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Removal of heavy metal ions from aqueous solutions by a local dairy sludge as a biosorbant

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Abstract

In this work, the removal of lead and cadmium from an aqueous solution by a local dairy sludge was investigated in a batch system. Biosorption of these heavy metals was studied as a function of solution initial pH, equilibrium time, temperature, biosorbent dose, biosorbent particle diameter and initial metal ion concentration. Maximum sorption was observed at a pH value of 5 and a temperature of 40 °C. Equilibrium uptake increased with increasing metal ion concentration for both metals with a maximum sorption capacity of a 148.6 mg/g for Pb (II) and 66.7 mg/g for Cd(II). The Langmuir model was found to better describe the sorption of lead ions with a correlation factor of 0.99 while Freundlich and Temkin models were better for Cd(II) sorption. The temperature increase from 20 to 40 °C enhanced the uptake of Pb(II) by 20% and Cd(II) by 5%. The sorption kinetics were compatible with the pseudo-second order model for the systems investigated. SEM micrographs were determined before and after sorption. Nitric and hydrochloric acids were used for the metals desorption. Pb(II) was better desorbed by nitric acid whereas Cd(II) was eluted slightly better by chlorhydric acid.

Keywords:

Heavy metals

Sorption

Dairy sludge

Isotherms

1. Introduction

Many industries produce significant amounts of heavy metal-laden wastewater, often discharged in the environment without any prior treatment, which may constitute a major source of pollution and health hazard. However, due to stringent legislation, heavy metal ion levels must be controlled before release into the environment [1] as they are classified as poisons since they accumulate in living species with a permanent toxic and carcinogenic effect. They are characterized by their persistence in the ecosystems, their non biodeterioration and their bioaccumulation along the food chain [2]. For these reasons, the presence of the heavy metal ions in the environment with concentrations not complying with pollution legislation is unacceptable and their removal from wastewater using different ways such as biosorption is increasingly attracting interest [3,4].

In many countries, dairy industries are often a large source of wastewater as they use activated sludge for their effluent treatment. The sludge formed during the aerobic biodegradation processes may lead to serious and costly disposal problems. This can be aggravated by the ability of sludge to adsorb specific organic compounds and even toxic heavy metals.

The use of the adsorbents able to trap micropollutants is an interesting starting step in order to decrease the degree of pollution [5–16]. Recently, a large number of works have studied the use of

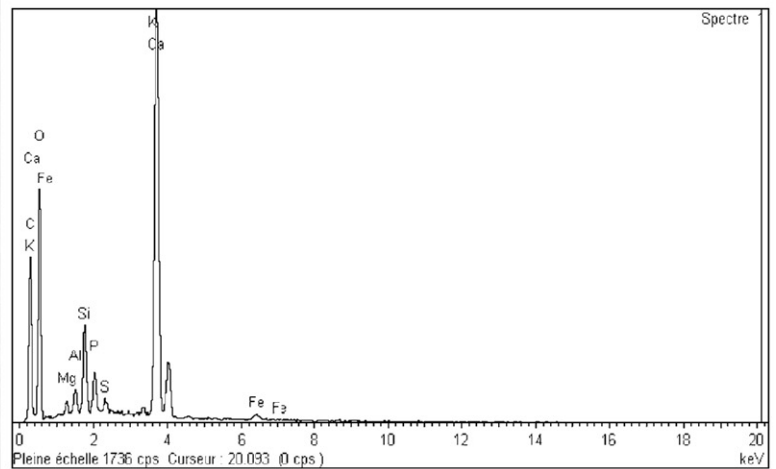
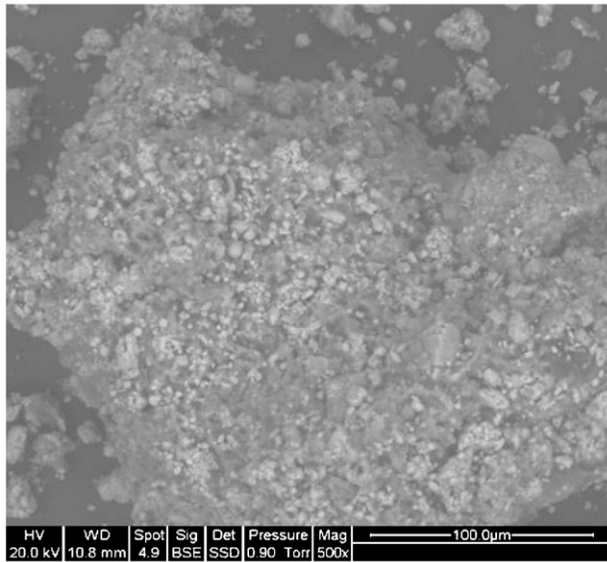
biosorbents (bacteria, algae and fungi, etc.) as an alternative or complementary sorbents to the existing standard adsorbents which are often expensive, ineffective and which generate great quantities of undesirable waste [17–21]. Living or dead microorganisms have been shown to be effective for the removal of the mineral micropollutants. However, alive cells are prone to the toxic effect of heavy metals and require also nutrients [22]. Hence, dead biomaterials can be more attractive [23] for metal removing applications. Activated sludges resulting from the stations of biological treatment can be good biosorbents of heavy metals because of their high content of microorganisms [24–27]. This work aimed at investigating the biosorption of Pb(II) and Cd(II) ions from aqueous solution by a local dairy sludge resulting from the water treatment processes [28–33]. The influence of pH, contact time, sorbent dose on biosorption were investigated. Experimental sorption isotherms were fitted to the Langmuir, Freundlich, and Temkin models. The pseudo first and second order models were used to study the sorption kinetics. Finally, acid desorption tests were performed.

2. Materials and methods

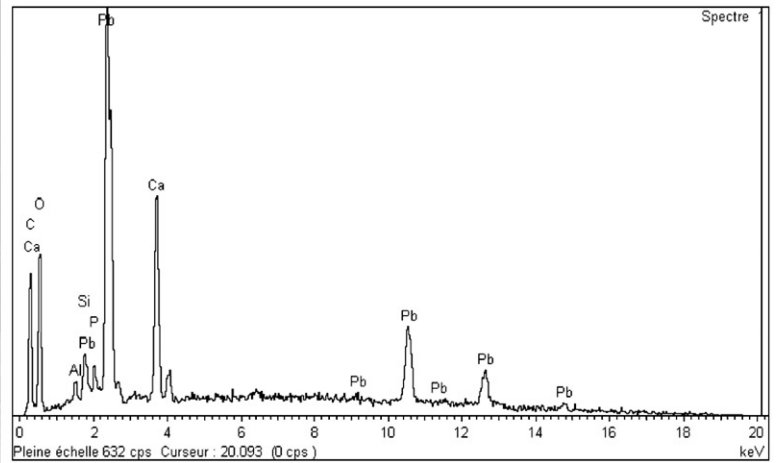
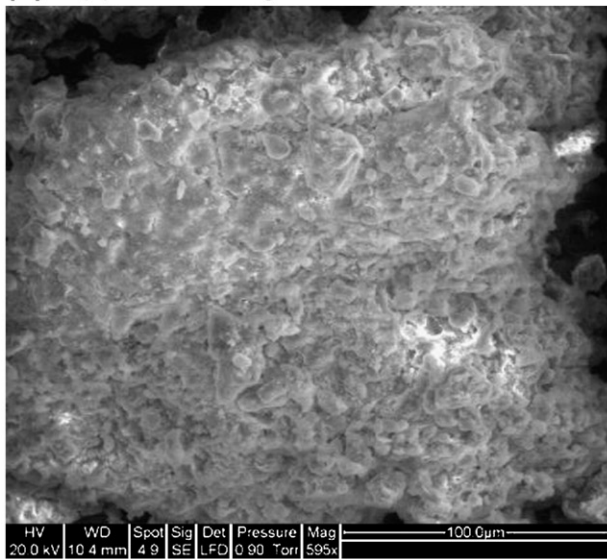
2.1. Preparation of metal ions stock solutions

Metal ions stock solutions were prepared from analytical grade PbCl₂ and CdCl₂, H₂O (Merck, Germany) and were further diluted as required with deionised water produced in the laboratory, then acidified at pH 5.

(a) Unloaded sludge



(b) Pb(II) loaded sludge



(c) Cd loaded sludge

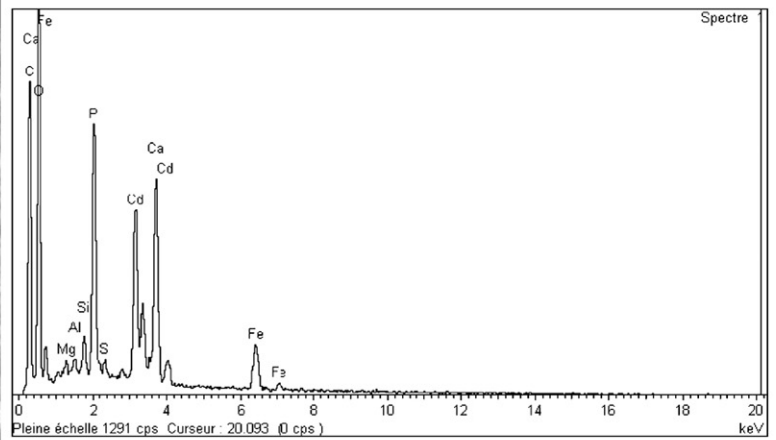
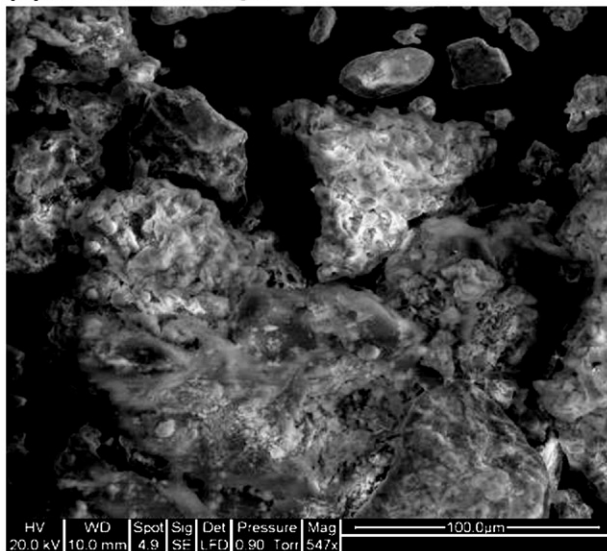


Fig. 1. Sludge SEM/EDX before and after lead and cadmium bio sorption: sludge (a), sludge-Pb (b) and sludge-Cd (c).

Table 1
Chemical composition of the dairy sludge (SEM/DEX).

Element	% Mass	% Atom
C	32.19	45.17
O	40.72	42.89
Mg	0.42	0.29
Al	0.64	0.40
Si	2.22	1.33
P	1.57	0.85
S	0.45	0.24
K	0.42	0.18
Ca	19.76	8.31
Fe	0.67	0.20
Sn	0.94	0.13
Total	100.00	

2.2. Biosorbent characterizations

The sludge was collected from drying beds of a nearby dairy plant, dried overnight at 383 K, ground and sieved, and finally kept in desiccators before use.

The organic fraction was determined by sludge calcinations to constant weight. Microbiological characterization revealed the presence of bacteria, fungi, and algae. Scanning electronic microscopy (SEM) and X-ray spectrometry were used to characterize the biosorbent.

2.3. Experimental procedure

2.3.1. pH effect

Initial pH was varied from a value of 2 to 6 by addition of concentrated hydrochloric acid or caustic soda as required to a suspension prepared by mixing 20 mg of biosorbent with 25 mL of solution of Pb(II) or Cd(II) (100 ppm). The resulting suspension was agitated magnetically for 48 h at 20 °C and the final pH value recorded.

2.3.2. Equilibrium isotherm models

For biosorption isotherms, a series of capped flasks containing 25 mL of metal ions solutions of known concentrations, varying from 10 to 500 mg/L were prepared. Identical amounts (20 mg) of sludge were added to the flasks and the resulting suspensions were agitated magnetically at 200 rpm and 20 °C for 48 h at a constant pH of 5. A 1.2 µm diameter filtration membrane was used to remove the biosorbent, and the filtrates were analysed by inductively coupled

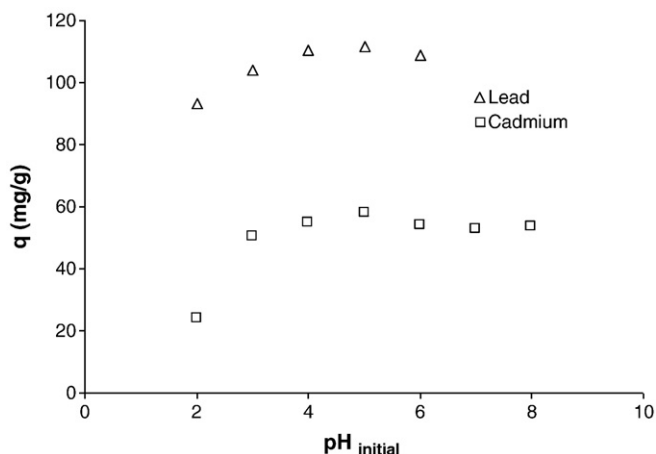


Fig. 2. Initial pH effect on Pb (▲) and Cd (◆) removal conditions ($C_i = 100$ mg/L, 20 °C, 200 rpm, particle size: 250–500 µm).

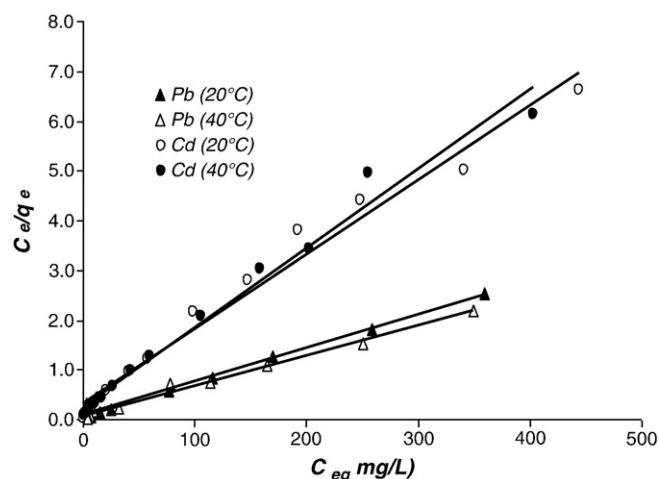


Fig. 3. Langmuir isotherms for Pb(II) and Cd(II) biosorption at (pH = 5; 20 and 40 °C).

plasma mass spectrometry (ICP-MS: 2000 spectrometer Jobin-Yvon, Longjumeau, France). The equilibrium adsorption capacity (or adsorption density), q_e , (mg/g) at different metal ions concentrations was determined using the following equation:

$$q_e = \frac{(C_0 - C_{eq})V}{1000m} \quad (1)$$

where C_0 is the initial (adsorbate) solute concentration (mg/L), C_{eq} is the equilibrium adsorbate concentration (mg/L), V is the volume of the liquid phase (mL), and m is the mass of the adsorbent sample (mg).

Three frequently used single-component adsorption models were considered: Langmuir, Freundlich and Temkin [34] models. The Langmuir isotherm may be expressed in its linearised form as:

$$\frac{C_{eq}}{q_e} = \frac{1}{Kb} + \frac{1}{b}C_{eq} \quad (2)$$

The linear plot of $C_{eq}/(q_e)$ versus C_{eq} yields the maximum adsorption capacity corresponding to complete monolayer coverage b (mg/g) and the Langmuir constant K (L/mg). The Freundlich model has been widely used to describe adsorption experiments. In this model, the uptake of metal ions occurs on a heterogeneous adsorbent surface. It is assumed that the stronger binding sites are occupied first and that the

Table 2

Langmuir, Freundlich and Temkin parameters for the biosorption of Pb(II) and Cd(II) by dairy sludge at pH 5.

Metal ions	Isotherm type								
	Langmuir			Freundlich			Temkin		
	b (mg g ⁻¹)	K (L g ⁻¹)	R^2	k_f (L g ⁻¹)	n	R^2	B	A (L g ⁻¹)	R^2
Lead									
20 °C	148.5	0.074	0.992	21.9	2.6	0.611			
40 °C	178.6	0.030	0.948	18.6	2.16	0.406			
Cadmium									
20 °C	66.7	0.049	0.980	16.2	4.10	0.967	7.926	1.772	0.967
40 °C	69.9	0.050	0.944	16.2	3.97	0.893	8.086	1.699	0.965

A quantitative chemical analysis was also performed at the "Service central d'analyse" at the National Centre for Scientific Research (CNRS), Solaize (France) after lead intake which revealed that level of calcium did not change after fixation and therefore ion exchange cannot account for the high sorption capacity as calcium is strongly linked to proteins as in caseins.

Table 3
Maximum uptake b (mg/g) for some biosorbents taken from literature.

	Pb(II)	Cd(II)	Ref.
Activated sludge	131.6	84.30	[28]
Fungal biomass	47.40	35.90	[17]
Phanerochaete chrysosporium	85.86	27.79	[18]
Algal biomass: Nostoc	93.46	–	[21]
Ulva Lactuca	34.70	29.20	[19]
Grape stalk waste	49.88	27.87	[10]
Dairy sludge	148.6	66.70	This study

These relatively high sorption capacities cannot solely be explained by the small surface area found around $1.2 \text{ m}^2/\text{g}$ but rather by the numerous and complex functional groups present on the sludge surface.

binding strength decreases with the increasing degree of site occupation. The linearised form of Freundlich equation is given by:

$$\log q_e = \log k_f + \frac{1}{n} \log C_e \quad (3)$$

where the parameters k_f and n can be obtained from the intercept and slope of the plot of $\log q_e$ versus $\log C_{eq}$.

The Temkin isotherm assumes that the fall in the heat of sorption is linear rather than logarithmic, as implied in the Freundlich equation. The linearised Temkin isotherm model has generally been applied in the following form

$$q_e = B \ln A + B \ln C_e \quad (4)$$

where, q_e (mg g^{-1}) and C_e (mg L^{-1}) are the amounts of adsorbed metal ion per unit weight of adsorbent and unadsorbed metal ion concentration in solution at equilibrium, respectively and $B = (RT)/b$. T the absolute temperature and R is the universal gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$). The constant b is related to the heat of sorption. If a plot of q_e versus $\ln C_e$ yields a linear line, A and B can be found.

2.3.3. Kinetic modeling

In order to examine the adsorption controlling mechanism, pseudo-first-order and pseudo-second-order kinetic models [35] were applied to experimental data of the studied metal ions. Kinetic experiments were conducted for different initial quantities ((0.5 g, 1.0 g and 2.0 g for Pb(II), and 1.0 g, 2.0 g and 4.0 g for Cd(II) respectively), and for particle diameters of $80 \mu\text{m}$, $125\text{--}250 \mu\text{m}$ and $250\text{--}500 \mu\text{m}$) of sludge to which identical volumes of Pb(II) or Cd(II) solutions (100 g/L) were added in stirred flasks for 72 h at a speed of

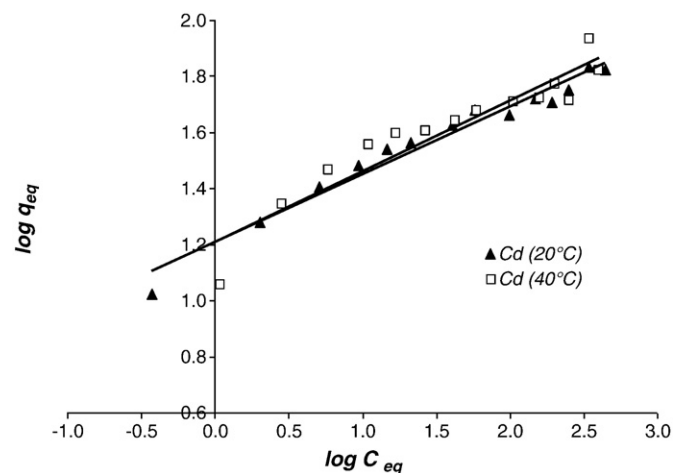


Fig. 4. Freundlich isotherm for Cd(II) biosorption at (pH=5; 20 and 40 °C).

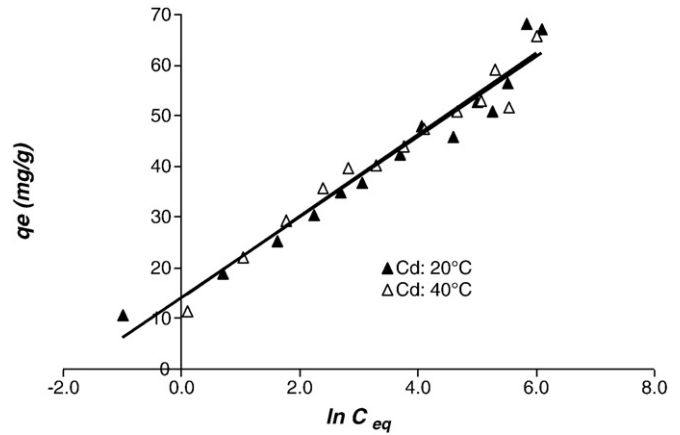


Fig. 5. Temkin isotherm for Cd(II) biosorption at (pH=5; 20 and 40 °C).

200 rpm, a pH of 5, and a temperature of 20 °C. Solution samples of 4 mL were withdrawn at regular intervals, filtered and the metal ions concentration measured. Similar tests were performed by varying the initial concentration of the metal ions (50, 100 and 200 mg/L) and the average particle diameter (<80 , $125\text{--}250$ and $250\text{--}500 \mu\text{m}$).

Effects of biosorbent dose, initial concentration and particle diameter on kinetics were also performed [36,37]. The pseudo first kinetic model for adsorption can be described by the following equation:

$$\log(q_e - q_t) = \log q_{e,1} - \frac{k_1}{2.303} t \quad (5)$$

where q_e and q_t (mg g^{-1}) are the amount of adsorbed metal ion at equilibrium and at time t respectively and k_1 (min^{-1}) is the rate constant of first order adsorption. The applicability of this kinetic model is suggested by the straight line of $\log(q_e - q_t)$ versus t . From the intercept and slope of the plot q_e and k_1 can be determined respectively.

The pseudo second order can be described by:

$$\frac{t}{q_t} = \frac{1}{k_2 q_{e,2}^2} + \frac{1}{q_e} t \quad (6)$$

where q_t (mg g^{-1}), is the amount of metal ion adsorbed at various times t (q_2 and k_2 are the maximum adsorption capacity (mg g^{-1}) and

Table 4
Kinetic parameters for the biosorption of Pb(II) and Cd(II) ions onto dairy sludge.

Conditions	Lead (II)			Cadmium (II)		
	q_e (mg/g)	$K_2 \cdot 10^{-3}$ ($\text{g mg}^{-1} \text{ min}^{-1}$)	R^2	q_e (mg/g)	$K_2 \cdot 10^{-3}$ ($\text{g mg}^{-1} \text{ min}^{-1}$)	R^2
Initial conc. (mg/L)						
50	45.87	3.5	0.9968	21.5	6.0	0.9999
100	88.50	0.49	0.9992	32.7	3.2	0.9999
200	117.6	0.27	0.9985	39.1	3.22	0.9998
Particle size (μm)						
80	76.90	1.2	0.999	5	5.0	0.9998
125–250	88.50	0.5	0.9992	3.2	3.2	0.9999
250–500	90.10	1.3	0.9996	1.5	1.5	0.9996
Sludge dose (g/L)						
0.5	112.40	0.67	0.9994			
1.0	98.00	0.18	0.9888	44.4	4.2	0.9999
2.0	43.10	16.5	0.9987	32.7	3.2	0.9999
4.0				21.8	4.8	0.9977

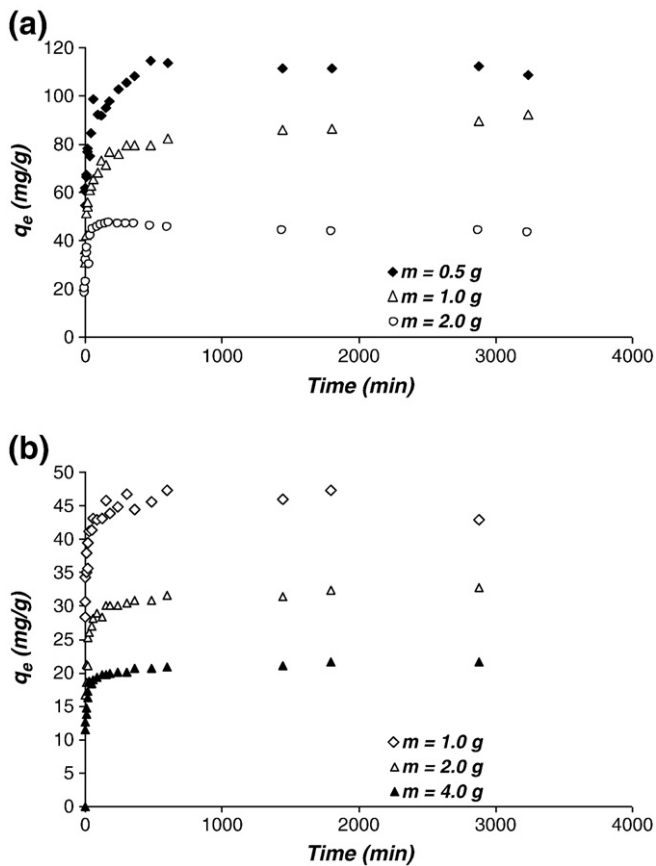


Fig. 6. Biosorption kinetics of Pb (a) and Cd (b) removals as a function of biosorbent dose.

the equilibrium constant rate for the pseudo-second-order adsorption ($\text{g mg}^{-1} \text{min}^{-1}$), respectively.

2.3.4. Metal ions desorption

Several methods have been developed that can strip metal ions from solid surface to a certain extent. They are based on desorption of metal ions using acids, bases, inorganic salts or solvents [38]. The recovery of lead and cadmium has been the subject of some investigations [39,40]. In order to determine the recovery rate, samples containing metal ions used during adsorption experiments were treated by hydrochloric and nitric acids (HCl and HNO_3) with various concentrations (0.1, 0.2 and 0.3 M). In each case, 20 mg of metal ion laden sludge were mixed with 25 mL of acid and agitated during 3 h at 20 °C for 200 rpm. The sample was centrifuged and the clear supernatant was filtered through a 1.2 μm diameter membrane and analysed for metal ion contents.

3. Results and discussion

3.1. Characterizations of biosorbent

The analysis of the sludge gave a 65% of organic matter content and a presence of aerobic germs, total coliforms, staphylococcal, the streptococcus lactic ones, bacterial spores, yeasts and moulds, algae and protozoa. The sludge analysis by Scanning Electron Microscopy before and after metals uptake is shown in Fig. 1 (a, b, c). The micrographs show the appearance of grains on biosorbent after adsorption whereas they were absent before the biosorption. The SEM observed grains were also characterized by energy dispersive X-ray spectrometry: EDX. Fig. 1b and c shows the signals of Pb(II) and Cd(II) on the surface of biosorbent. Table 1 summarizes the chemical

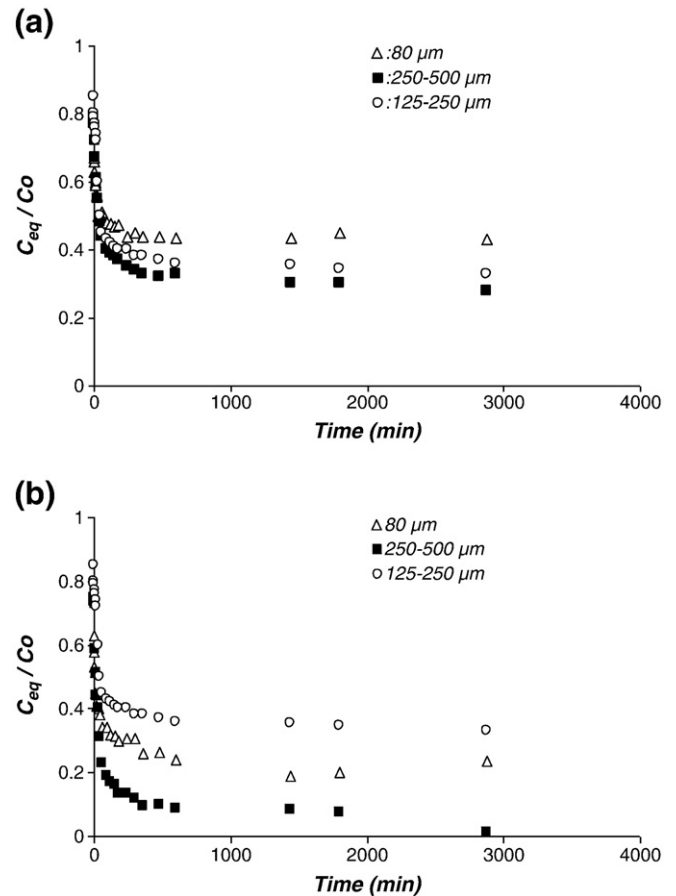


Fig. 7. Biosorption kinetics of Pb (a) and Cd (b) removals as a function of particles diameter.

composition of biosorbent used. Besides carbon and oxygen, high level of calcium was found in this sludge. The dairy wastewater is laden with lactoserum which is rich in calcium complexing proteins as in caseins, for instance.

3.2. pH effect

The effect of hydrogen ions concentration on biosorption of heavy metals has been the subject of many studies which showed the importance of this parameter on the solubility of the metal ions as well as on the ionization of the fixing sites [41]. In this work, pH was varied in order to determine its optimum value for maximum biosorption of lead and cadmium ions. As depicted in Fig. 2, the metal ions uptake ions was strongly affected by the pH of the medium as it increased with solution pH increase. The sharpest increase in maximum capacity (q_e) was obtained between pH values of 2 and 5, corresponding for the latter pH value to capacities of 111.8 mg/g and 58.1 mg/g for lead and cadmium, respectively. To avoid metal precipitation biosorption tests were not conducted beyond this maximum value of pH [31].

At low pH values, the high concentration of H^+ protons competes with and decreases the adsorption of positively charged metal ions [8,41] but an increase in the pH causes the ionization of the biosorbent surface functional groups and thus, increases the total negative charge which increases biosorption. The variation of the final pH as a function of the initial pH tests was also conducted. We found that the equilibrium pH stabilizes at around 5 for an initial pH of 5. The biosorbents would behave as buffers by modifying the pH of the medium [17].

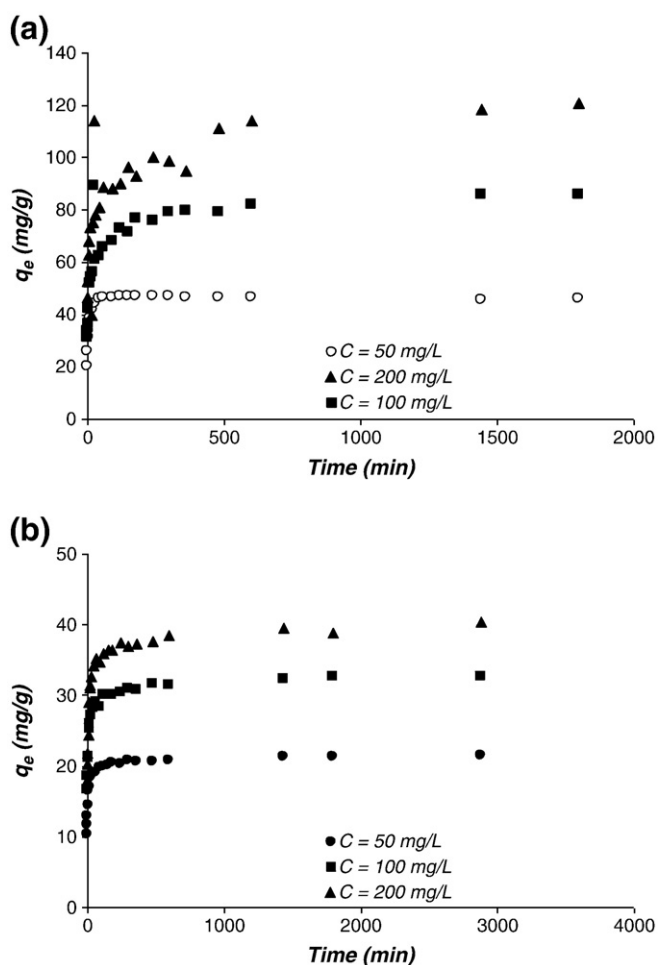


Fig. 8. Biosorption kinetics of Pb (a) and Cd (b) removals as a function of initial concentration.

3.3. Biosorption isotherms

The equilibrium adsorption isotherm which gives the capacity of the adsorbent at a fixed temperature is an important physicochemical quantity for evaluating an adsorption process. Three commonly used types of adsorption isotherms are considered here: Langmuir, Freundlich and Temkin adsorption isotherms [34].

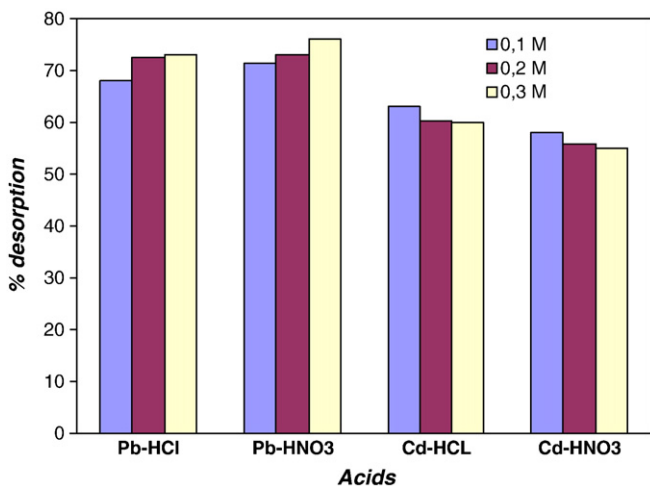


Fig. 9. Acid nature and concentration effects on Pb(II) and Cd(II) elution.

They correspond to the metal ions splitting between the liquid and solid phases at equilibrium. Fig. 3 shows the linear form of the Langmuir adsorption isotherm of Pb(II) and Cd(II) by dairy sludge at a pH of 5 and temperatures of 20 and 40 °C. Initially, the adsorption rate increases linearly with the increase in the concentration until equilibrium is reached corresponding to the maximum adsorption capacity for metal ions (saturation). The temperature increase to 40 °C enhanced the maximum capacity especially for Pb(II). Q_{max} at 40 °C is higher than at 20 °C (from 148.6 to 178.5 mg/g): It is an endothermic process as an increase in temperature would entail the appearance of new fixing sites leading to a higher Q_{max} . The values of the maximum capacity of adsorption b are shown in Table 2 compared with some values reported in literature for both metal uptakes, given in Table 3. The results obtained show a good correlation for the Langmuir model for both metals and a good affinity of this material for lead. The Freundlich model does not apply well, especially in the case of Pb at 40 °C at high concentrations (100 to 500 mg/l) as it is well known that it best fit slow concentration ranges. But at low concentrations it fitted well the experimental data with a determination coefficient R^2 higher than 0.98. As shown in Figs. 3–5 the three proposed models best fit the cadmium removal at both considered temperatures.

3.4. Kinetic studies

Sorption equilibria investigation is important for the determination of the sorption efficiency but cannot explain the mechanisms involved that is the reason why kinetic studies are performed.

The fitting of the intraparticle model may give an insight as to what step controls the sorption process. For the three parameters studied (initial concentration, sludge dose, particle diameter). Three distinct parts can be identified on the kinetic curves: The first one corresponds to the external diffusion, the second phase which is longer to intraparticle diffusion and the equilibrium step to a plateau like behavior. When more than one step are present, intraparticle diffusion is not the sole limiting step. Sorption itself can be accounted for by several interactions between the metal ions and the sorbent due to the numerous and complex surface functional groups present on the sludge.

The kinetics of biosorption, representing the rate of adsorption of the biosorbate controlled by the residence time in the solid-liquid interface is the principal characteristic defining the sorption efficiency [42]. The biosorption kinetic parameters of lead and cadmium found from a linear form of the pseudo-second order model are given in Table 4. The best fit model was selected based on the correlation coefficient, R^2 values (first order parameters are not shown as a figure since R^2 values are low). The second order model includes the different phases of the sorption process (external diffusion, intraparticle diffusion and sorption itself) and also its applicability suggests that a chemical process might control the sorption process but the mechanisms involved are not identified. In this case, the pseudo second-order kinetic model mechanisms describe well the biosorption of lead and cadmium with correlation coefficients greater than 0.998 for all the studied cases.

3.4.1. Effect of biosorbent dose

The sludge dose effect on Pb(II) and Cd(II) removal is shown in Fig. 6. The maximum uptake of the two metals was obtained at a sludge concentration of 0.5 g/L and 1.0 g/L respectively for Pb(II) and Cd(II). The increase of biomass dose decreases slightly the equilibrium time and prevents the metal ions from reaching the various sites of biosorption [27].

3.4.2. Effect of particle diameter

The biosorbent contact surface area with metal ions solution is important for biosorption process. Fig. 7 shows the effect of particle size on the biosorption. The quantity of metal remaining in the

solution increases slightly with a decrease in particle diameter, particularly at equilibrium.

3.4.3. Effect of initial concentration

The initial metal concentration constitutes a significant driving force allowing the metallic mass transfer between the aqueous and the solid phases [25]. The relationship between contact time and metal ion removal by the dairy sludge for three different initial concentrations is illustrated in Fig. 8 at a pH of 5 and for an adsorbent dose of 1 g/L and 2 g/L for Pb(II) and Cd(II), respectively. It can be seen from Fig. 9 that an increase in initial concentration results in an increase in the amount of metal removed. It can be concluded that the rate of binding with sludge is initially high, but it gradually decreases to reach equilibrium after a period of 500 min for both metal ions.

The result obtained for the biosorption kinetics of Pb(II) and Cd(II) onto the dairy sludge as a function of biosorbent dose, initial concentration and particle diameter are shown in Table 4. The various correlation coefficients being greater than 0.998 indicate that the pseudo-second order model best describes the metals ions biosorption and that a chemical biosorption process may be involved [43].

3.5. Metal ions desorption

Desorption experiments of lead and cadmium ions with nitric and hydrochloric acids were carried out in duplicate and are shown in Fig. 9. It can be seen that lead is better eluted with HNO₃ (0.3 M) yielding a desorption rate of 76.6% whereas cadmium was better recovered with HCl (0.1 M) with 62.5 % recovery rate. The smaller elution of Cd⁺⁺ ions with respect to Pb⁺⁺ may be explained by its fixation in depth the sorbent due its smaller ionic diameter. In the literature, both ions are reported to be well eluted by both HNO₃ and HCl.

4. Conclusions

The capacity of a dairy sludge to remove Pb(II) and Cd(II) was investigated. The room temperature maximum uptakes obtained at a pH of 5 for Pb(II) and Cd(II) were 148.6 and 66.7 mg/g, respectively. The temperature increase from 20 °C to 40 °C enhanced the maximum capacity especially for Pb(II) from 148.6 to 178.5 mg/g. The experimental adsorption data for both metal ions fitted reasonably well the Langmuir model, while, the Freundlich and Temkin models described well the Cd(II) biosorption. The lower values of R² show that the biosorption of lead is not well described by the Freundlich isotherm especially at higher concentration (>100 mg/L).

The biosorption kinetics for the metal ions studied at different initial solutions concentrations, dairy sludge loadings and particle diameter were best described using pseudo-second order suggesting a chemical process for the mechanism of biosorption between the metal ions and the sorbent. The tests of desorption showed that up to 76.6% of Pb(II) were recovered by HNO₃ (0.3 M) and 62.5% of Cd(II) by HCl (0.1 M). This study shows that this dairy sludge as a solid waste can be used as an alternative to cleanse heavy metal laden industrial wastewater.

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