sorption.

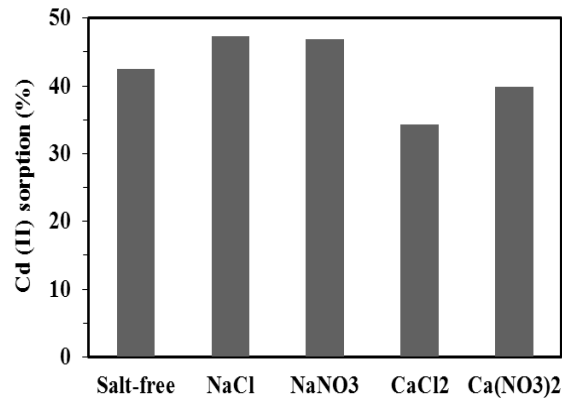


Fig. 6: Effect of the presence of salts (0.1 M) on Cd(II) sorption at pH 5 using dairy biosorbent (sorber dosage: 800 mg L⁻¹; C₀: 100 mg Cd L⁻¹, agitation time: 48 h).

D. Effect of Post-treatment of Dairy Sorbent on Sorption Properties

The effect of pretreatment of the dairy sorbent on biosorption of cadmium is shown in figure 7. We noticed that according to our working conditions the basic treatment has a not significant effect while the

acid action causes an increase in binding cadmium by the biosorbent. So in the initial concentration of 100 mg Cd (II) L⁻¹, the capacity of fixation is increased by 24 %. Gupta and Rastogi [33]— also observed an increase of 9 % of the fixation of the cadmium by an algae biomass (*Oedogonium* sp.).

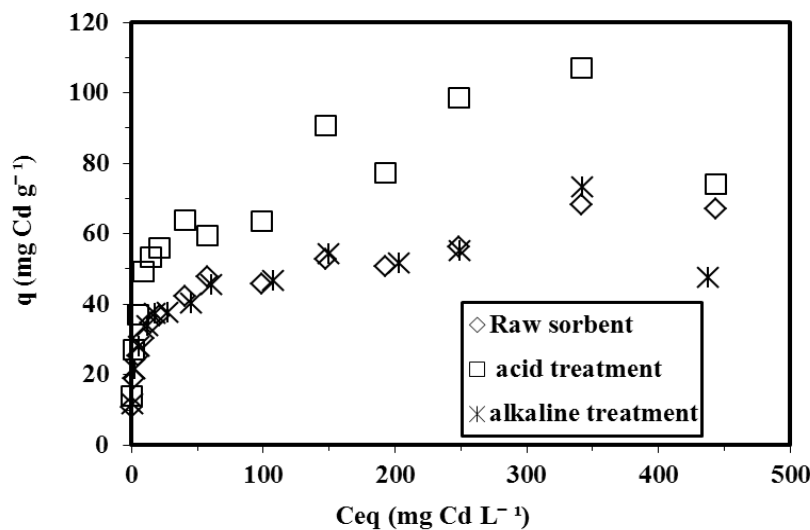


Fig. 7: Comparison of Cd(II) sorption isotherms for dairy sorbent (before and after acidic and alkaline treatment) at pH 5.

In another study of biosorption of Cu(II) and Ni(II) ions by *Chlorella vulgaris* having undergone a pretreatment by HCl, Mehta Tripathi and Gaur [34]—

noted an average increase of 39 % of the fixation capacities.

IV. CONCLUSIONS

The study of biosorption isotherms at different temperatures allowed evaluating the thermodynamics of the biosorption process: the reaction (non spontaneous) is endothermic; the negative value of entropy indicates that the sorption of cadmium decreases the randomness (disorder) at the interface solution/solid. The presence of Pb(II), Especially in

strong concentration, hardly influenced Cd(II) biosorption isotherm. Sodium salts (either chloride or nitrate) had a negligible impact on Cd(II) biosorption; calcium salts had a slightly greater effect on metal sorption, especially in the case of calcium nitrate. The modification of the biomass with alkaline treatment has a not significant effect while the acid treatment has caused an increase in biosorption. Previous work

has shown that dairy sludge can be used as a sorbent for Cd(II).

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