



Research Article

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**Removal of Mercury(II) from aqueous solution by modified
Triplochyton scleroxylon sawdust**

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ABSTRACT

The sawdust of a tropical wood, *Triplochyton Scleroxylon* (Ayous), has been used as a lignocellulosic biosorbent for removing mercury(II) ions from water. In this study, its adsorption capacity can be increased by previous treatment with hydroxide sodium solution. The efficiency of elimination of mercury(II) ions from water using unmodified and modified sawdust depends on contact time, pH and biosorbent dose. Biosorption is maximum at pH 7, and more than 88% and 94% removal mercury(II) ions were achieved within 1 h from a 10 mg L⁻¹ solution at neutral pH using unmodified and modified sawdust, respectively. Mercury adsorption kinetic was well fitted by a pseudo-second order model. Among the two isotherm models tested for the unmodified and modified sawdust, Langmuir model gave the best fit. The modified sawdust exhibited the best efficiency for mercury(II) ions removal from water. The alkaline treatment of sawdust improves the maximum adsorption capacity of mercury(II) from 5.32 to 6 mg g⁻¹ at pH 7. Both ionic strength of solution and metal co-cations decrease mercury(II) uptake by modified sawdust, with Na⁺ showing a more pronounced effect than Ca²⁺ and K⁺. Mercury(II) ions adsorbed on modified sawdust were better desorbed by EDTA than HCl and HNO₃. The maximum desorption ratio of 48% is achieved within 60 min using EDTA, and base treated sawdust reuse for two cycles operation showed a loss of 58%.

Key words: Mercury ions; Tropical sawdust; Alkaline treatment; Biosorption; Desorption

INTRODUCTION

The discharge of heavy metals in the hydrosphere is a serious problem for the environment. Increasing concentrations of these metals in the aqueous phase constitute a severe health hazard mainly due to their non-degradability and chemical toxicity. Numerous metals such as cadmium Cd(II), chromium Cr(VI), lead Pb(II), and mercury Hg(II) are very toxic and have harmful effects on human health. Increased intake of Hg(II) by human beings, for instance, causes neurological and renal disturbances and affects the foetal brain [1-3]. Various techniques have been developed to mitigate the concentration of mercury(II) from effluents (waters and wastewaters).

The most popular methods to remove mercury(II) from effluents are: chemical precipitation, ion exchange, reverse osmosis, electrocoagulation and adsorption [4-7]. Most commonly used adsorbents (activated carbons, zeolites and resins) for water treatment may be prohibitively expensive in some situations [1]. Therefore, efficient and affordable alternative adsorbents are urgently needed to mitigate the mercury(II) concentration from effluents.

In recent years, agricultural waste materials and by-products of lignocellulosic origin have been widely studied in the literature for their capacity to remove mercury from aqueous solutions. These include fungi [8], peat [9], bark [10], cellulose [11], coconut husks [12], rice husks [13], bagasse pith [14], moss [14], tree fern [16] and *Carica papaya* [17] but seldom sawdust. Sawdust is actually an efficient adsorbent that is effective to many types of pollutants such as dyes, oil, and other kind of heavy metals [18]. Sawdust has the advantage of being (i) low cost,

(ii) readily available, (iii) biodegradable and (iv) easily renewable. Its use for the treatment of polluted water is an attractive and promising option with a double benefit for the environment:

- It limits or reduces its uses as heating materials reducing thereby the release of an enormous quantity of carbon dioxide.
- It converts the wastes into useful and inexpensive sorbents for water purification.

The low cost adsorbent used in our study is tropical sawdust of *Triplochyton Sleroxylon*, locally termed as Ayous (Cameroon). This sawdust is a by-product of the wood industry. It contains various organic compounds (lignin, cellulose and hemicelluloses) with functional groups like polyphenolic, hydroxyl and carboxyl groups that might be useful for binding heavy metals ions [19-22]. However, to improve the biosorption capacity and reduce the release of soluble organic compounds contained in sawdust that induce an increase in the chemical and biological oxygen demand (COD, BOD) [22], sawdust need to be chemically modified. Biosorption mechanisms include ionic interactions and formation of complexes between metal ions and the functional groups of the cell wall components. Alkaline treatment is a simple chemical modification which improves an ion-exchange process; increases a surface area, average pore volume and pore diameter and converts carboxyl groups to carboxylate groups that serve as the binding sites for heavy metals (Lewis acids) [22-24].

In this study, natural sawdust and sawdust modified with sodium hydroxide have been used for biosorption of mercury(II) from aqueous solutions. The effects of several environment conditions such as agitation time, pH, ionic strength, electrolyte nature, etc., on mercury removal capacity were investigated and desorption characteristics including regeneration were also studied.

EXPERIMENTAL SECTION

1.1. Chemicals

All the solutions were prepared from deionized water and the following commercial compounds: mercuric nitrate ($\text{Hg}(\text{NO}_3)_2$, 99% Fluka), sodium chloride (NaCl , 99.5% Prolabo); potassium chloride (KCl , 99% Prolabo); calcium chloride ($\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$, 98% Prolabo); hydrochloric acid (HCl , 37% Prolabo); nitric acid (HNO_3 , 68% Prolabo); perchloric acid (HClO_4 , 70% Prolabo); sodium hydroxide (NaOH , 98% Prolabo); disodium ethylenediaminetetraacetate (Na_2EDTA , 98% Fluka).

1.2. Materials

The sawdust of *Triplochyton Scleroxylon* (Ayous), a species of locally available wood, was collected, crushed and the fraction with particle size under $90\ \mu\text{m}$ was used for experiments. Prior to use, Ayous powder was dried beforehand with drying oven at 105°C during 24 h.

Alkaline modification of Ayous powder was carried out as follows. 50 mL of NaOH 2M solution and 10 g of Ayous powder were placed in 50 mL beaker. Sealed beakers were shaken (250 rpm) for 6 h at different temperatures: 10, 20, 30 and 40°C . After reaction, the modified sawdust were filtered, washed firstly with HNO_3 1M and continuously with deionized water until the pH of the washed water became less than 7. The modified sawdust were dried in the open air for 3 days, and then dried in an oven at 55°C for 24 h. The quantity of residual NaOH of the filtrate was determined by potentiometry (pH). The amount of NaOH fixed by sawdust was calculated based on the difference of NaOH concentration in aqueous solution before and after treatment.

1.3. Mercury adsorption experiments

A $1000\ \text{mg L}^{-1}\ \text{Hg}^{2+}$ stock solution was prepared using $\text{Hg}(\text{NO}_3)_2$ (analytical grade) in deionized water (DI). All the solutions for mercury(II) removal experiments and analysis were prepared by appropriate dilution from the prepared stock solution. The mercury removal experiments were carried out by batch method at 250 rpm at room temperature ($28 \pm 2^\circ\text{C}$). The pH of the solution was adjusted with HNO_3 or NaOH . The kinetic study at $\text{pH } 6.90 \pm 0.10$ was carried out by stirring 40 mL of $10\ \text{mg L}^{-1}$ solution with 0.2 g of unmodified and modified sawdust at different time intervals (0-120 min). The effect of pH on the biosorption rate was investigated in the pH range 2.5-8.0. The effect of the biosorbent dose for mercury uptake capacity was studied in the range of 1-15 g L^{-1} . The biosorption isotherm at $\text{pH } 6.90 \pm 0.10$ was studied by varying the initial Hg^{2+} concentration from 1 to 50 mg L^{-1} . To investigate the selectivity for mercury ions, adsorption experiments for wastewater containing cations, such as Na^+ , K^+ , Ca^{2+} was performed with NaCl 0.1M, KCl 0.1M and CaCl_2 0.1M solutions. The effect of ionic strength was investigated by adding 0.05 to 1.00 M NaCl to mercury nitrate solution.

1.4. Analytical procedure

After adsorption of metal ions from aqueous solutions, the aqueous phases were separated from the biosorbents and the concentration of Hg(II) ions in these phases was measured by voltamperometry method. The analyses were conducted using a μ -autolab type potentiostat from Ecochemie (Netherland). The technique used is anodic redissolution in pulse differential mode. The measurements were performed in a three-electrode system comprising the Au working electrode, Pt auxiliary electrode and a calomel saturated electrode serving as reference electrode. The supporting electrolyte consisted of 10^{-3} M NaCl, 10^{-3} M EDTA and 2×10^{-4} M HClO₄. All measurements were carried out at room temperature, the potential ranging from 0.4 to 0.9 V at 50 mV s^{-1} [7].

The specific amount of Hg(II) adsorbed onto biosorbent was calculated from the following equation:

$$Q_e = \frac{(C_0 - C_e)}{W} \times V \quad (1)$$

where Q_e is the equilibrium adsorption capacity (mg g^{-1}); C_0 and C_e are respectively the initial and the equilibrium concentrations (mg L^{-1}), V is the volume of the aqueous solution (L), and W is the mass (g) of the adsorbents.

1.5. Mercury desorption experiments

Desorption of mercury(II) was performed by 0.1 M EDTA, 0.5 M HNO₃ and 0.5 M HCl solutions. The biosorbent loaded with mercury ions were placed in desorption medium and stirred at 250 rpm for 2 h at room temperature (28 ± 2 °C). The desorption kinetic of mercury(II) by 0.1 M EDTA has been also evaluated. In order to determine the possibility of re-using the modified Ayous, consecutive adsorption-desorption cycles were repeated 2 times by using 0.5 M EDTA solutions. Desorption ratio was calculated from the amount of metal ions adsorbed on modified sawdust and the final Hg(II) ions concentration in the desorption medium.

2.6. Theoretical approach

2.6.1. Adsorption isotherms

An adsorption isotherm represents the sorption capacity (Q_e) in function of metal concentration in solution (C_e) at equilibrium. Modeling of the equilibrium data has been done using the Langmuir and Freundlich isotherms.

The Langmuir adsorption model is based on the assumption of surface homogeneity such as equally available adsorption sites, monolayer surface coverage and no interaction between adsorbed species [25]. The mathematical description of this model is

$$Q_e = \frac{K_L Q_m C_e}{1 + K_L C_e} \quad (2)$$

where K_L is Langmuir constant (L mg^{-1}) and Q_m is maximum Hg(II) adsorbed (mg Hg(II) g^{-1} adsorbent).

The Freundlich isotherm is based on the multilayer adsorption of an adsorbate onto the heterogeneous surfaces of an adsorbent [26]. This empirical equation takes the form:

$$Q_e = K_F C_e^{1/n} \quad (3)$$

where K_F is the Freundlich constant that indicates the adsorption capacity and n is a constant that indicates the adsorption intensity.

2.6.2. Kinetics models

To express the mechanism of mercury adsorption onto sawdust, the following kinetic model equations were used.

The Pseudo-First-Order rate equation of Lagergren is one of the most widely used for the sorption of an adsorbate from a liquid phase [27]. It may be represented as follows:

$$\frac{dQ_t}{dt} = K_1(Q_e - Q_t) \quad (4)$$

where Q_e and Q_t are the adsorption capacity (mg g^{-1}) at equilibrium and time t respectively, K_1 (min^{-1}) is the rate constant of pseudo-first order biosorption.

The initial biosorption rate h_1 (mg (Hg(II)) $g^{-1} min^{-1}$) from the pseudo-first order sorption is defined as:

$$h_1 = K_1 Q_e \quad (5)$$

The h_1 and Q_e values were determined from a plot of $\ln(Q_e - Q_t)$ against t .

The Pseudo-Second-Order model describes the biosorption of some metal ions onto the biosorbent. This model assumed that the biosorption follows the Langmuir equation. The kinetic rate equations can be written as follows [27]:

$$\frac{dQ_t}{dt} = K_2(Q_e - Q_t)^2 \quad (6)$$

where K_2 ($g\ mg^{-1}(Hg^{2+})\ min^{-1}$) is the equilibrium rate constant of the second order sorption.

The initial biosorption rate h_2 (mg (Hg(II)) $g^{-1} min^{-1}$) from the pseudo-second-order equation is defined as:

$$h_2 = K_2 Q_e^2 \quad (7)$$

The Q_e and h_2 values were determined from a plot of t/Q_t versus t .

RESULTS AND DISCUSSION

3.1. Alkaline treatment

Fig. 1 shows the evolution of NaOH uptake by sawdust versus temperature. It appears that the quantity of NaOH fixed by the sawdust depends on the chemical modification temperature. The maximum yield of the saponification is observed for a temperature of 30 °C (3.6 mmol NaOH per gram of sawdust). An increase in the modification temperature above 30 °C causes a decrease in the amount of NaOH fixed by the sawdust. This may be due to a partial destruction of material because of thermal deactivation of the acidic groups on its surface [27]. Our studies have shown that sawdust treated with NaOH at 30 °C presents a best biosorption capacity of mercury(II) ions. Sawdust treated at 30 °C was thus used for the rest of experiments.

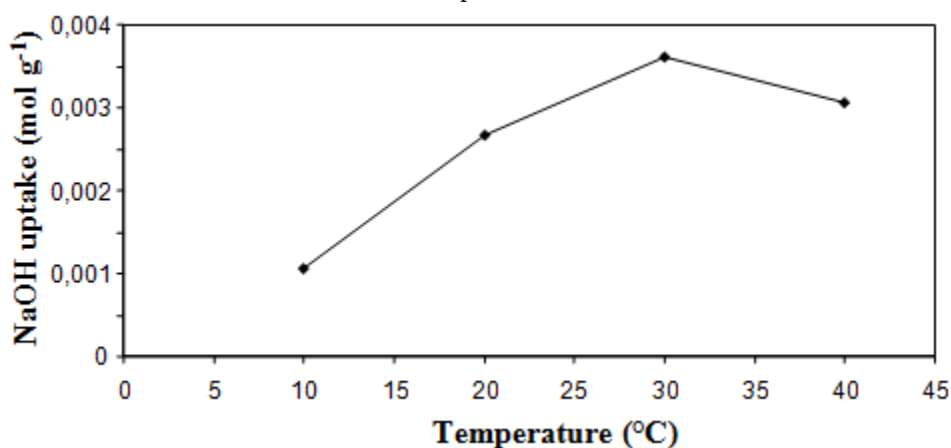


Fig. 1: Effect of temperature on NaOH uptake by sawdust

3.2. Biosorption characteristics

3.2.1. Adsorption rate

To establish an appropriate contact time between the biosorbent and mercury ions solution, sorption capacities of Hg(II) ions were measured as a function of time. As can be seen from Fig. 2, mercury uptake of base treated sawdust is higher than that of untreated sawdust, implying that alkaline treatment improved the sorption capacity of Ayous sawdust.

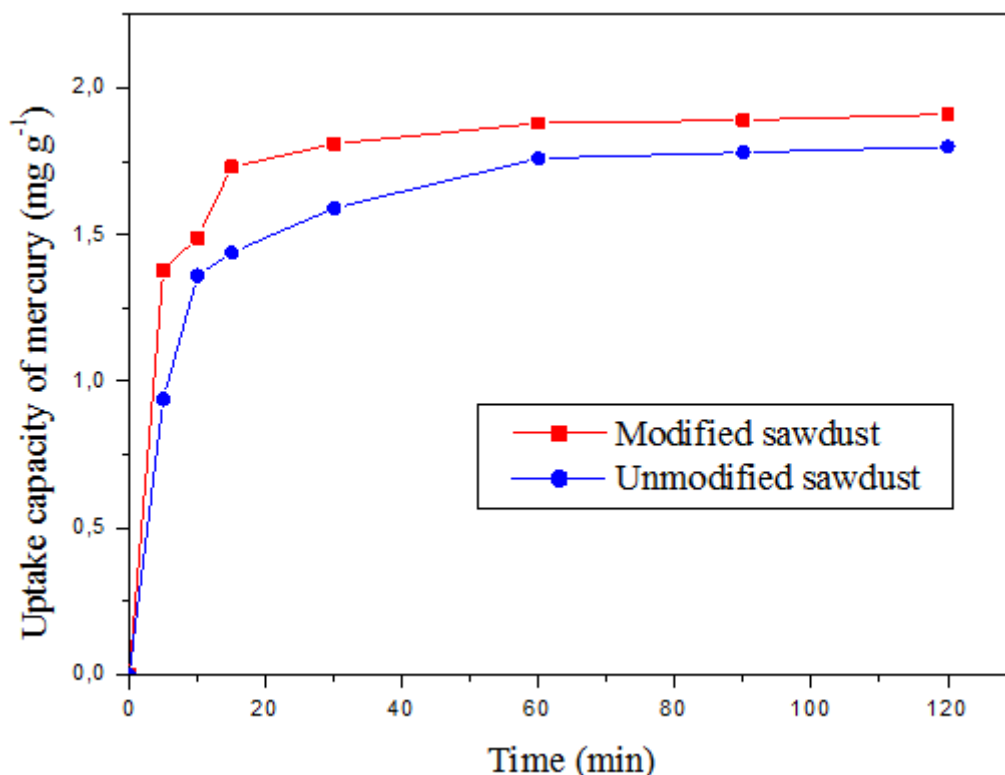


Fig. 2 : Effect of agitation time on mercury uptake capacity using unmodified and modified Ayous (initial concentration: 10 mg L⁻¹, biosorbent dose: 5 g L⁻¹, pH: 7, agitation rate: 250 rpm, temperature: 28 ± 2 °C).

Generally, the Hg(II) uptake was fast at the beginning of adsorption and saturation levels were completely reached about 30 min for modified sawdust and 60 min for unmodified one. After these equilibrium periods, the amount of adsorbed metal ions on the biosorbents did not significantly change with time. The constants values at the equilibrium plateau are 1.80 mg g⁻¹ and 1.91 mg g⁻¹ for unmodified and modified sawdust respectively. The rapid metal uptakes were certainly due to the availability of active sites on biosorbent surfaces, whereas the observed equilibrium plateau corresponds to a slow step of biosorption during which there are saturation of active sites and establishment of pseudo-balance between adsorption and desorption rates [29, 30]. After 2 h, the biosorption rate of Hg(II) ions is 90% and 95% for unmodified and modified sawdust respectively.

3.2.2. Effect of pH on the biosorption capacity

The pH of the aqueous solution is an important parameter that controlled the biosorption process [30, 31]. Fig. 3 shows the effect of pH on mercury(II) ions removal efficiencies of unmodified and modified sawdust.

The amount of adsorbed Hg(II) increases with pH to attain a maximum at pH 7 thereafter it decreases with further increase in pH. The percentage of sorption increases from 59% at pH 2.5 to 88% at pH 7 for unmodified sawdust and from 25% at pH 4 to 94% at pH 7 for modified sawdust. The maximum adsorption capacity of Hg(II) at pH 7 were found to be 1.76 mg g⁻¹ for unmodified Ayous and 1.88 mg g⁻¹ for base treated sawdust. Decrease in removal of Hg(II) at lower pH may be due to the higher concentration of H⁺ ions. These H⁺ ions can protonate the sorption sites of sawdust or compete with Hg(II) ions. Decrease in biosorption at higher pH is due the formation of hydroxy species such as Hg(OH)₂ or [Hg(OH)]⁺. Several researchers have investigated the effect of pH on biosorption of mercury by using different kind lignocellulosic materials. For example, maximum biosorption of Hg(II) was obtained at pH 8 using eucalyptus bark [30] whereas it was obtained at pH 6 using base treated *Acacia arabica* [31]. However, it should be observed that at pH lower than 6, unmodified sawdust is more effective than modified sawdust for the elimination of Hg(II) from aqueous solution, while at pH greater than 6, the tendency is reversed. Kilic et al. [4] also observed that at pH 5.8, waste activated sludge treated by a boiling solution of 0.5 N NaOH was less effective for mercury removal than the unmodified waste activated sludge.

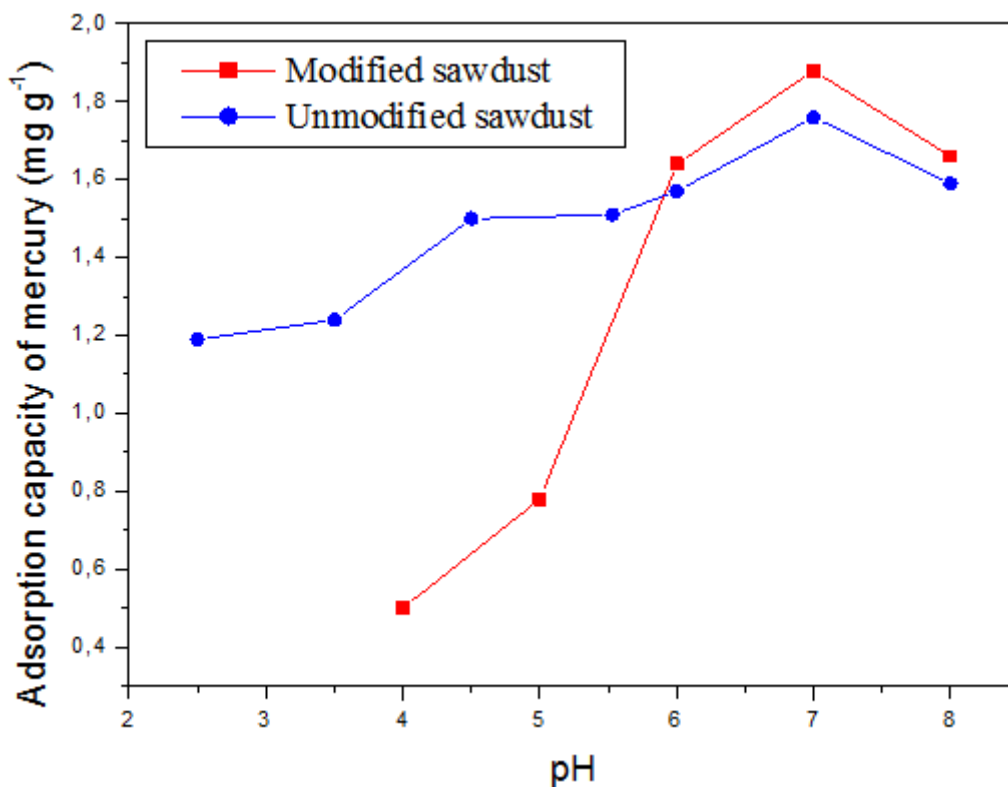


Fig. 3: Effect of pH on the mercury biosorption capacity using modified and unmodified sawdust (initial concentration: 10 mg L⁻¹, biosorbent dose: 5 g L⁻¹, time: 60 min, agitation rate: 250 rpm, temperature: 28 ± 2 °C).

3.2.3. Effect of biosorbent dose

As is indicated in Fig. 4, it is apparent that mercury(II) adsorption increased gradually with increasing adsorbent dose, to a maximum of 10 g L⁻¹ for treated sawdust and 12.5 g L⁻¹ for untreated sawdust.

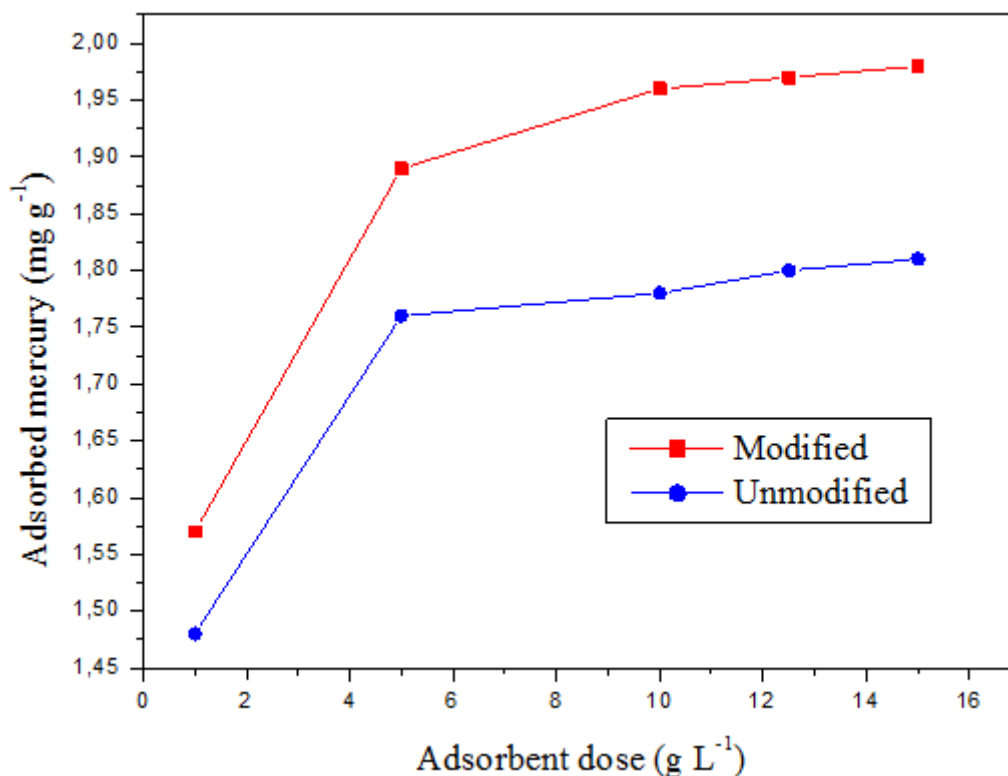


Fig. 4: Effect of adsorbent dose on the mercury biosorption capacity using modified and unmodified sawdust (initial concentration: 10 mg L⁻¹, pH: 7, time: 60 min, agitation rate: 250 rpm, temperature: 28 ± 2 °C).

After this maximum equilibrium value, the uptake efficiency of mercury did not increase with increasing adsorbent dose. The higher the sorbent dose is, the greater is the availability of the exchangeable sites [32]. As adsorbent dose increased from 1 to 15 g L⁻¹, the adsorption capacity of mercury ions increased from 1.48 to 1.81 mg g⁻¹ for unmodified Ayous and 1.57 to 1.98 mg g⁻¹ for modified Ayous. Thus treatment of sawdust improves the adsorption of mercury of 10% for an adsorbent dose of 12.5 g L⁻¹.

3.2.4. Effect of Hg(II) concentration

The effects of initial concentration of Hg(II) on the biosorption capacity onto unmodified and modified sawdust is shown in Fig. 5.

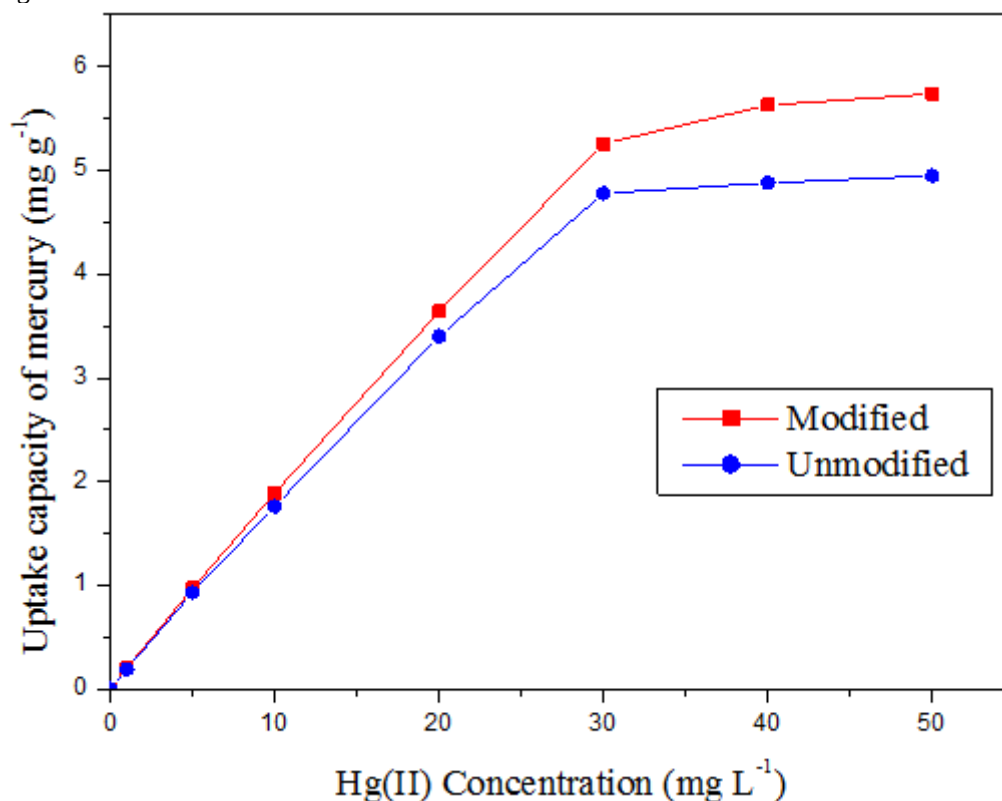


Fig. 5: Adsorption isotherms of the mercury biosorption using modified and unmodified sawdust (biosorbent dose: 5 g L⁻¹, pH: 7, time: 60 min, agitation rate: 250 rpm, temperature: 28 ± 2 °C)

It can be seen from the figure that adsorbed Hg(II) increased first with the increasing of equilibrium concentration of Hg(II) ions then reached a plateau value at about an equilibrium Hg(II) concentration of 30 mg L⁻¹ using unmodified sawdust and 40 mg L⁻¹ using modified sawdust. The plateau represents the saturation of the active binding sites of the reactive functional groups on the surfaces of sawdust. At lower initial concentrations (less than 5 mg L⁻¹), sufficient adsorption sites are available for adsorption of mercury(II) ions. Therefore, the biosorption is independent of treatment of sawdust and of initial concentration.

3.2.5. Effect of metal co-cations

In general, different kinds of salts are mixed in real wastewater and it's necessary to investigate the selectivity of the biosorbent for mercury(II) ions. From the results of the influence of electrolyte nature on the mercury biosorption (Fig. 5), it appears that Hg(II) removal is greatly affected by each of three electrolytes used (NaCl, KCl and CaCl₂) at a concentration of 0.1 M. The mercury(II) removal rate decreases from 94.1% (in deionised water DI medium) to 59% (in KCl medium), to 57.1% (in CaCl₂ medium) and to 33.5% (in NaCl medium). It is possible that cations (Na⁺, Ca²⁺ and K⁺) may compete with mercury(II) ions for electrostatic binding onto base treated sawdust. Indeed, these cations are hard acids and can form ionic complexes with hard bases such as carboxylate ions in base treated sawdust [32]. Na⁺ cation caused the greatest percentage decrease in mercury(II) biosorption among the cations used. The effect of co-cations in lowering mercury(II) biosorption by modified sawdust followed the order Na⁺ > Ca²⁺ > K⁺. Inbaraj *et al.* [34] obtained the order Ca²⁺ > Na⁺ > K⁺ in lowering mercury(II) biosorption by extracellular biopolymer poly (γ-glutamic acid).

3.2.6. Effect of ionic strength

The ionic strength of the solution is of significance for its effect on the adsorbent. From the preceding study, the NaCl solution is that which caused the decreases of mercury adsorption uptake. It was used to study the influence of the ionic strength on the sorption efficiency of mercury(II) ions using modified Ayous. It can be seen from Fig. 6 that the sorption of mercury decreases with an increase of NaCl concentration and reaches a plateau for higher NaCl concentration.

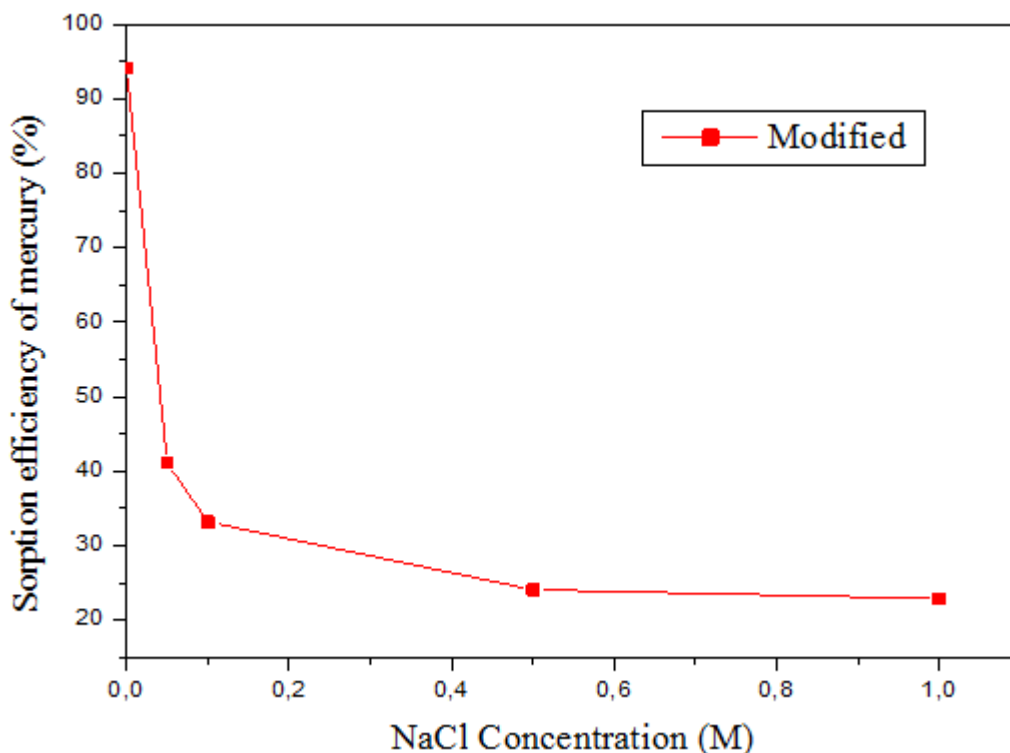


Fig. 6: Effect of ionic strength on the mercury sorption efficiency using modified sawdust. (time: 60 min, initial concentration: 10 mg L⁻¹, biosorbent dose: 5 g L⁻¹, pH: 7, agitation rate: 250 rpm, temperature: 28 ± 2 °C).

The increase in ionic strength between 0 and 1M decreases the sorption percentage from 94.1% to 22.9%. The adverse effect of ionic strength on mercury(II) uptake onto base treated sawdust suggests that the electrostatic attraction is the fundamental mechanism on biosorption process.

3.2.7. Biosorption kinetic modeling

In order to examine the controlling mechanism of biosorption process such as mass transfer and chemical reaction, kinetics models were used. The Lagergren first-order and the pseudo-second order were applied for the biosorption of Hg(II) ions on the unmodified and modified sawdust. The plots of Lagergren and pseudo-second order, respectively both for unmodified and modified sawdust were done but they are not presented here. The comparison of experimental biosorption capacities and the theoretical values estimated from the above two equations are presented in Table 1.

Table 1: Comparison of the Lagergren and pseudo-second order kinetic constants for the biosorption of Hg(II) on unmodified and modified sawdust. (Initial concentration: 10 mg L⁻¹, biosorbent dose: 5 g L⁻¹, pH: 7, agitation rate: 250 rpm, temperature: 28 ± 2 °C)

Sawdust	Experimental Q _e (mg g ⁻¹)	Lagergren				Pseudo-second order			
		K ₁ (min ⁻¹)	Q _e (mg g ⁻¹)	h ₁ (mg g ⁻¹ min ⁻¹)	R ²	K ₂ (min ⁻¹)	Q _e (mg g ⁻¹)	h ₂ (mg g ⁻¹ min ⁻¹)	R ²
Unmodified	1.80	4.4 × 10 ⁻²	0.82	3.6 × 10 ⁻²	0.9709	15.1 × 10 ⁻²	1.85	51.7 × 10 ⁻²	0.9985
Modified	1.91	3.9 × 10 ⁻²	0.48	1.9 × 10 ⁻²	0.9292	17.9 × 10 ⁻²	1.95	68.1 × 10 ⁻²	0.9977

We observed that beyond 25 min, sorption of Hg(II) both by unmodified and modified Ayous does not follow the lagergren equation, while the plots of pseudo-second order are the straight lines. These observations are confirmed by the results of Table 1. The correlation coefficients of the pseudo-second order model are higher than those of Lagergren model. It was noticed that the calculated values of Q_e from the Lagergren model are very lower than the experimental values. Thus, the biosorption does not follow the Lagergren reaction. The coefficient values of the

pseudo-second order exceed 0.99 and the calculated sorption capacity values determined from the pseudo-second order model were more consistent with experimental values of sorption capacity. Therefore, the pseudo-second order model represents better the sorption kinetic of Hg(II) from aqueous solution using unmodified and modified Ayous. This suggests that the chemisorption might be the rate-limiting step that controls the biosorption process.

3.2.8. Biosorption isotherms

Fig. 7 (a and b) show the linearization of Langmuir and Freundlich isotherms respectively, for the mercury(II) biosorption onto unmodified and alkaline treated sawdust.

The isotherm parameters obtained from these models are given in Table 2. The applicability of a particular isotherm model is judged from the regression coefficient value (R^2). From results of Table 2, the Langmuir isotherm model presents the greatest values of R^2 (0.9970 and 0.9987 for unmodified and modified sawdust, respectively). Therefore, the biosorption process of mercury(II) ions onto unmodified and modified sawdust could be described by the Langmuir model.

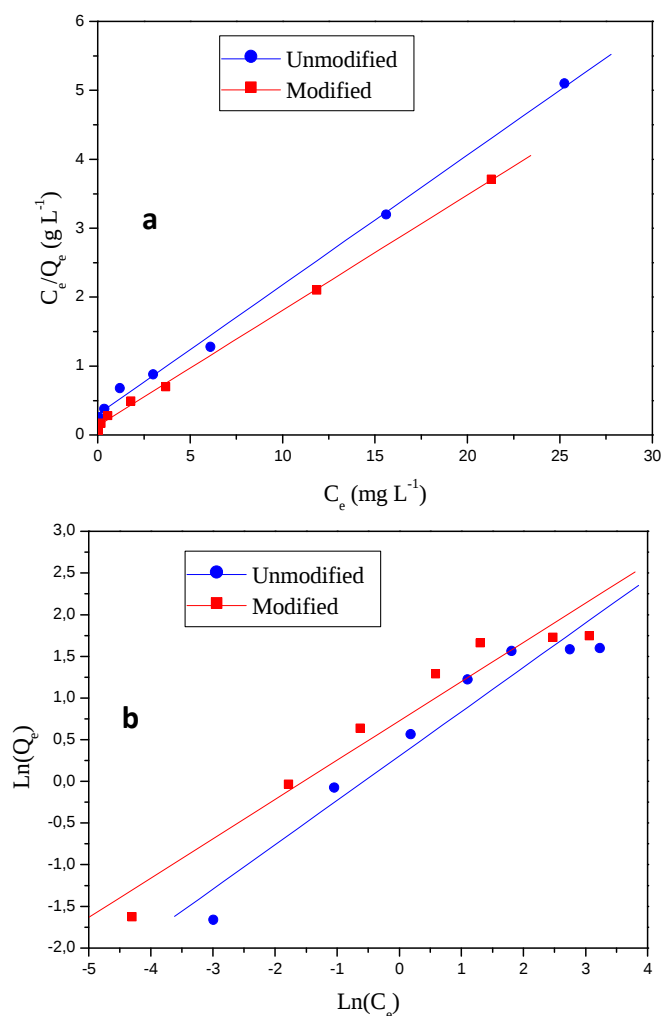


Fig. 7: Linearization of Langmuir (a), Freundlich (b) isotherms for unmodified and modified sawdust (time: 60 min, biosorbent dose: 5 g L⁻¹, pH: 7, agitation rate: 250 rpm, temperature: 28 ± 2 °C).

As determined from the Langmuir equation, the maximum biosorption capacities (Q_{max}) for mercury(II) ions using unmodified and modified sawdust are 5.31 and 6.01 mg g⁻¹, respectively. The alkaline treatment of sawdust improves the maximum adsorption capacity of mercury(II) ions of 13%.

Table 2: Freundlich and Langmuir parameters for adsorption isotherms of mercury(II) onto unmodified and modified Ayous. (Time: 60 min, biosorbent dose: 5 g L⁻¹, pH: 7, agitation rate: 250 rpm, temperature: 28 ± 2 °C)

Adsorbents	Freundlich			Langmuir		
	n	K _F	R ²	Q _{max} (mg g ⁻¹)	K _L (L mg ⁻¹)	R ²
Unmodified	1.88	1.36	0.9307	5.31	0.64	0.9970
Modified	2.12	2.07	0.9419	6.01	1.24	0.9987

The essential characteristic of the Langmuir equation can be described by a separation factor or equilibrium constant R_L , which is defined as:

$$R_L = \frac{1}{1 + K_L C_0} \quad (8)$$

where C_0 is the initial Hg(II) concentration (mg L⁻¹). The value of R_L indicates the nature of biosorption as unfavourable ($R_L > 1$), linear ($R_L = 1$), favourable ($0 < R_L < 1$) or irreversible ($R_L = 0$). In this work, the R_L values calculated for initial mercury concentration of 10 mg L⁻¹ are 0.135 and 0.075 for unmodified and modified sawdust, respectively. These values suggest the favorable adsorption of mercury onto studied biosorbents. Sorption is more favourable for modified sawdust than unmodified sawdust, which can be explained by the high affinity between mercury(II) ions and the carboxylate groups created by the alkaline treatment on the sawdust surfaces.

3.3. Desorption and reuse

A desorption study is also important since it is useful in the recycling of the adsorbent and recovery of metal. In this study, extractant reagents like 0.1 M EDTA, 0.5 M HCl and 0.5 M HNO₃ were used for desorption of mercury(II) ions from base treated sawdust. Desorption ratio of mercury ions using EDTA was about 48%, while HNO₃ and HCl were showed about 15% and 11% of the adsorbed mercury(II) ions, respectively. Therefore, it appears that EDTA is the best desorbent for mercury(II) ions from modified sawdust. This can be attributed to the strong chelating properties of EDTA which forms with mercury(II) ions the complexes like HgY²⁻. EDTA was then selected to carry out future investigations on the mercury(II) ions desorption studies.

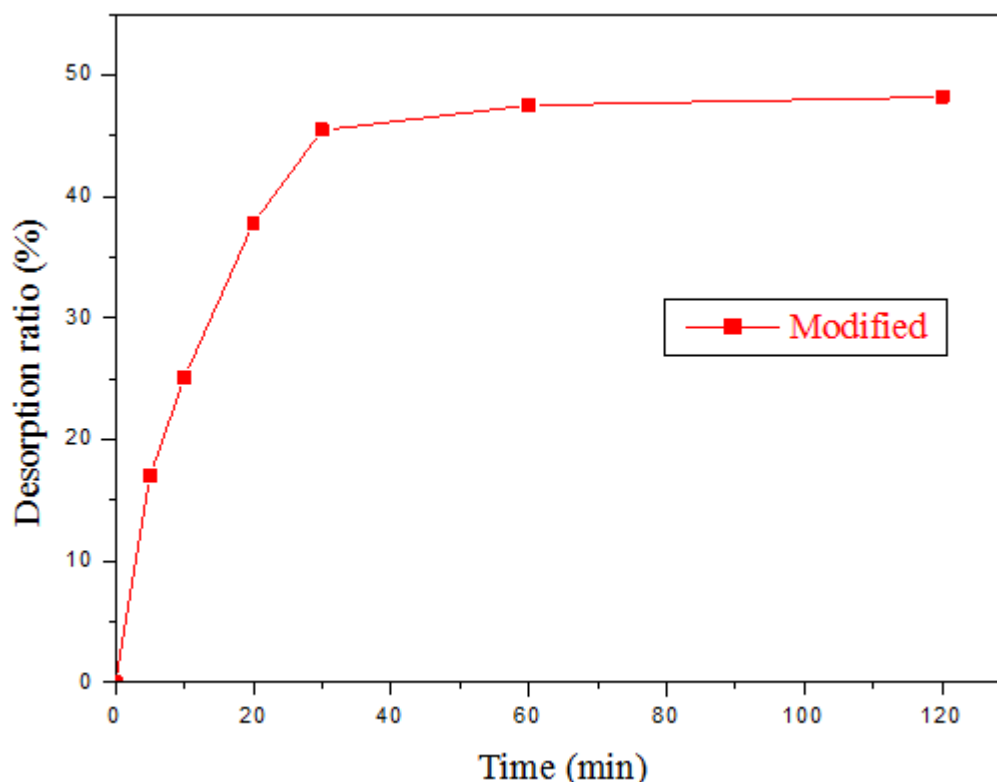


Fig. 8: Kinetic desorption of mercury(II) ions from modified sawdust using 0.1 M EDTA. (agitation rate: 250 rpm, temperature: 28 ± 2 °C)

The effect of time on desorption ratio of mercury(II) ions from modified sawdust using 0.1 M EDTA was studied. As shown in Fig. 8, desorption ratio of mercury(II) ions increased with time, and then tends to reach a plateau. Most of the desorption was completed within 60 min. The low value of maximum desorption observed (48%) would be

due to the insufficient breaking by EDTA of the strong affinity of mercury(II) ions with negatively charged groups (hydroxyl or carboxylate groups) present on the base treated sawdust.

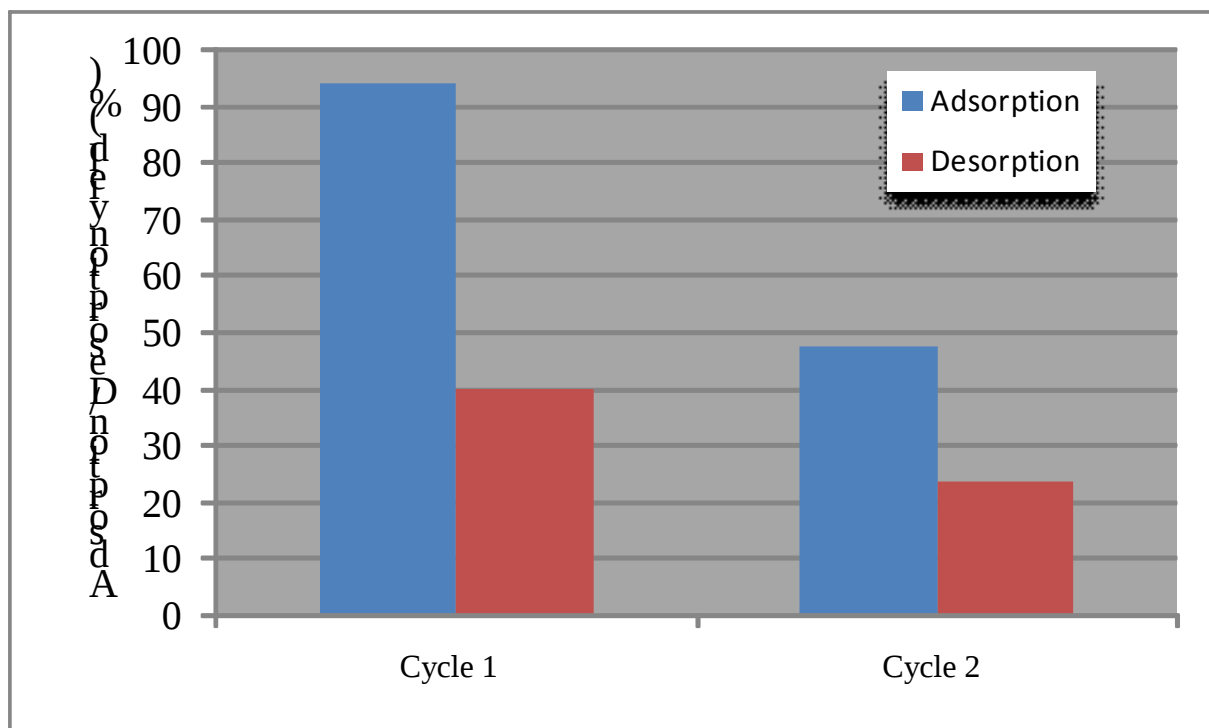


Fig. 9: Adsorption-desorption cycle of mercury(II) ions from modified sawdust using 0.1 M EDTA. (time: 60 min, agitation rate: 250 rpm, temperature: 28 ± 2 °C)

In order to obtain the reusability of the modified sawdust, adsorption-desorption cycle of mercury(II) ions was repeated 2 times by using the same preparations. From Fig. 9, the adsorption capacity of Hg(II) decreases from 94% to 40% (which corresponds to a loss of adsorption capacity of 58%) while the desorption capacity decreases from 48% to 24%. The modified sawdust can thus be recycled, but with poor yield. This can be explained by an incomplete desorption of the modified sawdust initially charged with Hg(II) ions.

CONCLUSION

The goal of this work was the valorization of the sawdust from *Triplochyton Scleroxylon* wood as a biosorbing agent for the removal of Hg(II) ions from the aqueous solution. The adsorption capacity of sawdust was increased by an alkaline treatment and the maximum NaOH uptake was observed for a temperature of 30 °C. The experimental results show that base treated sawdust yielded a higher biosorption capacity for Hg(II) than unmodified sawdust. The adsorption process is dependent on numerous factors such as the contacting time, the biosorbent dose, the solution pH, the Hg(II) initial concentration, the ionic strength and the metal co-cations. In particular, mercury(II) adsorption onto unmodified and modified sawdust was fast during the first 20 min and thereafter it slowly reached a pseudo-equilibrium in 60 and 30 min for unmodified and modified sawdust, respectively. The biosorption kinetic followed the pseudo-second order model, which indicates that mercury removal might be a chemisorptions process. For all the biosorbent, biosorption is maximal at pH 7 and the Hg(II) uptake are 1.80 and 1.91 mg g⁻¹ at neutral pH during 60 min using unmodified and modified sawdust, respectively. The biosorption isotherms were better fitted by Langmuir model. The alkaline treatment of sawdust improves the predicted maximum Hg(II) adsorption capacity from 5.32 to 6 mg g⁻¹ at pH 7. Both ionic strength of solution and metal co-cations decrease mercury(II) uptake by modified sawdust, with the order Na⁺ > Ca²⁺ > K⁺. Mercury(II) ions adsorbed on modified sawdust were better desorbed by EDTA than HCl and HNO₃. The maximum desorption ratio of 48 % is achieved within 60 min using EDTA, and base treated sawdust reuse for two cycles operation showed a loss of 58%.

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