



Research article

Biosorption of nickel ions Ni^{2+} by natural and modified *Pinus caribaea* Morelet sawdust



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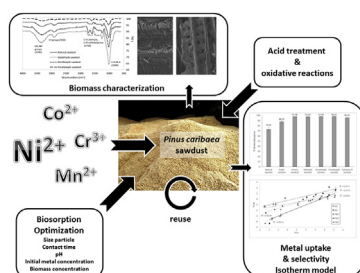
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HIGHLIGHTS

- *Pinus caribaea* sawdust is an effective biosorbent of metallic trace elements.
- High Ni^{2+} removal efficiency was observed at pH 8 with 5 g/L of biosorbent.
- Equilibrium adsorption was described by Freundlich and Langmuir isotherms.
- Pine sawdust is a reusable biosorbent with good desorption capacity.
- Efficiency of acidified and oxidized adsorbents.

GRAPHICAL ABSTRACT



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ABSTRACT

The potential of *Pinus caribaea* Morelet sawdust for the removal of nickel ions (Ni^{2+}) and other metallic trace ions (Co^{2+} , Cr^{3+} , Mn^{2+}) from aqueous solutions was investigated under batch conditions. Several parameters such as size of particles, contact time, pH, initial metal and biomass concentrations, desorption conditions and reusability were evaluated on natural biomass. Biosorption was fast, effective (73%) and biomaterial can be reused after five cycles. To enhance the removal capacity of nickel, pine sawdust was modified by acidic and oxidative treatments. Cellulosic residues from sawdust sequential extraction showed great biosorption capacity (96%). In the presence of a metal mixture, oxidized sawdust had better selectivity for Cr^{3+} ions than for Ni^{2+} . *Pinus caribaea* biomass could be an environmental, inexpensive and renewable material for the depollution of water laden with metallic trace elements.

1. Introduction

Pollution by trace metals and their bioaccumulation in ecosystems is a global problem. Metals are particularly present in rivers and groundwater because of natural processes (rocks alteration and soil erosion) and anthropogenic activities which lead to uncontrolled discharges of urban, industrial and agricultural wastewater (Lakherwal, 2014).

New Caledonia is a South Pacific island characterized both by soils naturally rich in metallic trace elements and by nickel mining and industrial activities of worldwide importance (Losfeld et al., 2015). One third of the main island is covered by ultramafic rocks rich in transition elements as iron, nickel, cobalt, manganese or chromium which can be released in surface waters (Gunkel-Grillon et al., 2014). In this archipelago, nickel and chromium are two elements found in the urine of

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populations exposed to concentrations above international reference values, in particular in children (St-Jean et al., 2018).

To reduce the potential health risks associated to metals chronic exposure through the consumption of drinking water and for the removal of trace metal elements in aqueous solution, several treatment methods have been described (Lakherwal, 2014; Volesky, 2001; Lin and Juang 2002). Among them, biosorption have the advantages of being low cost, ecological, flexible, simple to implement and the possibility to be reuse (Volesky et al., 2003; Torres, 2020; Gupta et al., 2015; Demirbas, 2008; Veglio and Beolchini, 1997; Bailey et al., 1998).

Forestry by-products such as sawdust and bark have many advantages because they are abundant, generally not toxic, and the macromolecules that compose them are known to bind metal ions (Gupta et al., 2015; Basso et al., 2002; Shukla et al., 2002). In particular, the biomass from trees of the genus *Pinus* has been described as good biosorbent for removing metallic trace elements (Gundogdu et al., 2009; Argun et al., 2005; Uzun et al., 2003). For example, the *Pinus halepensis* untreated sawdust traps cadmium, copper and lead in aqueous solutions (Semerjian, 2010 and 2018). For the removal of nickel (II) from aqueous environment, a review describes various agricultural solid wastes used as biosorbent like peanut hulls, pine bark or pine cone (Raval et al., 2016). Another example is the used of treated mahogany sawdust as biosorbent for the removal of nickel from aqueous solution (Chanda et al., 2021).

In the context of the bioresource use and circular economy perspective, our work is focused on *Pinus caribaea* Morelet, a native conifer from Central America and Caribbean islands. This species was widely planted for timber production in tropical regions including New Caledonia, where it is nowadays the most exploited wood. This work investigates the use of sawdust from *P. caribaea* as a biosorbent material for Ni^{2+} removal and other metallic trace elements Co^{2+} , Cr^{3+} , Mn^{2+} ions from aqueous solutions. This study allows the determination of optimal conditions (pH, contact time, initial Ni^{2+} and biomass concentration) based on batch experiments. Isotherms of Langmuir and Freundlich have been compared and kinetic parameters have been calculated by pseudo-second-order models. Extraction of parietal components of sawdust was carried out to evaluate the biosorption capacity of cellulosic material. In addition, the selectivity of sawdust has been evaluated according to four metals in solution (Ni^{2+} , Cr^{3+} , Co^{2+} and Mn^{2+}) taken separately or in mixture to take into account the behaviour of biosorbent in more realistic conditions.

The impact of different chemical treatments of natural sawdust was furthermore investigated in this work. Two treatments and three oxidations of sawdust were carried out by acidic and oxidation methods. The aim was to improve the capacity of nickel Ni^{2+} removal compared to the natural biomass. The modification using an environmentally friendly technique was chosen to evaluate the selectivity of this material.

2. Materials and methods

2.1. Preparation of biosorbent material

2.1.1. Raw material

Pine tree sawdust used in this work was from *P. caribaea* Morelet. The material for the preparation of biosorbent was obtained from local garden center. Before use, pine sawdust was washed in deionized water to remove surface impurities and then dried in an oven (Memmert Universal Oven UF1060 marque) at 40 °C for 4 days. Then, sawdust was ground into fine particle in a blender (Knife Mill GM 300) and sieved in a second crusher (Polymix PX-MFC 90 D) to the particles size required (0.2 or 0.5 mm).

2.1.2. Extraction of polymers

The parietal polymers of wood were obtained through successive extractions. The first step allows to get extractables like circulating

sugars, tannins, mineral elements by an 80% hydroethanolic solution mixed with 10 g of sawdust powder. The solution was stirred for 7 min through Soxhlet apparatus. The residue was obtained by filtration and washed with ethanol 80%. For pectins, lignins, hemicelluloses and cellulosic residue extractions, protocols have been used according to the literature (Astier, 2010).

2.1.3. Modification of biomass

Five biomass modifications have been carried out by washing the sawdust (5 g, 0.2 mm) with different reagents following chemical protocols optimized from the literature (Hachem et al., 2012; Astier, 2010; Varmat and Chavan, 1995).

The acidic sawdust (S_H^+) was obtained by washing the adsorbent material in a solution of H_2SO_4 (0.1 M) under stirring for 2 h at 50 °C.

Fenton oxidized sawdust (S_F) was obtained by washing sawdust in 500 mL of water at 25 °C for 2 h. After filtration, a mixing solutions of hydrogen peroxide 50 mM and iron sulfate 0.5 mM was equilibrated in biomass at pH 3 by adding H_2SO_4 solutions (0.1 M). The solution was stirred at 25 °C for 1 h. Finally, the biomass was filtered, washed and then stirred in a H_2SO_4 solution (0.1 M) for 1 h.

The oxidation techniques to get dialdehyde (S_{CHO}), di-carboxylic ($\text{S}_{\text{COOH}(2)}$) and tri-carboxylic ($\text{S}_{\text{COOH}(3)}$) sawdust have been optimized from polysaccharide oxidation described in the literature (Hachem et al., 2012; Varmat and Chavan, 1995). Therefore, di-carboxylic sawdust ($\text{S}_{\text{COOH}(2)}$) was obtained by reaction of 1.5 g of dialdehyde sawdust (S_{CHO}) in 600 mL of sodium chlorite (0.3 M). Tri-carboxylic sawdust ($\text{S}_{\text{COOH}(3)}$) was obtained from 3 g of $\text{S}_{\text{COOH}(2)}$ in 300 mL of solution containing TEMPO (2,2,6,6-tetramethylpiperidin-1-yl)oxyl (0.24 mmol), sodium bromide (3.63 mmol) and sodium hypochlorite (7.26 mmol). Aldehyde functions formed on the biomass after oxidation are determined using the Cannizzaro reaction (Pommerening et al., 1992). Indeed, 100 mg of modified sawdust was suspended in 20 mL of sodium hydroxide (0.1 M) and the solution was stirred at 70 °C for 15 min. The excess of sodium hydroxide was neutralized by 0.05 M hydrochloric acid.

2.2. Characterizations of natural and modified adsorbent material

The functional groups on the surface of natural and modified biomass were identified by Fourier Transform Infrared (FTIR) spectrometer, ATR Frontier by PerkinElmer (spectrum range of 400–4000 cm^{-1}). The morphology and surface of natural and modified sawdust particles were observed by a scanning electron microscope (SEM, JSM-IT300 LV/LA).

The PH_{PZC} (Point of zero charge) of natural sawdust was determined by adding amounts of biosorbent at different pH values (Tran et al., 2017). In series of centrifuge tubes (50 mL), the pH was adjusted with 0.1 M HCl and 0.1 M NaOH as needed, to obtain the appropriate pH range of 2, 3, 4, 5, 6, 7, 8, 9, 10 and 11. These pH values are denoted as the initial pHs (pH_i). 100 g of sample were added and solutions were completed with deionized water. The solutions ns were shaken on a mechanical platform shaker at 250 rpm for 24 h and the final pH in each tube were measured and denoted as pH final (pH_f). The PH_{PZC} was obtained from the plot of ΔpH ($= \text{pH}_f - \text{pH}_i$) versus pH_i or the plot of PH_f versus PH_i . Experiments were carried out in triplicate and the mean value was recorded.

2.3. Preparation of metal ions solutions and analytical methods

A solution containing 5 g/L Ni^{2+} ions was prepared from a solution of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Sigma-Aldrich) in a volumetric flask with deionized water. The working solution was carried out by appropriate dilutions with varying concentration (mg/L) of the mother solution at a given pH. Other metals solutions were prepared in the same way from solutions of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and $\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ respectively.

An Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES 730ES Varian) was used to analyze metal ions concentrations in experimental aqueous solutions. A reference scale of Ni^{2+} solutions at

known concentrations was realized in the range among 0.005–20 mg/L as a calculus base for the ICP-OES to determine further concentrations. Samples with an initial Ni²⁺ concentration higher than 20 mg/L were prepared by adequate dilution to avoid any error during the analyzing process.

2.4. Biosorption

The biosorption of Ni²⁺ on the pine sawdust was studied through batch technique by studying the effect of particle size, pH, contact time and initial adsorbate concentration. The general method was as follows: 10 mL of nickel solutions at varying concentrations (0.5–1000 mg/L) was in reaction with biomass (1–20 mg) at pH 5 for the first batch. Values of pH of solutions were adjusted to desire levels (pH = 1 to 9) using diluted NaOH or HCl solutions.

The suspension in the tube was stirred at 25 °C on a mechanical platform shaker at 250 rpm for 16 h to reach equilibrium. The influence of contact time on adsorption efficiency were investigated by shaking the tubes at different times (10 s–360 min). Biomass was removed by vacuum filtration through 0.45 μm nitrocellulosic membrane, and the concentration of Ni²⁺ ions in the filtrate was analyzed using ICP-OES. All the biosorption experiments were repeated in triplicate.

Compared to the initial metal concentration, the adsorption efficiency in the following Eq. (1) was calculated as a percentage of adsorbed metal in equilibrium. Adsorption capacity is the amount of metal adsorbed per mass unit of sawdust according to Eq. (2).

$$\text{Metal removal efficiency(\%)} = \frac{(C_i - C)}{C_i} \times 100 \quad (1)$$

$$q(\text{mg/g}) = \frac{(C_i - C) \cdot V}{m} \quad (2)$$

where, C_i and C are the initial and equilibrium concentrations of metals ions (mg/L) in solution, q is the adsorption capacity (mg/g) or the mass of metal ion solution adsorbed per unit mass of sawdust (mg/g), V is the volume of solutions (L) and m is the sawdust mass (g).

2.5. Desorption

The Ni²⁺ ions retained by pine sawdust have been extracted by experiments in a batch system by investigating different concentrations of two acids: hydrochloric acid (0.01, 0.1 and 0.5 M) and sulfuric acid (0.005, 0.05 and 0.25 M). Previously dried, the biomass loaded with Ni²⁺ ions was stirred for 16 h in 10 mL of HCl or H₂SO₄ solutions. The solution was filtered through 0.45 μm nitrocellulose membrane and analyzed by ICP spectrometer to determine the amount of Ni²⁺ desorbed.

2.6. Adsorption isotherm models

The relationship between the amount of Ni²⁺ ions adsorbed and its equilibrium concentration in aqueous solution was established by models of Langmuir and Freundlich which are the most commonly used (Langmuir, 1918; Freundlich, 1907). Experiments were conducted at different concentration of biomass (1–20 g/L) with different Ni²⁺ initial concentration (0.5–200 mg/L).

2.7. Adsorption kinetics

Most adsorption systems were reported to follow a pseudo second-order kinetic models (Ho and McKay, 1999). Experiments were carried out at various periods ranging from 10 s to 360 min at two pH values to study the effect of acidic and basic conditions.

2.8. Biosorption of a mixture of metals (Co²⁺, Cr³⁺, Mn²⁺, Ni²⁺)

The biosorption capacities of natural and Fenton oxidized sawdust were assessed for the removal of metal ions Co²⁺, Cr³⁺, Mn²⁺ and Ni²⁺ ions from aqueous solutions. Metal solutions were evaluated separately and in a mixture under optimum parameters previously determined (initial metal ion concentration = 5 mg/L (alone or in a mixture), 5 g/L of pine biomass, pH = 8).

2.9. Biomass recycling

To evaluate the reusability of natural pine sawdust, biosorption-desorption cycles were repeated five times using the same concentrations (5 g/L of sawdust). 5 mg/L of initial Ni²⁺ concentration solution was used for biosorption and desorption was performed with 10 mL of 0.1 M HCl solution for 16 h.

3. Results and discussion

3.1. Physicochemical characterization of natural and modified sawdust

3.1.1. Fourier Transform Infrared (FTIR) spectroscopy

The infrared spectra of the natural and modified pine sawdust were carried out to determine the type of functional groups present in the sawdust surface (Figure 1). All spectra shared characteristic absorption bands around 1600–1700 cm⁻¹, 2900 cm⁻¹ and 3300 cm⁻¹ which has been assigned respectively to the stretching vibrations of carbonyl group (C=O), C–H and OH stretching. Nevertheless, we can observe some modifications after the different chemical treatments. Thus, aldehydes groups (S_{CHO}) in pine sawdust is associated to bands around 2855–2849 cm⁻¹ (vibrational stretching of C–H bands) and 1700 cm⁻¹ (C=O) higher than natural sawdust (Stuart, 2005). Bands attributed to COOH groups present at 1500–1600 cm⁻¹ (C=O), and 1200 cm⁻¹ (C–O) are higher in dicarboxylic and tricarboxylic spectra. Generally, band intensities increase in the same direction as the sawdust oxidation degree. The oxidation of aldehyde functions in carboxylic acid function is reflected in a decrease of band intensity around 1740 cm⁻¹ versus a wide band around 1600 cm⁻¹ for dicarboxylic and tricarboxylic sawdust spectra. The presence of band for dicarboxylic sawdust is translated by a non-complete reaction because all aldehydes haven't been oxidized. The spectra of acidified sawdust allow to observe a little increase in the intensity of the band around 1700 cm⁻¹ (C=O aldehyde) as a sign of the disappearance of hemiacetal functions in acid treatment. For Fenton oxidized sawdust, the band characteristic of aromatic rings (1600 cm⁻¹ stretching of C=C) was decreased following degradation.

3.1.2. Scanning electron microscopy (SEM) analysis and energy dispersive X-Ray (EDX) spectroscopy

The microscopic analysis SEM confirms the difference in structure between natural and modified sawdust (Figure 2). Natural sawdust had fibrous and rough surface with heterogeneous structure similar to a spongy aspect. The obtained S_{H+} presented many pits and fissures, possibly because of the powerful dehydrating of sulfuric acid. Oxidized sawdust S_F, S_{CHO} and S_{COOH} had irregular, heterogeneous surface characterized by cracks, the pore volume increase. Thus, oxidized reagents disturb the surface of sawdust making them more available to metals. The adsorption mechanism occurring in pores considers interactions such as electrostatic attraction, hydrogen bonding, surface precipitation, cation exchange. These interactions depend on the characteristics of the porous adsorbents and adsorbate (Tran et al., 2017).

The EDX spectroscopy gives an overview of the sawdust elemental composition before and after nickel biosorption (Table 1s, Fig 1s and 2s in supplementary data). The natural sawdust contains atoms on its surface like carbon and oxygen present in the structural polymers of wood.

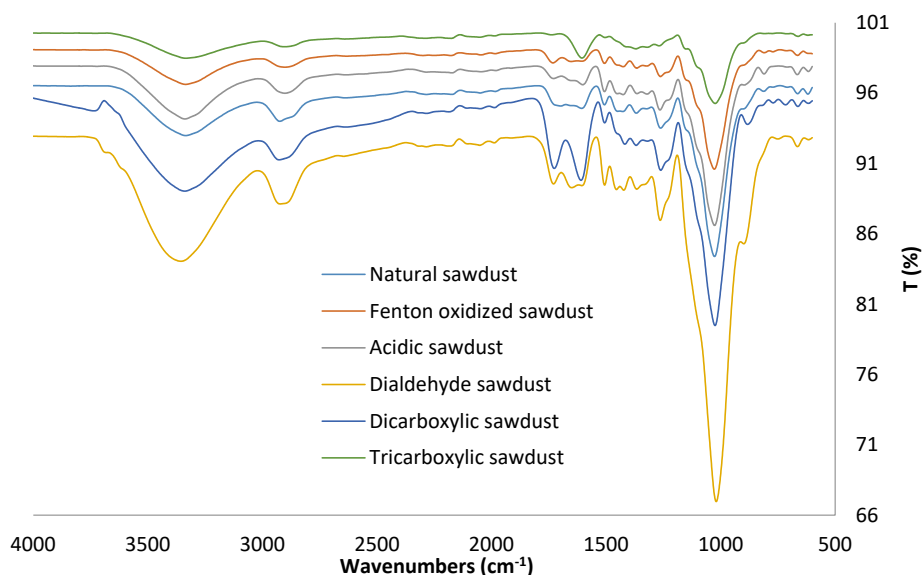


Figure 1. FTIR spectra of natural, treated and oxidized sawdust.

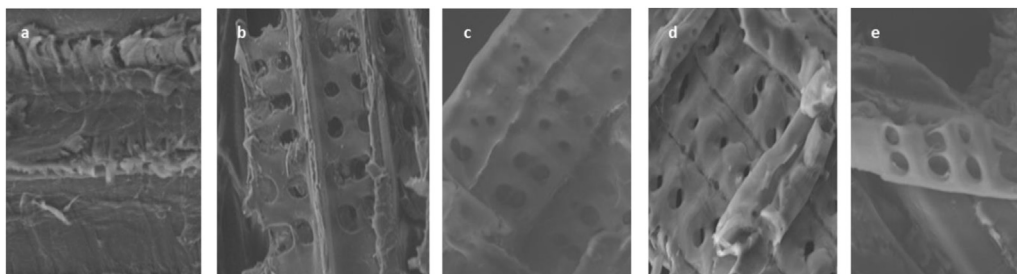


Figure 2. Characterizations by SEM of natural sawdust (a) at 1600x, treated SH+ (b), SF (c) at 650x and oxidized sawdust SCHO (d), SCOOH (e) at 650x.

Other elements are present such as minerals: calcium, manganese, silicon, iron or copper. These elements were naturally absorbed by the biosorbent in its environment. For example, manganese and calcium are found in *P. caribaea* needle samples in works of Carrions et al. (1987). Chlorine and nickel appear in addition on the sawdust after biosorption, chlorine comes from the HCl acid added during pH adjustment. This experiment shows that nickel is present on the surface of pine sawdust after biosorption of 5 mg/L of nickel solution. This element is not the only one present on the surface of the sawdust, which raises the question of the occupation of active sites (Supplementary Data).

3.1.3. Point of zero charge determination

The point of zero charge (pH_{PZC}) of natural sawdust in aqueous solution was obtained by plotting pH final against pH initial or (pH initial – pH final) against pH initial according to Figure 3. For this biomass, the pH_{PZC} was around 4.6. At a pH less than pH_{PZC} , the biosorbent is protonated and the surface positively charged, is able to capture anions. When pH is higher than pH_{PZC} , the biosorbent surface is negatively charged and becomes a trap for the cations. The nickel (Ni^{2+}) is more easily trapped in basic environment. The mechanism involved is electrostatic interaction (Tran et al., 2017).

3.2. Modification yield and quantitative dosage

3.2.1. Modification yield

The mass yields obtained were 92.4, 93.8, 95.0 and 92.0% respectively for S_{H+} , S_F , S_{CHO} , and S_{COOH} . A low loss of mass was observed, the sawdust is reactive to oxidation even after several steps.

3.2.2. Quantitative determination of aldehyde functions (S_{CHO})

The oxidation reaction of polysaccharides by sodium hydroxide was confirmed through the determination of the aldehyde functions present on the sawdust. The Cannizzaro reaction involves the action of base on the aldehyde functions leading to the establishment of a stoichiometric ratio between the concentration of hydroxyl ions consumed and the initial concentration of the dialdehyde groups. The aldehyde functions rate was 12.7 mmol per gram of oxidized pine sawdust. Compared to the estimated value (4.08 mmol) this value is higher, which suggesting that the oxidation was reacted on other polysaccharides.

3.3. Factors affecting efficiency of Ni^{2+} biosorption on sawdust

3.3.1. Initial concentration of Ni^{2+} and size of particles

High metal removal was attained (80%) at Ni^{2+} ions concentration of 0.5 mg/L (Figure 4). The biosorption of metal ions has stabilized for higher concentration of Ni^{2+} because of saturation of binding sites on the adsorbent. In this case, the additional number of metal ions in solution was competing for a limited number of adsorption sites (Ucun et al., 2003).

3.3.2. Adsorbent concentration

Experiments was carried out with sawdust concentrations ranging from 0 to 20 g/L and different Ni^{2+} concentrations (10–100 mg/L) at pH 8 for 16 h. The percent removal of metal ions was increased in the same direction than the mass of sawdust until a quantitative retention for the adsorbent mass of 5 g/L in Figure 5. It is apparent that the Ni^{2+} adsorption evolves with the weight of sawdust because of an increase of

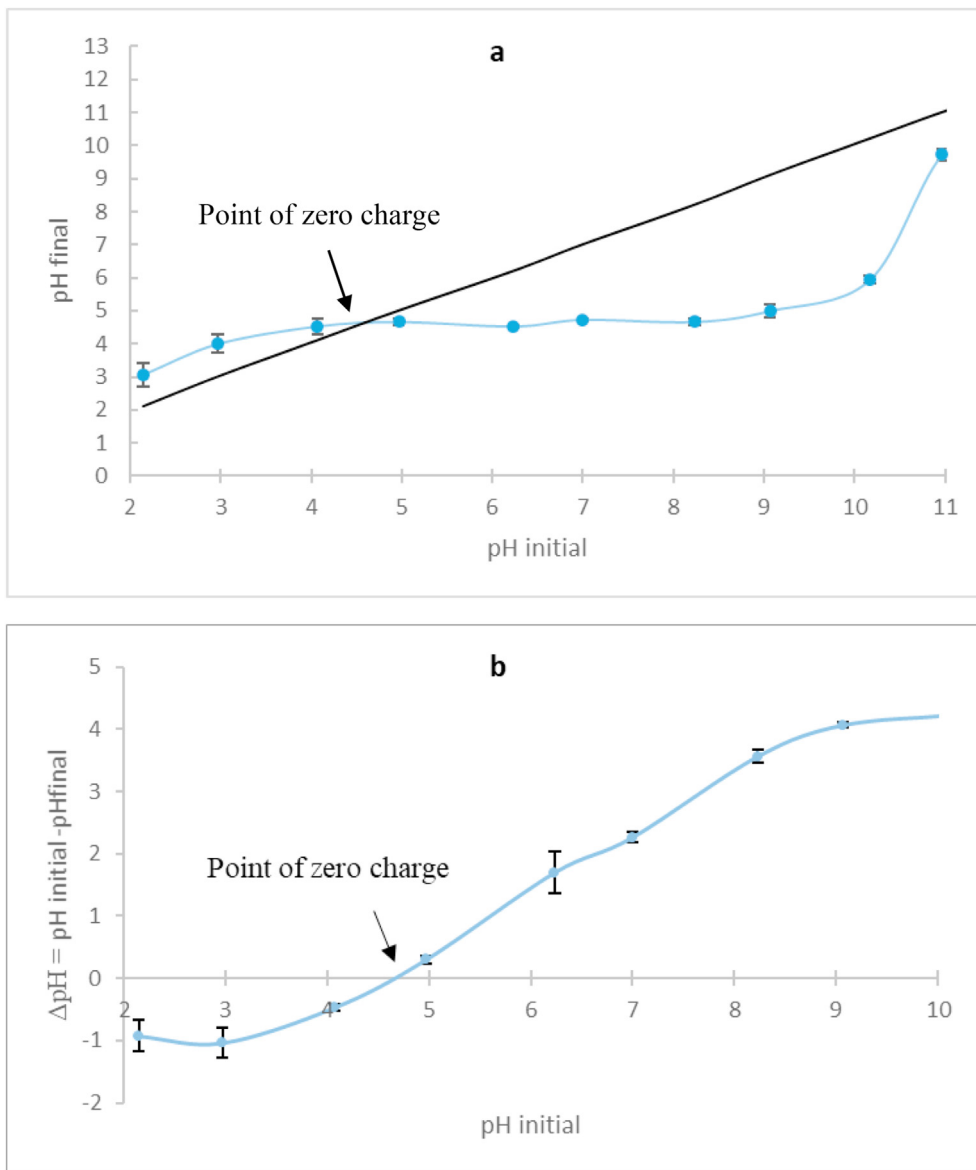


Figure 3. Point of zero charge of natural sawdust, pH final against pH initial (a) and Δ pH against pH initial (b).

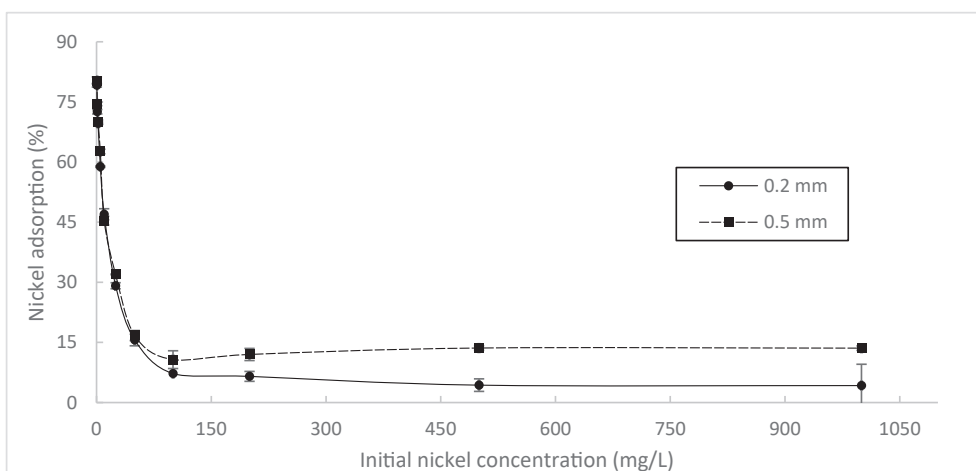


Figure 4. Effects of initial concentration of Ni²⁺ and size of particles.

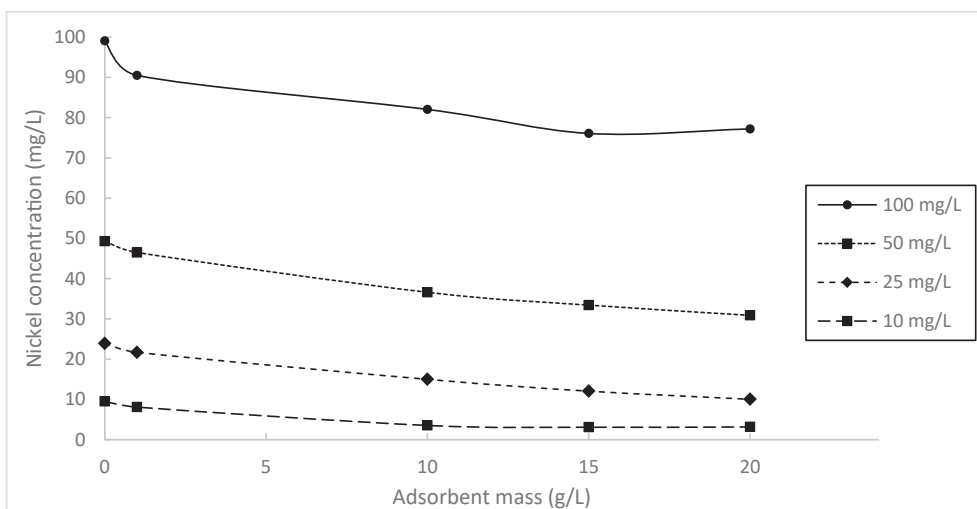


Figure 5. Effect of adsorbent mass.

availability of exchangeable sites. At a moment, the maximum adsorption efficiency of a metal was achieved even after additional added of binding sites from sawdust. Thus, the adsorption efficiency decreases with the increases of the quantity of biomass.

3.3.3. pH of suspension

As an important parameter in the sorption process, pH can act on the functional groups and the charges affecting interactions between ions in solution (Akmal et al., 2012).

Under highly acidic conditions (pH 1–3), the amount of Ni^{2+} uptake was minimal (<0.2 mg/g) while the sorption was enhanced in the pH ranging of 3–9, showing a maximum adsorption at pH 9 (Figure 6). At lower pH values, high concentration of hydronium ions are in competition with Ni^{2+} ions for the active sites on the sawdust surface positively loaded. When pH increase, the competing effect of hydronium ions decreased, Ni^{2+} ions have electrostatic attraction with the surface of sawdust, negatively loaded, allowing a favorable process for the metal ions adsorption (Shukla et al., 2002 and 2005).

Nickel have four different species Ni^{2+} , $\text{Ni}(\text{OH})^+$, $\text{Ni}(\text{OH})_2$ and $\text{Ni}(\text{OH})_3$ but the predominant species is Ni^{2+} at pH 9 (Gonsalvesh et al.,

2016). When the pH increased above pH 9, the percentage of nickel removal decreased by the fact that soluble hydroxyl complexes are formed at higher pH.

The increase observed around pH 4 seems to confirm the acidic character of the unmodified pine sawdust surface that corresponds to pKa of aromatic carboxylic acids. Indeed, Salazar J.J et al. described a high concentration of acid groups, mainly phenolic groups present in the surface of the main components of pine sawdust (Salazar-Rabago et al., 2017).

3.3.4. Contact time

Under basic condition Figure 7(a), a maximum adsorption rate (90%) was achieved instantly and then slowly decreased until equilibrium was reached (2 h, 70% of biosorption). The formation of soluble hydroxyl complexes can lead to decrease of adsorption (Shukla et al., 2005).

Under acidic condition (pH 4), the adsorption rate was increased during the first 5 min and reach equilibrium after 1h according to Figure 7(b). An adsorption efficiency of 57% was recorded for 50 mg/L. The equilibrium in acidic conditions was reached more rapidly but at lower percentage of adsorption as compared to the basic condition.

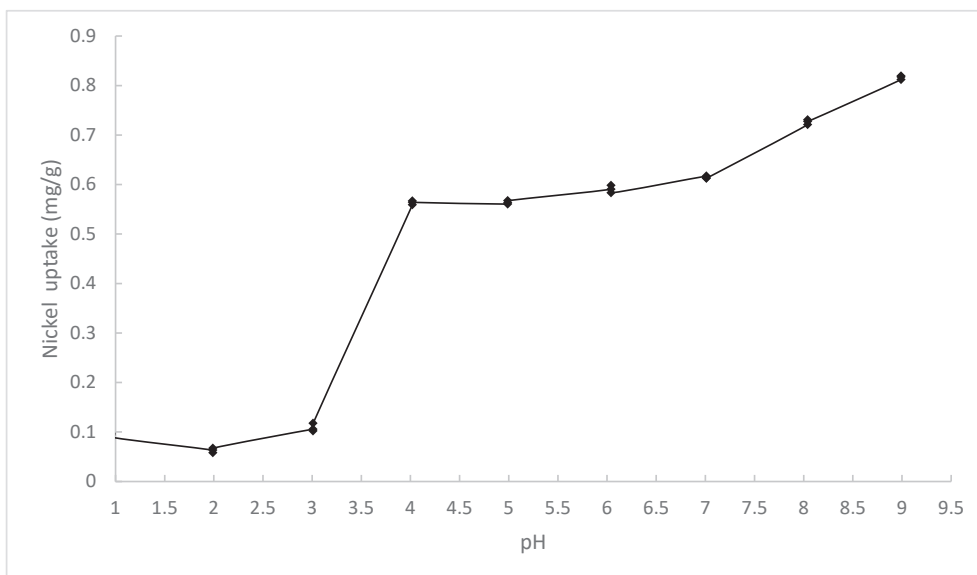


Figure 6. Effect of pH for the adsorption of 50 mg/L of Ni^{2+} in sawdust (5 g/L).

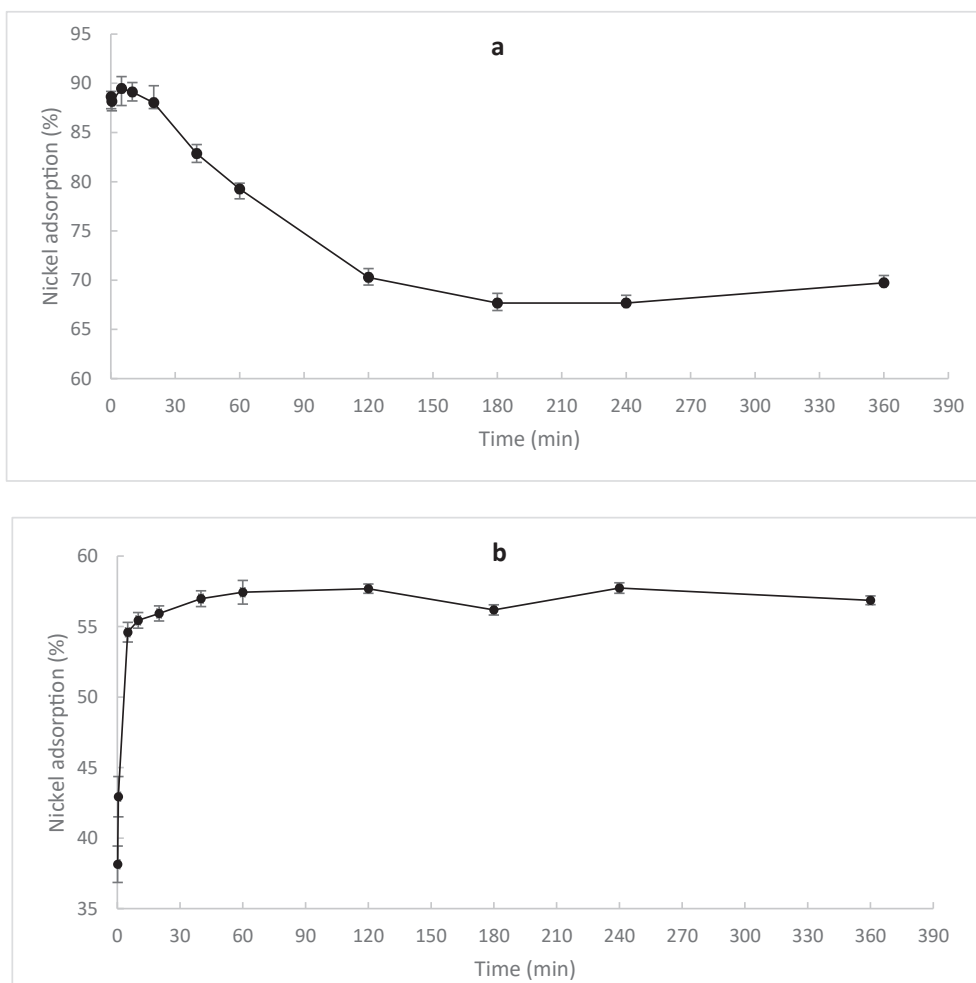


Figure 7. Effect of contact time under basic (a, pH 8) or acidic (b, pH 4) conditions in 5 g/L of adsorbent.

3.4. Adsorption isotherms

3.4.1. Langmuir isotherm

Langmuir isotherm is valid for monolayer adsorption capacity onto a surface containing a finite number of equivalent adsorption sites. This model respects the following assumptions: the number of active sites on the surface of the adsorbent is fixed and has the same energy, desorption is possible, no other adsorption can occur on the occupied site and no interaction between the adsorbed species. The following nonlinear and linear forms (Eq. 3 and Eq. 4) model this isotherm (Langmuir, 1918).

$$\frac{q_e}{q_{max}} = \frac{b \cdot C_e}{1 + b \cdot C_e} \tag{3}$$

$$\frac{C_e}{q_e} = \frac{1}{b} \cdot \frac{1}{q_{max}} + \frac{1}{q_{max}} \cdot C_e \tag{4}$$

Where q_e and q_{max} (mg/g) are the amount of metal ions adsorbed per unit mass of the adsorbent at equilibrium and at maximum respectively, b (L/mg) is the adsorption equilibrium constant related to the affinity of the binding sites and C_e (mg/L) is the adsorbate concentration at equilibrium.

The separation factor R_L is employed for isotherms that obey the Langmuir model at different initial adsorbate concentrations. This equation is presented below (Eq. 5).

$$R_L = \frac{1}{1 + b \cdot C_0} \tag{5}$$

where C_0 (mg/L) is the initial concentration of the adsorbate. The separator factor is commonly used to evaluate the adsorbent capacity. If $0 > R_L > 1$, the adsorption is favorable while if $R_L = 0$, $R_L = 1$ and higher than one, the adsorption is unfavorable (Fu et al., 2007).

Table 1 presents the values of Langmuir parameters for nonlinear and linear modeling and separator factor R_L . The non-linear parameters were

Table 1. Parameters of Langmuir isotherm models for Ni²⁺ adsorption on *P. caribaea* sawdust, comparison of linear and nonlinear models.

Sawdust (g/L)	Langmuir linear parameters			Langmuir nonlinear parameters		Comparison		R_L
	q_{max} (mg/g)	b (L/mg)	R^2	q_{max} (mg/g)	b (L/mg)	Δq_{max}	Δb	
1	5.692	0.067	0.869	7.274	0.018	1.582	0.049	0.937–0.982
10	1.890	0.097	0.994	1.952	0.067	0.062	0.03	0.597–0.912
15	1.705	0.071	0.994	1.696	0.073	0.009	0.002	0.478–0.484
20	1.439	0.073	0.988	1.367	0.086	0.072	0.013	0.366–0.407

calculated according to the method described by Tran et al. (2017). The q_{max} values (number of active sites on the biosorbent) are higher when the concentration of sawdust is low and the R_L values are between 0 and 1 so the adsorption is favorable.

The linearization used for Langmuir is the form $(C_e/q_e = f(C_e))$ which shows a reliable similarity with the nonlinear fit. The parameter values appear to be close for the linear and non-linear fit and the largest differences in values are found for low biosorbent concentrations (1 g/L). Recent work has provided a critical analysis of the linear model. Indeed, the dispersion of the points is arranged according to a Gaussian distribution and the error distribution is uniform at all points. However, according to a non-linear model, this rarely happens with adsorption isotherms. In our linearization, C_e is in both x and y and the correlation is overestimated. The linearization leads to a good fit but is not only significant of Langmuir hypotheses. Thus, high R^2 values do not prove that the Langmuir mechanism occurs exclusively and is no sufficient to compare the experimental values and isotherm parameters (González-López et al., 2021; Tran et al., 2017). Hence, the nonlinear model allows a reliability of the parameters (Figure 8).

3.4.2. Freundlich isotherm

The Freundlich isotherm implicates a removal of metal ions on a heterogeneous adsorbent surface. The model is suitable for multilayer adsorptions and describes a reversible adsorption process (Freundlich, 1907). The equation of Freundlich is expressed in nonlinear and linear forms in Eq. (6) and Eq. (7) respectively.

$$q_e = K_f \cdot C_e \cdot 1/n_f \tag{6}$$

$$\text{Log } q_e = \log K_f + \frac{1}{n_f} \cdot \log C_e \tag{7}$$

where, $K_f ((\text{mg/g})/(\text{mg/L})^n)$ is the constant related to adsorption capacity, n_f is the Freundlich equilibrium constant, a parameter related to adsorption intensity.

Linearization of Freundlich model by logarithmic form allows the determination of constants K_f and n_f by the plot of $\log q_e$ versus $\log C_e$.

Table 2 summarize Freundlich isotherms constants for Ni^{2+} adsorption in pine sawdust and allows the comparison of nonlinear and linear models. The K_f relative to the adsorption capacity increases when the

Table 2. Parameters of Freundlich isotherm models for Ni^{2+} adsorption on *P. caribaea* sawdust, comparison of linear and nonlinear models.

Sawdust (g/L)	Freundlich linear parameters			Freundlich nonlinear parameters		Comparison	
	K_f (mg/g)	n_f	R^2	K_f (mg/g)	n_f	ΔK_f	Δn_f
1	0.545	2.487	0.912	0.325	2.380	0.22	0.107
10	0.128	3.399	0.850	0.047	2.444	0.081	0.955
15	0.04	1.514	0.928	0.035	2.234	0.005	0.72
20	0.003	1.538	0.957	0.020	2.58	0.017	1.042

The n_f values higher than 1 highlights a physical process. The values for the exponent n in the range of 0–10 suggest favourable adsorption (Kumar, 2006a). The K_f values is lower in the non-linear fit than linear fit. The comparison of the parameters shows that the values are close and the greatest difference is found for the concentrations of 1 and 20 g/L.

biosorbent concentration is low. These results showed the decrease of efficiency of Ni^{2+} removal despite the addition of adsorbent and the increased of Ni^{2+} concentration in solution.

3.5. Adsorption kinetic study

Kinetic models aim to understand the interactions between the adsorbent and the adsorbate, and to provide information on the complex mechanism of adsorption. The pseudo-second order models (PSO) is the most commonly used equation and suppose that the rate-limiting step involves chemisorption (González-López et al., 2021). The two equation (nonlinear and linear) Eq.8 and Eq. 9 respectively are presented below.

$$q_t = \left(\frac{q_e^2 \cdot k^2 \cdot t}{1 + q_e \cdot k^2 \cdot t} \right) \tag{8}$$

$$\frac{t}{q_t} = \frac{1}{q_e^2 \cdot k^2} + \left(\frac{1}{q_e} \cdot t \right) \tag{9}$$

where k (l/min) is the second-order rate constant, t (min) the time, q_t and q_e (mg/g) are the amounts of adsorbate uptake per mass of adsorbent at any time t (min) and at equilibrium respectively.

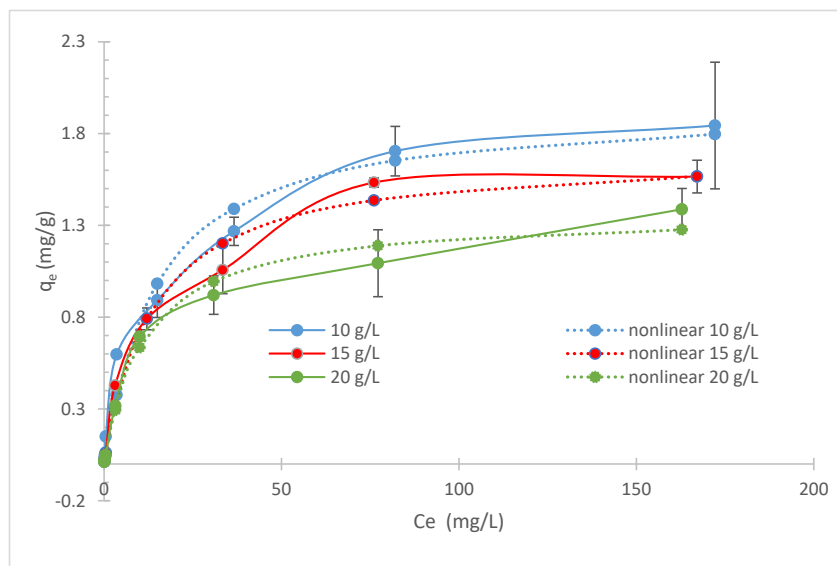


Figure 8. Curves fitting of non-linear Langmuir equation.

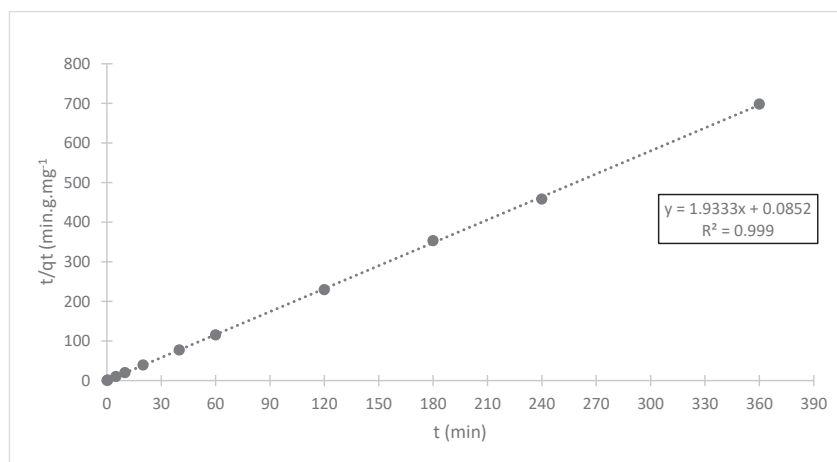


Figure 9. Pseudo-second-order plot of Ni^{2+} adsorption on *P. caribaea* sawdust.

The linear form describes the kinetic of Ni^{2+} biosorption with a high correlation coefficient ($R^2 > 0.999$) for initial metal concentration of 5.0 mg/L according to Figure 9. The linearized models help for predicting the initial k and q_e for non-linear models. Hence, the second-order rate constant (k) was 43.96 and the theoretical amount of adsorbed metal ions at equilibrium was measured at 0.517 mg/g (q_e , calculated), whereas the experimental value was 0.798 mg/g (q_e , experimental).

This linearized equation give a good fit but t is in the two axis so the correlation is overestimating and could positively change the conditions (González-López et al., 2021). Because of the error distribution, non-linear regression is preferred (Figure 10).

The maximal rate was obtained in the first minutes and the adsorption stabilizes.

3.6. Study of desorption of Ni^{2+} ions

After desorption, the biosorbent should recover its original form as well as its adsorption capacities. Desorption process requires effective, cheap and non-destructive reagents for the biomass. Dilute solutions of hydrochloric acid HCl and sulfuric acid H_2SO_4 were selected as eluents to desorb Ni^{2+} ions from the metal-loaded pine biomass. Under acidic conditions, protons displace metal cations such as Ni^{2+} from the binding sites of the pine sawdust.

The percentage of Ni^{2+} ions removal from pine sawdust surface with HCl was constant (Figure 11), but the highest desorption were observed

for 0.01 and 0.1 M of HCl (82.0 and 81.0 % respectively). For 0.5 M of HCl, the Ni^{2+} desorption was bitten decreased. For the three concentrations of H_2SO_4 , the best rate of desorption is observed for a concentration of 0.01 M showing that higher concentrations of sulfuric acid were less efficient in releasing Ni^{2+} ions. Sulfuric acid globally presented lower desorption capacities than hydrochloric acid. However, a complete desorption of Ni^{2+} ions by using HCl or H_2SO_4 could not be obtained, which might be due to metal ions being trapped in the intrapore of the sorbent's surface and therefore, difficult to be released (Serencam et al., 2008). Finally, 0.1M of HCl was selected for the other experiments of this study.

3.7. Evaluation of removal capacity of modified sawdust

Cellulose is the main component of sawdust (73.1%) and better adsorbs Ni^{2+} ions in solution (96.0%) than natural pine sawdust (Figure 12). This result is confirmed by the literature, which confirms the high removal capacity of cellulosic polysaccharides and in particular, hydroxyl groups on their surface (Gupta et al., 2015; Basso et al., 2002). Studies of Basso and al. have proved that the presence of cellulose and hemicelluloses in plant biomass improved the biosorption potential (Basso et al., 2002).

As a heterogenous material, sawdust contains numerous cations like calcium and sodium naturally fixed on the ion exchange sites, which reduce the retention capacities of metal in solution (Hawari and

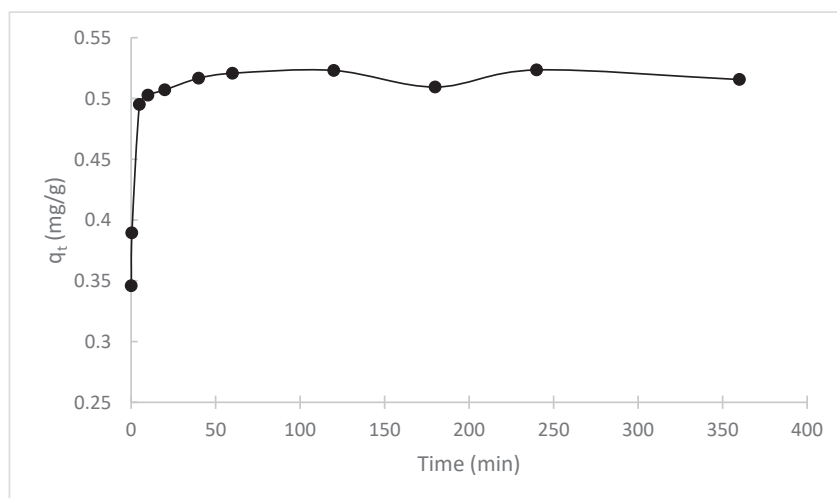


Figure 10. Non-linear regression of Pseudo-second order in acid condition.

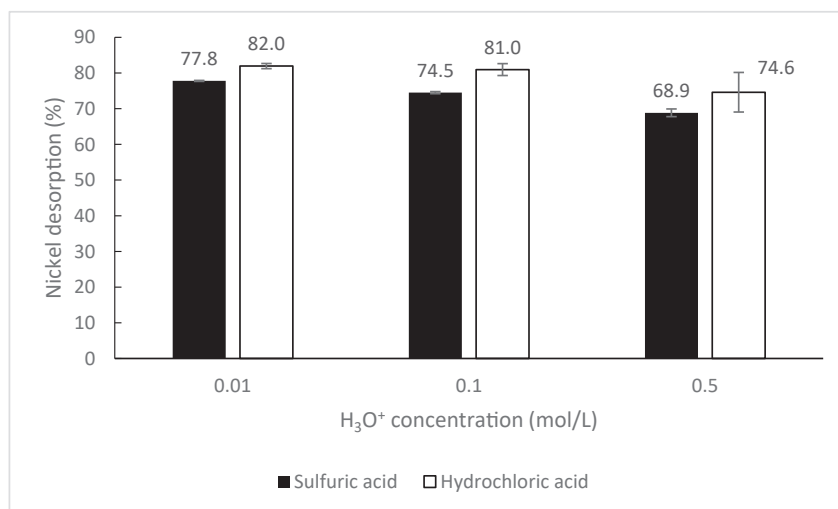


Figure 11. Ni²⁺ desorption efficiency of sawdust with HCl or H₂SO₄ treatments.

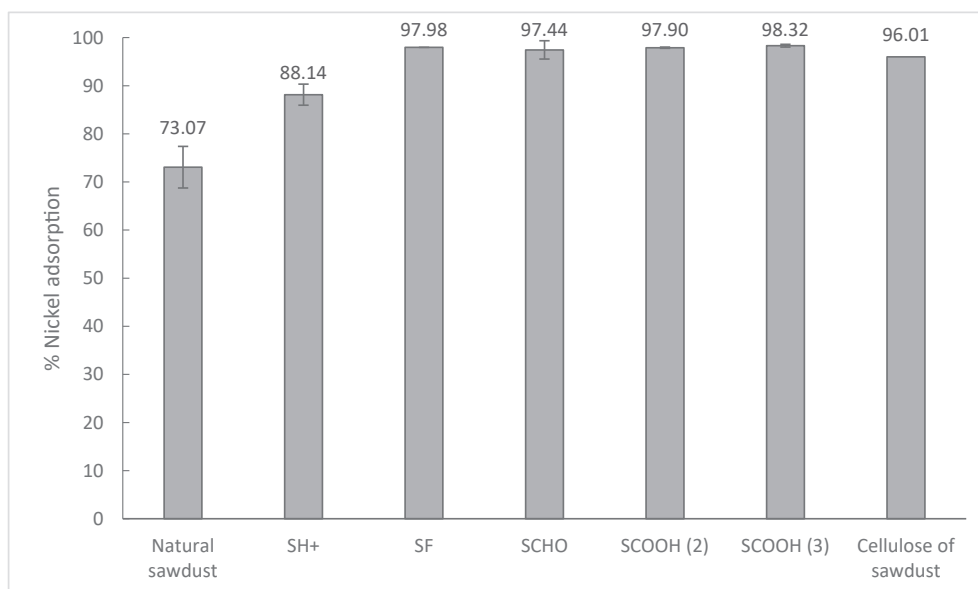


Figure 12. Ni²⁺ adsorption on modified sawdust SH⁺ (acidified), SCHO (di-aldehyde), SCOOH (2) (di-carboxylic), SCOOH (3) (tri-carboxylic) compared to natural sawdust and isolated cellulose.

Mulligan, 2005). To overcome this drawback, this material was stabilized through chemical activation, for example by treatment with acid or oxidative degradation. These chemical modifications aim to adding functional groups on the polysaccharide structure or treatments that modifying the physicochemical surface properties. Adsorption results depend on the chemical modification as well as the metal considered. Compared with natural sawdust according to Figure 13, all modifications were more effective for the Ni²⁺ uptake. Acid treatment seems to be less effective than oxidized reactions. Mentioned above, the surface S_H⁺ sawdust seems to be damaged compared to smooth surface of oxidized pine sawdust. All of these modifications are characteristics of increasing surface area making the sites more accessible. The adsorption maximum of 98.3% was observed for tricarboxylic sawdust. This result confirms the proportionality between the number of carboxylic acid functions formed and the amount of ions bounds (Vinicius et al., 2007). The chemical nature and spatial arrangement of binding sites can influence the binding of cations to organic matter. Indeed, carboxylic sites attached to adjacent carbon atoms and spaced on a ring, are more selective to multivalent cations (Talibudeen and Greenland 1981).

3.8. Biosorption of Co²⁺, Cr³⁺ and Mn²⁺ ions by natural and Fenton oxidized sawdust

As a chemical process for wastewater treatment, oxidation by Fenton's reagents is based on the catalytic decomposition of H₂O₂ in presence of iron salts (Fe²⁺). As a cost-effective source of hydroxyl radical (OH.), this method has many advantages as simplicity of design, safe operation, high efficiency, availability and short reaction time (Neyens and Baeyens, 2003). Figure 13 shows that metal adsorption was different as function of active sites and functional groups on the surface of the biosorbent. This behavior is attributed to selectivity of biosorption, which depend on characteristic of metal ions such as electronic charge of the valence layer, the counter ions in solutions, hydration enthalpy, ionic radius, coordination number, electron configuration or electronegativity (Gorgievski et al., 2013; Zeraatkar et al., 2016).

For single metal uptake (Figure 13,b), natural pine sawdust showed a greater affinity than for Cr³⁺ (84.1%) followed by Ni²⁺ (72.6%) whereas Fenton oxidized pine sawdust had better adsorption capacity for

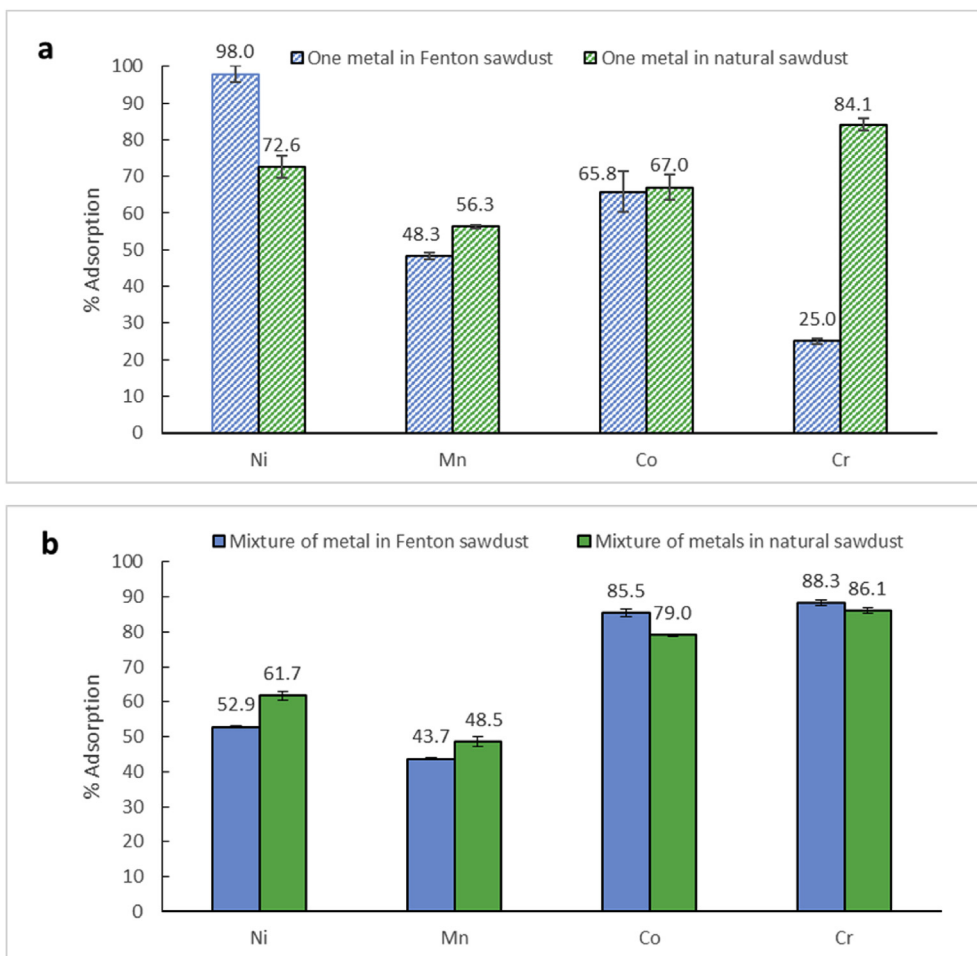


Figure 13. Selectivity of metals (Ni^{2+} , Mn^{2+} , Co^{2+} , Cr^{3+}) in natural versus Fenton oxidized sawdust in a mixture of four metals (a) and separately (b) at 5.0 mg/L.

Ni^{2+} (98.0%) followed by Co^{2+} (65.8%). Oxidation under Fenton conditions was the most favorable treatment for the adsorption of nickel in solution. As the metals are usually found in mixture in nature, experiments with a mixture of four metals were conducted (Figure 13, a). Sawdust is a complex material with many possible binding sites. In a

mixture, metal is competed with another inducing selectivity according to the available sites on sawdust surface. Results show that in the presence of a mixture of these four metals, natural sawdust and Fenton oxidized sawdust had great affinity for Co^{2+} and Cr^{3+} . Affinity of metal ion for biosorbent takes into consideration all properties of metal ion.

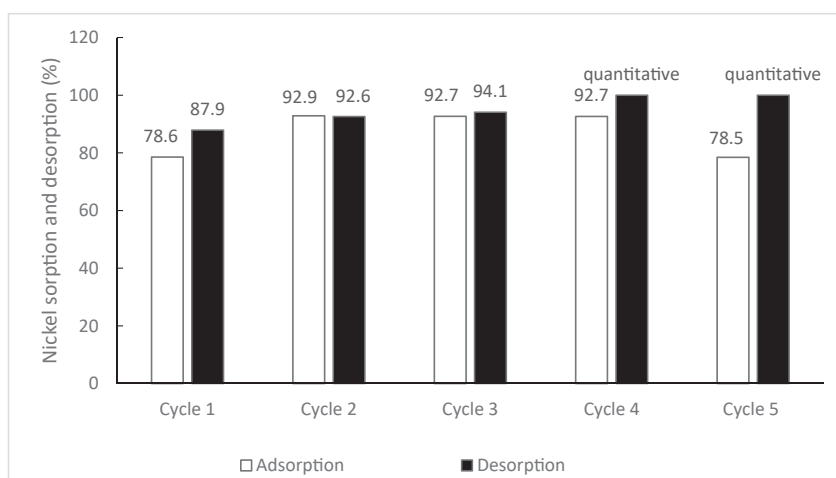


Figure 14. Reuse of natural pine sawdust for Ni^{2+} biosorption-desorption cycles (initial Ni^{2+} concentration = 5.0 mg/L, sawdust concentration = 5.0 g/L, pH = 8, desorption solution: 10 mL of 0.1 HCl at 16 h).

3.9. Biomass reusability cycles

After the first cycle, the biosorption of natural pine sawdust capacity increased then barely changed before decreasing after the fifth cycle according to Figure 14.

On the contrary, the desorption efficiency slowly increased until quantitative desorption after the fourth cycle. These results disagree with results obtained in other studies in which HCl decreases metal adsorption capacity of the biosorbent in successive cycles by damaging metal binding sites (Mehta and Gaur 2005). Desorption using HCl solution can cause a change in sawdust structure as seen in acidic treatment modification, thus gradually increasing the capacity of biosorption in the first cycles. This structural modification in acidic conditions can also explain the increase of Ni²⁺ desorbed which could come from initial ions accumulated into intrapore of the biosorbent during previous cycles.

4. Conclusion

P. caribaea sawdust is an ecological, available, inexpensive and effective biosorbent to reduce in aqueous solutions metallic trace elements (Ni²⁺, Co²⁺, Cr³⁺, Mn²⁺) which are present in rivers and groundwater of New Caledonia. Our work defined the optimal parameters (pH, particle size, biomass and initial concentration) for Ni²⁺ and adsorption rate was reaching equilibrium in short time. From a sustainable development perspective, we proven than *Pinus caribaea* sawdust can be reuse in five cycles after regeneration with a good efficiency. Biomass modifications by acid treatment and oxidative reactions can be accomplished in good yields and improve the metal binding capacities on sawdust. Selectivity of metals on natural sawdust versus Fenton oxidized sawdust is highlighted for Ni²⁺ and Cr³⁺ while variation are observed when metals are in mixture. *P. caribaea* sawdust could thus become an attractive material for the development of water purification techniques by biosorption for depollution installations adapted to the context of tropical islands producing this *Pinus* species in forestry. Many studies focus on the use of biomass to remove heavy metals from water but rarely lead to concrete applications because the treatment of biomass to remove metals require acidic environment and thus generates new waste. Metallurgical extraction techniques have evolved over the last decades with the emergence of hydrometallurgy. This technique currently applied in New Caledonia involve the use of acidic aqueous solutions for the recovery of metals from ores. Our results thus fit in an island context for which a technical solution could be associated with industrial metallurgical complexes to recycle the biomasses used to decontaminate water.

Declarations

Author contribution statement

Cynthia Sinyeue: Conceived and designed the experiments; Performed the experiments; Contributed reagents, materials, analysis tools or data; Wrote the paper.

Théophile Garioud & Monika Lemestre: Performed the experiments; Contributed reagents, materials, analysis tools or data.

Michaël Meyer: Performed the experiments.

Frédérique Brégier & Vincent Chaleix: Contributed reagents, materials, analysis tools or data.

Vincent Sol: Conceived and designed the experiments; Contributed reagents, materials, analysis tools or data.

Nicolas Lebouvier: Conceived and designed the experiments; Performed the experiments; Contributed reagents, materials, analysis tools or data.

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Data availability statement

Data included in article/supplementary material/referenced in article.

Declaration of interests statement

The authors declare no conflict of interest.

Additional information

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