Desalination and Water Treatment
www.deswater.com

doi: 10.5004/dwt.2020.24768

173 (2020) 367–382
January

Removal of cadmium and copper from aqueous media by biosorption on cattail (*Typha angustifolia*) leaves: kinetic and isotherm studies

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Received 25 September 2018; Accepted 5 August 2019

ABSTRACT

The aim of the present study is the characterization and evaluation of heavy metals, cadmium and copper, removal ability of cattail (*Typha angustifolia*) leaves (CL) as a novel biosorbent from aqueous media under various operating conditions in a batch process. The CL were characterized by X-ray diffraction, scanning electron microscope, Fourier transform infrared spectrometer, isoelectric potential (pH_{zpc}) and Boehm titration method. Batch experiments were performed to examine the effect of operating parameters such as temperature (25°C–55°C), initial solution pH (3–6), ionic strength (0–5 g/250 mL), stirring speed (0–600 rpm), biosorbent dose (0.3–1.5), biosorbent particle size (0.18–1.5 mm), contact time (0–70 min) and initial concentration (25–300 mg/L) of metal ions on the removal of cadmium and copper. It was found that the equilibrium time at initial concentrations from 25 to 300 mg/L was from 10 to 30 min and from 5 to 25 min, respectively, for copper and cadmium. This shows a good kinetic property of *Typha angustifolia*. The kinetics data of biosorption for both metal ions were studied by applying Lagergren pseudo-first-order, Blanchard pseudo-second-order, Elovich, Natarajan–Khalaf and intraparticle diffusion models. The obtained results indicate that the biosorption system of both metals on CL obeyed pseudo-second-order kinetics model ($r \geq 0.996$) and the diffusion mechanism reveals that intraparticle diffusion ($r \geq 0.990$) is not the only rate limiting step. Additionally, the biosorption isotherm data were analyzed by four isotherm models Langmuir, Freundlich, Harkins–Jura and Flory-Huggins models. Equilibrium data can be well described by the Langmuir model for both metal ions, showing maximum monolayer biosorption capacity (q_m) of 97.80 and 113.46 mg/g at 25°C for copper and cadmium, respectively. Furthermore, thermodynamic parameters such as $\Delta G°$, $\Delta S°$ and $\Delta H°$ were calculated, and the results suggest that the biosorption is spontaneous, a physical process for both metals. Complete regeneration of the CL was obtained even after three cycles. These results reveal that the CL (*Typha angustifolia*) are suitable biosorbent materials for the removal of heavy metals from aqueous media.

Keywords: Biosorption; Cattail (*Typha angustifolia*) leaves; Characterization; Heavy metals; Modeling; Desorption

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1. Introduction

Heavy metal contamination exists in aqueous waste streams of many industries, such as metal plating facilities, mining operations, textiles, storage batteries, ceramics, glass and tanneries. The soils surrounding many military bases are also contaminated and pose a risk of metals groundwater and surface water contamination [1]. Some heavy metals are associated with these activities such as cadmium, chromium, uranium, mercury, copper, nickel, lead and zinc. But, heavy metals are not biodegradable and tend to accumulate in living organisms which bind to protein-binding sites by displacing original metals from their natural binding sites and result in distortion of cells. Heavy metals such as lead, mercury, arsenic, copper, zinc and cadmium are highly poisonous when they enter into the biological system. The oxidative stress in living cells and biological macromolecules is chiefly due to binding of heavy metals to the DNA and nuclear proteins [2]. So, untreated effluents may have an adverse impact both on human and environmental health, causing various diseases and disorders [1].

According to the World Health Organization (WHO), the most toxic metals are chromium, cobalt, nickel, lead, zinc, mercury, cadmium and copper [3]. The United States Environmental Protection Agency (US EPA) has determined that drinking water should not contain more than 1.3 mg/L of copper [4–6] while the WHO limit for copper ions in drinking water is 0.05 mg/L [6]. However, the drinking water guideline value recommended by WHO, AWWA (American Water Works Association), FDA (Food and Drug Administration) and EPA (Environmental Protection Agency) is 5×10^{-3} mg Cd/L [5–8]. Therefore it is very important to remove these heavy metals from water environment, in order to protect the environment and offer people a better quality of life. In this approach, several scientific studies have shown that popular processes such as membrane filtration, solvent extraction, carbon adsorption, reverse osmosis, precipitation as hydroxides or carbonates, capture on synthetic ion exchangers [9,10] and several biological processes were used for the cause. However, these methods are expensive mainly in developing countries and may generate a huge amount of waste, which leads to disposal problems. Moreover, these methods are not sufficient to remove heavy metals present in low concentration (<100 mg/L) and can even fail to achieve legal limits [11]. For that reason, there is an imperative requirement to develop an inventive process, which can remove heavy metals economically from aqueous solution.

Recently, the biosorption process is receiving increasing attention in becoming an attractive and promising technology [11]. Biosorption occurs as a result of a combination of several mechanisms, including Van der Waals attraction, electrostatic attraction, complexation, ion exchange, covalent binding, adsorption and microprecipitation [12]. The study of biosorption which utilizes natural materials or industrial and agricultural wastes is of great importance from an environmental point of view, as it can be considered as an alternative technique for removing toxic pollutants from wastewaters. Several low-cost biosorbents have been studied in the literature for their ability to remove heavy metals such as potato peel [11], fly ash [13], *Tectona grandis* [14], *Moringa oleifera* seed [10], *Hevea brasiliensis* [15], Okoume sawdust [16], peanut husk [17], pine bark [18], eucalyptus bark [19], mulch [20], luffa fruit fiber [21], red pine sawdust [22] and others.

The cattail is one kind of grass, it makes up the genus *Typha* of the family Typhaceae, which grow in wetlands throughout the world and are commonly also known as bulrush or raupo. The genus consists of 10 species (*Typha angustifolia*, *Typha latifolia*, *Typha domingensis*, *Typha capensis*, etc.) which occur commonly in wet soil, marshes, swamps and shallow fresh and brackish waters, throughout the world. The cattail can grow up to 3–4 m in height [23]. It has a potential to be used for bioremediation of polluted wastewater as they tolerate high amounts of pollutants and are capable of taking up chemical pollutants and heavy metals with no visual toxic symptom including chlorosis and necrosis when exposed to metal stress. They also have some level of tolerance to salinity. Chemical and morphological properties of cattail are summarized in Table 1 [24]. The morphological characteristics of cattail leaves from another study [25] show that they have a structure of light weight cantilever beam, exhibiting excellent mechanical properties (rigid) to maintain stability in severe weather, with low density and with high porosity (around 96%). Therefore, there is an increased interest in studying them further. Nevertheless, studies involving the use of *Typha angustifolia* leaves untreated for the removal by sorption of organic or mineral pollutants such as heavy metals or dyes from aqueous phase still are scarce. Indeed, only one work have been published using *Typha angustifolia* leaves untreated as an original low-cost biosorbent for removal of dye (malachite green) from aqueous solutions until now [26]. Although *Typha angustifolia* is available abundantly in nature and is renewable, its potential and economic source compared with other natural sorbents is still underutilized.

Thus, the aim of the present study is to characterize the cattail (*Typha angustifolia*) leaves untreated in order to complete what has not been studied in our previous work and to investigate the potential of *Typha angustifolia* leaves as a novel biosorbent for the removal of heavy metal ions, cadmium and copper, from synthetic aqueous media in batch process. The kinetics data concerning the biosorption of cadmium and copper on CL can be fitted to Lagergren pseudo-first-order, Blanchard pseudo-second-order, Elovich, Natarajan–Khalaf and intraparticle diffusion models. Equilibrium isotherm data were analyzed by four equations, namely the Langmuir, Freundlich, Harkins–Jura and Flory–Huggins models. Additionally, thermodynamic parameters such as $\Delta G°$, $\Delta S°$ and $\Delta H°$ were determined for this study. The biosorption

Table 1
Chemical and morphological properties of cattail (*Typha*) [24]

Component	Composition
Holocellulose (%)	71.0
Klason lignin (%)	16.8
Pentosane (%)	33.6
α Cellulose(%)	34.4
Extractive (%)	39.1
Ash (%)	3.7
Fiber length (mm)	1.3
Fiber diameter (μm)	12.0

parameters obtained using the present biosorbent will be compared with the ones presented in the literature. Finally, in order to evaluate the *Typha angustifolia* leaves untreated as an economic and effective biosorbent, desorption experiments were investigated using HCl as a desorbing agent.

2. Materials and methods

2.1. Preparation and characterization of CL (*Typha angustifolia*) as biosorbent

The collected leaves of cattail *(Typha angustifolia)* were washed with distilled water several times to remove dirt particles and water soluble materials. The washed materials were then completely dried in an oven at 50°C for 5 d [26]. The dried leaves were then cut into small pieces, crushed and the particle size distribution of CL was analyzed by the conventional dry sieving technique which it shows that approximately 50% (d_m, mean diameter) of all particles are ≤2 mm. However, in this study the particle size of CL sieved to desired mesh size (0.5–1.25 mm) except for biosorbent particle size studies. Finally, the obtained material was then dried in an air circulating oven at 50°C for 7 d and stored in a desiccator until use [26]. Principle characteristics of the CL *(Typha angustifolia)* were determined and the results are summarized in Table 2. The surface functional groups of the CL *(Typha angustifolia)* were determined by the Boehm method and using a (Shimadzu FTIR-8400S, Japan) Fourier transform infrared spectrometer analysis, which the spectra were recorded from 4,000 to 400 cm^{-1} by preparing KBr pellets for sample preparation. The pressed KBr disc employed for this purpose was prepared using approximately 1 mg of sample and 200 mg of KBr. The isoelectric potential or point of zero charge (pH_{pzc}) of the CL characteristics was determined by using the solid addition method and also was determined by zeta potential analysis, which zeta potential at various pH values was measured. Mineralogical analysis was conducted on powder samples with an X-ray diffractometer employing CuKα radiation. In addition, scanning electron microscopy (SEM) analysis was carried out on the CL to study the surface morphology before and after metals biosorption.

2.2. Preparation of aqueous metal ions solutions

The stock solutions (1,000 mg/L) of metal ions, copper and cadmium, were prepared by dissolving their corresponding sulfate salts ($CuSO_4{\cdot}5H_2O$ and $CdSO_4{\cdot}8H_2O$) in distilled water. The solution was further diluted to the required concentrations before use. All the chemicals used were of analytical reagent grade and were obtained from Sigma-Aldrich and Fluka (USA).

Table 2
Principal characteristics of CL (*Typha angustifolia*)

Porosity (%)	79.87
Apparent specific gravity	0.32
Absolute specific gravity	1.59
Mean diameter, d_m, (mm)	≤2
Point of zero charge (pH_{pzc})	5.20
SSA (m^2/g)	52.47

2.3. Biosorption experiments

In this study, all experiments were performed separately for each metal. Biosorption experiments were carried out by adding 0.3 g of CL to 250 mL of each metal ion solution in a conical flask. The mixture of each metal ion was agitated for 70 min with a stirring speed of 400 rpm at 25°C. Samples of the mixture were withdrawn at suitable time intervals, filtered through a filter paper for separating the CL, with the aid of a suction pump. The metal concentration in the filtrate was analyzed using atomic adsorption spectrophotometer. Effect of parameters such as temperature (25°C–55°C), contact time (0–70 min), initial pH (3–6), ionic strength (0–5 g/250 mL), stirring speed (0–600 rpm), biosorbent dose (0.3–1.5), biosorbent particle size (0.18–1.5 mm), initial metal ions concentration (25–300 mg/L) on the removal of metal ions by CL was studied.

The effect of initial pH of the solution for each metal ions was analyzed over a pH range from 3 to 6. The pH of the solution was adjusted by either 0.1 N NaOH or 0.1 N H_2SO_4 solutions using a pH meter (AD1030, ADWA instruments, Romania, Europe). Moreover, the biosorption studies were conducted in batch experiments as a function of contact time in the range of 0–70 min, metal ions concentration in the range of 25–300 mg/L, temperature in the range of 25°C–55°C and ionic strength in the range of 0–5,000 mg of NaCl/250 mL. The amount of each metal ion biosorbed on CL at time t, q_t (mg/g), was determined using Eq. (1):

$$q_t = \frac{(C_0 - C_t)V}{W} \tag{1}$$

where C_0 and C_t (mg/L) are the liquid phase concentrations of metal ions at initial and any time, respectively, V (L) is the volume of the solution and W (g) is the mass of the used biosorbent.

Biosorption equilibrium experiments were conducted for each metal by adding a fixed amount of CL into a number of flasks containing a definite volume at different initial concentrations without changing pH. The flasks were placed in a thermostatic water bath in order to maintain a constant temperature (25°C) and after agitating flasks more than 70 min to ensure equilibrium was reached for the higher concentrations and determined the maximum amount, that is, capacity biosorbed with a constant stirring speed of 400 rpm, and after the reaction mixtures were filtered and analyzed.

The amount of biosorption at equilibrium, q_e (mg/g), was calculated by:

$$q_e = \frac{(C_0 - C_e)V}{W} \tag{2}$$

where C_e (mg/L) is the liquid phase concentrations of heavy metals at equilibrium time.

All biosorption experiments were conducted in triplicate and the mean values were used.

3. Results and discussion

3.1. Characterization of CL

The infrared spectroscopy technique was used to identify the functional groups on the CL *(Typha angustifolia)*, which can be responsible for binding metal ions, and to explain metal–biosorbent interactions. FT-IR spectra for CL before and after metal ions sorption are shown in Fig. 1. The FTIR spectrum of CL in natural form (Fig. 1) shows an intense absorption peak at 3,670 cm^{-1} representing the –OH stretch of phenol group of cellulose and lignin. The peaks at 2,920 and 2,857 cm^{-1} can be assigned to –CH and $-CH_2$ stretch of aliphatic compound. The peaks detected at 1,735 and 1,606 cm^{-1} were recorded to the carbonyl group (C=O) of carboxylic acid or ester [27] and C=C stretch of phenol group, respectively. In the spectrum, other functional groups were also found at 1,431, 1,263, 1,035 and 874 cm^{-1} that can be attributed to –C–O group or $-CH_2$ deformation, Si–C stretch, C–O stretch of cellulose, lignin and hemicelluloses [28] and C–N stretch, respectively. Consequently, the Fourier transform infrared spectrometer (FTIR) analysis indicated the presence of functional groups such as –OH, −C–O, C=O and C=C on the surface of the CL. The Boehm method (Table 3) quantitatively proved these results. These results show that several types of surface groups exist, that is, phenolic, carboxylic, carbonylic, etc. From acid sites, the phenolic groups were the dominant acidic oxygenated groups. In addition, the total acid groups were higher than the total basic groups. Subsequently, these results confirmed the nature of the CL surface. Similar results have been reported by Sivarajasekar et al. [29] unlike those obtained by Naushad et al. [30]. The FTIR spectrum after metal ions biosorption, shown in Fig. 1, indicates that the peaks due to above functional groups are slightly affected in their position and intensity, which indicated that the functional groups on surface of CL participated in the metals biosorption. For example, the FTIR spectrum of biosorption of cadmium (Fig. 1) shows a band at 3,425 cm^{-1} assigned to OH^- stretching vibration and its peak intensity is lower than that of FTIR spectrum of CL, however, for the FTIR spectrum of biosorption of copper shows a band at 3,745 cm^{-1} also assigned to OH^- stretching vibration and its peak intensity is higher than that of FTIR spectrum of CL.

Based on the FTIR spectrum analysis and the results of Boehm titration method, the mechanism for the biosorption of metal ions on CL can be explained. The analysis of FTIR indicates that OH and COOH are present on CL surface, and know that in aqueous media, all the hydroxyl and carboxylic groups are deprotonated consequently, the surface of CL is negatively charged and hence positively charged metal ions (Cu^{2+} or Cd^{2+}) can interact with O^- and COO^- sites present on CL by electrostatic attraction.

The point of zero charge (pH_{zpc}) of a biosorbent is the pH at which the biosorbent surface has electrical neutrality. At this value, the acid or basic functional groups no longer contribute to the pH of the solution [31]. The pH_{zpc} of CL was calculated using the solid addition method [31,32], and was determined to be 5.20. This method was found to be similar to that studied by some authors [2,12,31–34]. This result of pH_{zpc} was confirmed by Zeta potential experiment (5.23) (Fig. 2).

The surface morphology of the CL (*Typha angustifolia*) before and after metal ions biosorption was observed using scanning electron micrograph analysis. The SEM images of CL sample before and after copper and cadmium uptake at bar length equivalent to 50 μm, working voltage 5 kV with 1,500× magnification are shown in Fig. 3. As presented in this, CL displayed an irregular, dense and porous surface texture before biosorption (Fig. 3a) providing a large exposed surface area for the biosorption of metal ions. However, the porous and rough texture disappeared after interaction with copper (Fig. 3b) and cadmium (Fig. 3c), which indicates a

Table 3
Concentration of acid and basic groups on CL surface

Concentration groups	Value (mequiv/g)
Carboxylic	0.25
Lactonic	0.16
Phenolic	1.85
Carbonylic and quinonic	0.83
Acid	3.09
Basic	0.12
Total	3.21

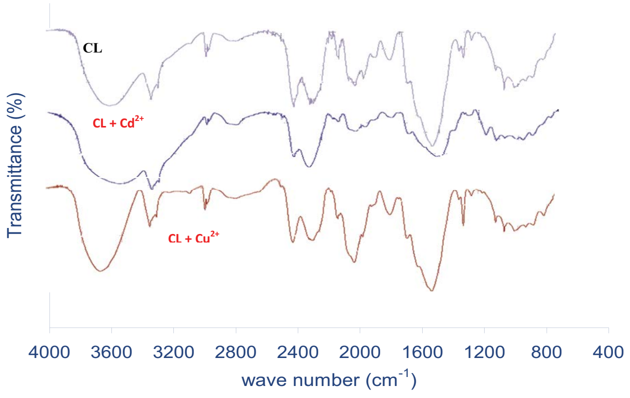

Fig. 1. FTIR spectra of CL (*Typha angustifolia*) before and after metals biosorption.

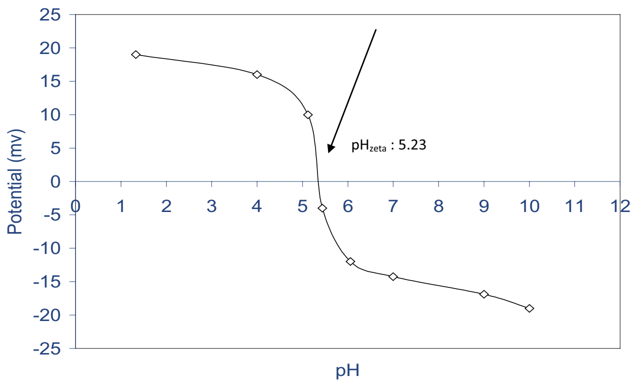

Fig. 2. Zeta potentials of CL as a function of solution pH, and determined points of zero charge.

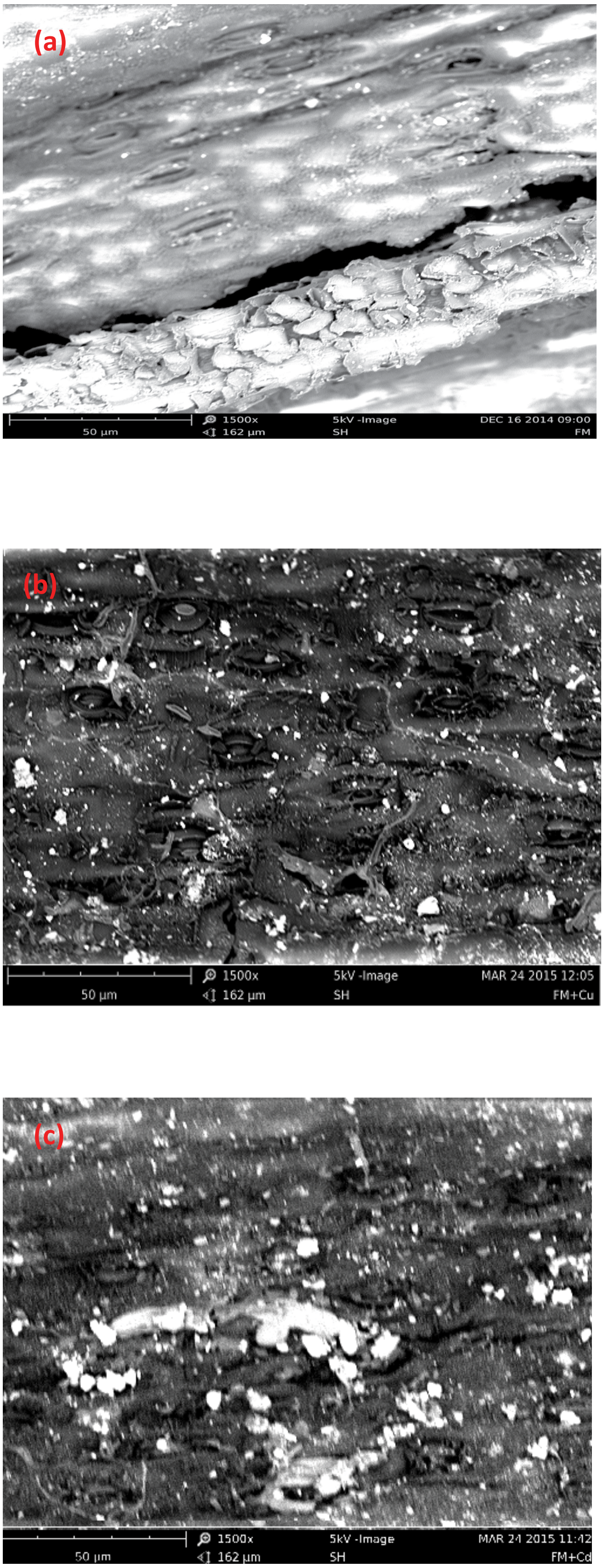

Fig. 3. SEM micrograph (×1,500) of CL before (a) and after (b) copper and (c) cadmium biosorption.

smooth surface texture and the CL (*Typha angustifolia*) surface has a higher tendency to catch and biosorb the copper and cadmium.

Mineralogical analysis of CL was conducted by X-ray diffraction, which showed no apparent diffraction peaks (data not shown), indicating that CL (*Typha angustifolia*) was X-ray amorphous. Similar result was reported using modified peat for adsorption of phosphate [35].

3.2. Biosorption kinetic studies

3.2.1. Effect of temperature

Temperature has a great effect on the biosorption process. The effect of temperature on the biosorption of each metal ion was studied by contacting 0.3 g of biosorbent with 250 mL of metal ion solution of 200 mg/L initial concentration into flasks. The flasks were placed in a thermostatic water bath in order to maintain a constant temperature (25°C, 35°C, 45°C or 55°C) and stirring was provided at 400 rpm to ensure equilibrium was reached. Fig. 4 shows the biosorption of metals on CL. It was observed that the biosorption of copper decreases with the increase in temperature from 25°C to 55°C. This indicates that the biosorption process of copper on CL is exothermic in nature. As the temperature increases, the physical bonding between the copper ions and the active sites of the biosorbent weakens. In contrast, in the case of cadmium, the removal is an endothermic process because it was observed that the biosorption of cadmium increases with the increase in temperature from 25°C to 55°C. Similar results were reported using different biosorbents for the removal of copper and cadmium [11,19,21,33]. However, Dekhil et al. [36] indicated that the removal of cadmium by the macro alga *Caulerpa racemosa* was an exothermic process.

3.2.2. Effect of initial solution pH

The initial pH of metal ions solutions is one of the most important parameters controlling the biosorption process. The experiments were carried out at a fixed biosorbent dose of 0.3 g, temperature of 25°C, initial metal ions concentration

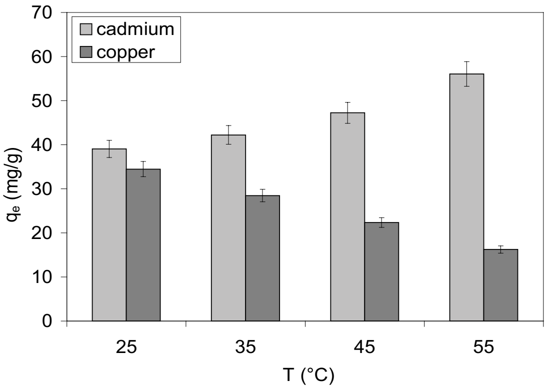

Fig. 4. Effect of temperature on the biosorption of cadmium and copper on CL (conditions: C_0: 200 mg/L; biosorbent dosage: 0.3 g; stirring speed: 400 rpm; pH_{copper}: 5; $pH_{cadmium}$: 6, *T*: 25°C–55°C, error bars: 5%).

of 200 mg/L and varying pH in the range of 3.0–5.0 for copper and in the range of 3.0–6.0 for cadmium for different time intervals. This pH range was chosen in order to avoid metal solid hydroxide precipitation and thus biosorption studies at these pH values could not be performed because the biosorbent was deteriorated with the accumulation of metal ions [37]. Fig. 5 shows the effect of initial pH on the biosorption of both metals, and it was observed that the removal of both metal ions increases with increasing pH, from its minimum at pH 3.0 to its maximum at pH 6.0. The biosorbed amount at equilibrium increased from 18.28 to 34.47 mg/g for copper when the pH increased from 3.0 to 5.0 and from 23.14 to 39.05 mg/g for cadmium when the pH increased from 3.0 to 6.0. The variation in the removal of both metal ions on CL with respect to pH can be elucidated by considering the surface charge of the biosorbent material and the speciation of copper and cadmium. According to the cadmium speciation diagram, Cd^{2+} is the predominant ionic species at pH less than 7.0. Hence, cadmium was biosorbed on the CL as Cd^{2+} for all the carried experiments. Also, according to the copper speciation diagram, at the pH values varying in the range of 3.0 to 5.0, there are three species of copper present in solution. In the acidic pH (≤3.0), copper should be predominantly present as Cu^{2+}, at pH between 4.0 and 5.0, Cu^{2+} and $CuOH^{+}$ are present in solution in large amount, but $Cu(OH)_2$ in small amount. At pH > 5.0, precipitation of $Cu(OH)_2$ prevents biosorption studies, similar observations were already reported [5]. On the basis of the point of zero charge, pH_{zpc}, of the biosorbent, it was possible to explain the influence of the solution pH on the metal ions uptake. At lower pH ($pH < pH_{zpc}$), CL surface is positively charged, concentrations of H^{+} were high and they compete with positively charged for each species metal ions as indicated, for vacant biosorption sites causing a decrease in metal ions uptake. At $pH > pH_{zpc}$, the surface of the CL gets negatively charged and favors uptake of each metal ions species. Consequently, the optimum pH for the biosorption of copper was 5.0 but for the biosorption of cadmium was 6.0. Similar results were already found by some authors [11,19,38].

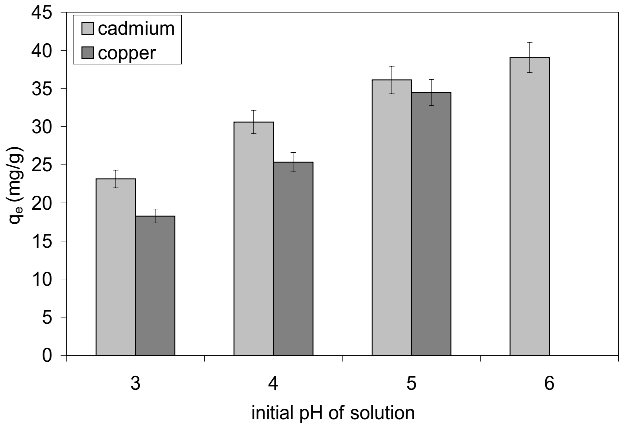

Fig. 5. Effect of initial pH on the biosorption of cadmium and copper on CL (conditions: C_0: 200 mg/L; biosorbent dosage: 0.3 g; stirring speed: 400 rpm; pH: 3–6, T: 25°C, error bars: 5%).

3.2.3. Effect of ionic strength

There are a number of studies showing the changing of the removal order of metal ions with the concentration of various electrolyte types in metal ions medium. The presence of salt or co-ions in solution can affect the biosorption of ions. The effect of ionic strength on the biosorption of both metal ions on CL was studied with a constant initial concentration of 200 mg/L, biosorbent mass of 0.3 g, temperature of 25°C, stirring speed of 400 rpm and different concentrations of sodium chloride (0–5,000 mg/250 mL). Fig. 6 shows that for each metal ion, the biosorbed amount decreased with the increase in concentration of salt (NaCl) in the medium. The biosorbed amount at equilibrium decreased from 34.47 to 12.18 mg/g for copper and from 39.05 to 17.14 mg/g for cadmium as the concentration of NaCl in the medium was increased from 0 to 5,000 mg/250 mL. This occurrence can be explained that as when the ionic strength was increased, the electrical double layer surrounding the biosorbent surface was compressed, which would lead to a decrease in the electrostatic potential. This indirectly resulted in a reduction of the Coulombic free energy, and a decrease in metal ions biosorption [11]. Similar results have been reported for removal of copper by potato peel [11] and for removal of cadmium by fiber fruit luffa [21] but unlike those obtained for removal of cadmium by curcumin formaldehyde resin [30].

3.2.4. Effect of stirring speed

The effect of stirring speed was studied by varying the stirring speed between 0 and 600 rpm while maintaining the initial metals concentration constant (200 mg/L). The amount of copper biosorption increases from 8.97 to 39.41 mg/g and of cadmium increases from 10.07 to 43.65 with an increase in stirring speed from 0 (without stirring) to 600 rpm, respectively (Fig. 7). The increase of stirring speed increases the removal efficiency by decreasing the thickness of the diffusion layer around the biosorbent surface. The change in the biosorbed amount for both metals was insignificant compared with the dissipated energy, when the stirring speed

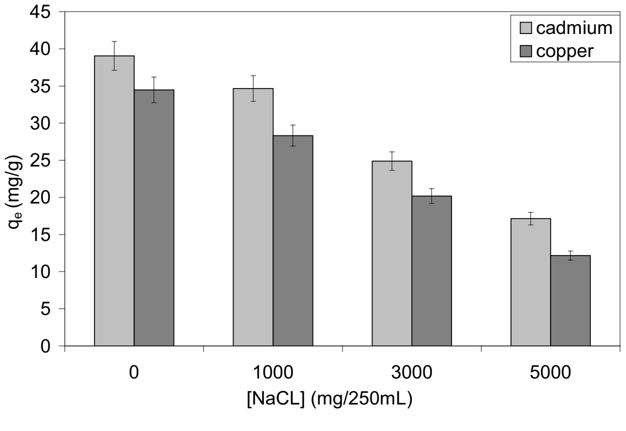

Fig. 6. Effect of salt concentration on the biosorption of cadmium and copper on CL (conditions: C_0: 200 mg/L; biosorbent dosage: 0.3 g; stirring speed: 400 rpm; pH_{copper}: 5 $pH_{cadmium}$: 6, T: 25°C, error bars: 5%).

increased from 400 to 600 rpm, the amount of copper biosorption increases from 34.47 to 39.41 mg/g and of cadmium increases from 39.05 to 43.65 mg/g. Therefore, all subsequent experiments were conducted at a stirring speed of 400 rpm. Similar results have been reported in biosorption of heavy metals [11,16].

3.2.5. Effect of biosorbent dose

In order to establish the effect of biosorbent dose the biosorption of copper and cadmium, the batch equilibrium studies at different dose values were carried out in the range of 0.3–1.5 g/250 mL. The experiments were carried out at 200 mg/L initial metal concentration with pH (5) for copper and pH (6) for cadmium at 25°C ± 2°C for equilibrium time and a constant stirring speed of 400 rpm. Fig. 8 shows the effect of biosorbent dose on the biosorption of both metals, and it was observed that the biosorption capacity was lesser at higher biosorbent doses. This is due to greater availability of the exchangeable sites or surface area at a higher concentration of the biosorbent [39,40]. Thus, with increasing biosorbent dosage, the amount of each metal biosorbed by unit weight of biosorbent becomes reduced, thus causing a decrease in biosorption capacity with increasing biosorbent dosage. On the other hand, the results (figure not shown) indicate that an increase in the biosorbent dose resulted in increase in the percentage removal due to the increase in the number of biosorption sites [41].

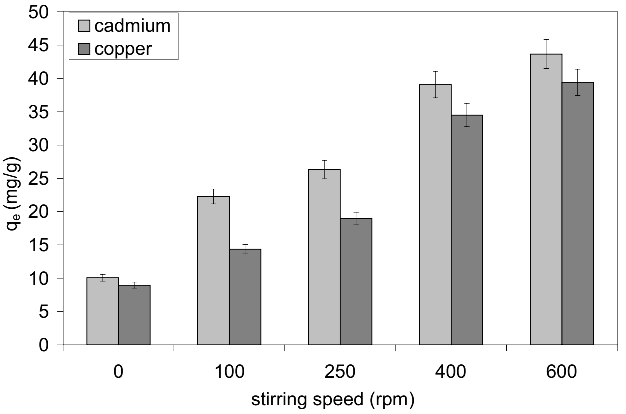

Fig. 7. Effect of stirring speed on the biosorption of cadmium and copper on CL (conditions: C_0: 200 mg/L; biosorbent dosage: 0.3 g; stirring speed: 0–600 rpm; pH_{copper}: 5 $pH_{cadmium}$: 6, T: 25°C, error bars: 5%).

3.2.6. Effect of biosorbent particle size

The effect of particle size of CL *(Typha angustifolia)* on the copper and cadmium removal was studied by varying the particle size from 0.18 mm at 1.5 mm, keeping all other parameters constant. Fig. 9 shows the biosorption equilibrium of both metal ions at three different particle sizes. It was observed from this figure, the removal is enhanced as the particle size decreases for both metals. The amount of copper biosorption equilibrium decreases from 49.81 to 20.24 mg/g and from 52.53 to 28.76 for cadmium with an increase in particle size of CL from 0.18 to 1.5 mm, respectively. This is because the smaller particles have more surface area and access to the particle pores is facilitated when their size is small. It is moreover believed that the breaking up of large particles to form smaller ones opens some tiny sealed channels, which might then become available for biosorption, and so the biosorption by smaller particles is higher than that by larger particles [42]. In the literature, similar results were observed for the biosorption of ion metals on different biosorbents [11,16,43].

3.2.7. Effect of initial metal ions concentrations and contact time

The experiments were carried out at a fixed biosorbent dose (0.3 g), natural pH for copper and cadmium, stirring speed of 350 rpm, temperature of 25°C and at different initial metal ion concentrations (from 25 to 300 mg/L) for different time intervals (0–70 min). Fig. 10 shows the effect of initial metal ions concentrations and contact time on metal

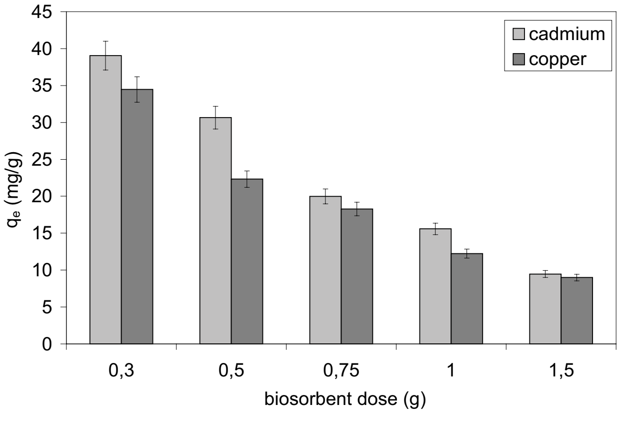

Fig. 8. Effect of dosage biosorbent on the biosorption of cadmium and copper on CL (conditions: C_0: 200 mg/L; biosorbent dosage: 0.3–1.5 g; stirring speed: 400 rpm; pH_{copper}: 5 $pH_{cadmium}$: 6, *T*: 25°C, error bars: 5%).

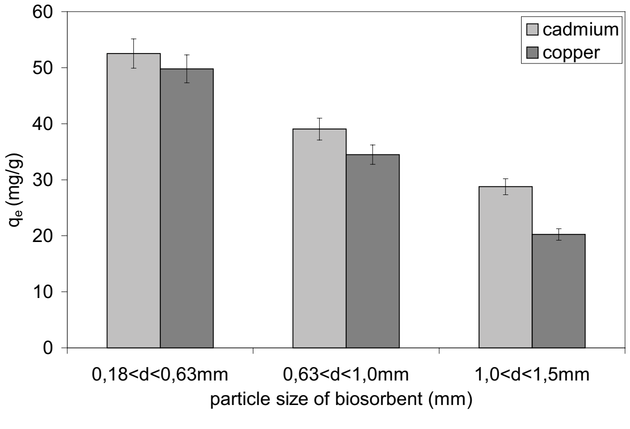

Fig. 9. Effect of biosorbent particle size on the biosorption of cadmium and copper on CL (conditions: C_0: 200 mg/L; biosorbent dosage: 0.3 g; stirring speed: 400 rpm; pH_{copper}: 5 $pH_{cadmium}$: 6, *T*: 25°C, error bars: 5%).

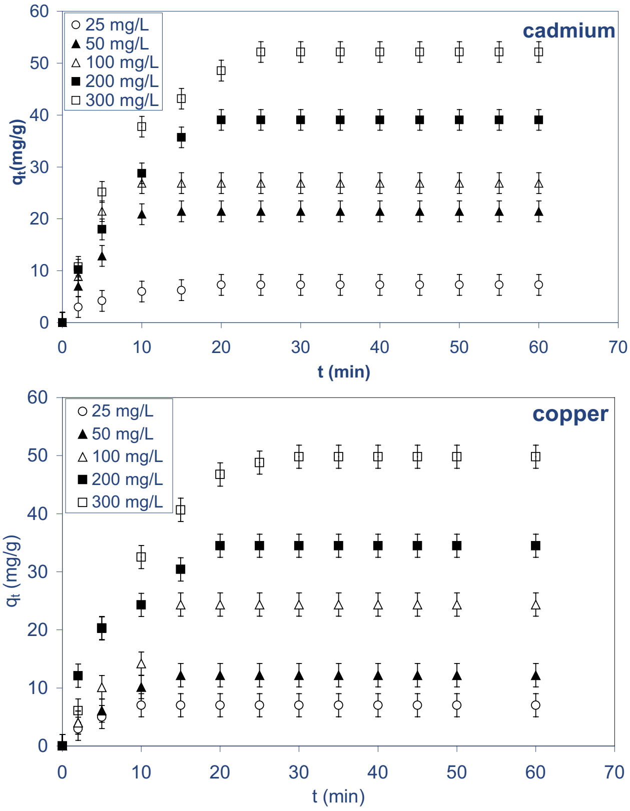

Fig. 10. Effect of initial concentration and contact time on the biosorption of cadmium and copper on CL (C_0: 25–300 mg/L; CL dosage: 0.3 g; stirring speed: 400 rpm; pH_{copper}: 5 $pH_{cadmium}$: 6, T: 25°C, error bars: 5%).

ions uptake. For the different concentrations tested, it can be observed that the biosorption capacity increased with time and reached a constant value where no more metal ions were removed from the solution. It can be observed that the biosorption for both metal ions at different concentrations is rapid in the initial stages (first few minutes) and gradually decreases with the biosorption progress until the equilibrium is reached; similar observations have further been obtained in the biosorption of copper by Awuala et al. [6]. As the surface biosorption sites become exhausted, the rate of uptake is controlled by the rate of transport from the exterior to the interior sites of the biosorbent particles [44]. As a result of the above observations, it was indicated that the biosorption process for both metal ions on CL was to be dependent on concentration of biosorbate up to some extent. The initial rate of biosorption was greater for higher initial metal ion concentrations, because the resistance to the metal uptake decreased as the mass transfer driving force increased. The biosorbed amount at equilibrium increased from 5.23 to 49.81 mg/g and 7.18 to 52.14 mg/g as the concentration increased from 25 to 300 mg/L, respectively, for copper and cadmium. The kinetic results showed that the curves of contact time are single and continuous leading to equilibrium. These curves indicate the possible monolayer coverage for both metal ions on the surface of CL [26]. In the literature, similar results have been found by other authors [4,45]. Furthermore, Fig. 10 reveals that the biosorption of both metals was a rapid process, which the contact time required to reach the equilibrium at initial concentrations from 25 to 300 mg/L was from 10 to 30 min and from 5 to 25 min, respectively, for copper and cadmium. This shows a good kinetic property of *Typha angustifolia*. However, in all subsequent experiments the equilibrium time was maintained after 1 h, which was considered sure that full equilibrium was attained for the removal of both metal ions on CL. Cirik et al. [46] have studied the biosorption of copper and cadmium on marine algae and have reported that the equilibrium was established to be lower than 60 min for both metal ions studied.

The experimental results for different initial metal ions concentrations were modeled by the Lagergren pseudo-first-order [11], the Blanchard pseudo-second-order [21], the Elovich [47], the Natarajan–Khalaf [48] and the intraparticle diffusion (Weber and Morris) [47] models.

The best-fit model was selected based on the magnitude of the regression correlation coefficient (r) as a first criterion, that is, the kinetic model giving a value of r closest to unity is deemed to provide the best fit and the experimental amount biosorbed at equilibrium (q_e) will be close to the theoretical (calculate) amount biosorbed as a second one.

The Lagergren equation was used to investigate the suitability of pseudo-first-order kinetic model and to obtain the rate constants. This equation can be written as:

$$\ln q_e - q_t = -k_1 t + \ln q_e \tag{3}$$

where q_e (mg/g) and q_t (mg/g) represent the biosorbed amount of metal ions at equilibrium and at any time t, respectively, and k_1 (min^{-1}) is the rate constant.

The plot of $\ln(q_e - q_t)$ vs. t gives a straight line for the Lagergren pseudo-first-order biosorption kinetics (figure not shown). The slope of plot was used to determine the equilibrium rate constant, k_1, and the intercept for the biosorption at equilibrium, q_e. The k_1 values, the correlation coefficients, the calculated biosorbed amount ($q_{e,\text{cal}}$) and experimental ($q_{e,\text{exp}}$) values for both metals were collected in Table 4. As seen that the linear regression correlation coefficient (r) values were found to be higher, (≥0.982) for copper and (≥0.989) for cadmium, however, it was observed (Table 4) that the experimental ($q_{e,\text{exp}}$) values were not in agreement with the calculated ($q_{e,\text{cal}}$) values obtained from the linear plots for both metal ions. Consequently, these results have shown that the experimental data do not agree with the Lagergren pseudo-first-order kinetic model. Generally the first-order equation of Lagergren was applicable over the initial stage of the adsorption processes [21].

The kinetic data were analyzed using the Blanchard pseudo-second-order model which can be linearized in the following form:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \tag{4}$$

where k_2 (g/mg min) is the rate constant for the pseudo-second-order kinetics, q_e and q_t represent the biosorbed amount of metal ions (mg/g) at equilibrium and at any time t, respectively. $h = k_2 q_e^2$ is the initial biosorption rate (mg/g min). The values of k_2 and $q_{e,\text{cal}}$ were calculated from the intercepts ($1/k_2 q_e^2$) and slopes ($1/q_e$) of the plots of t/q_t vs. t, respectively

Table 4
Parameters of the kinetic models for the biosorption of copper and cadmium on CL (*Typha angustifolia*) at different concentrations

Model	Initial copper concentration (mg/L)					Initial cadmium concentration (mg/L)				
Lagergren pseudo-first-order	25	50	100	200	300	25	50	100	200	300
$q_{e\,(\text{exp})}$ (mg/g)	5.23	12.18	24.35	34.47	49.81	7.18	21.68	26.87	39.05	52.14
$q_{e\,(\text{cal})}$ (mg/g)	16.45	4.76	33.15	28.89	72.17	2.18	19.69	40.13	36.35	63.79
k_1 (min^{-1})	0.231	0.178	0.084	0.124	0.160	0.156	0.277	0.401	0.155	0.130
r	1	0.983	0.987	0.982	0.987	1	0.989	1	0.997	0.994
Blanchard pseudo-second order										
k_2 (g/mg min)	0.132	0.032	0.016	0.019	0.021	0.199	0.010	0.066	0.072	0.089
$q_{e\,(\text{cal})}$ (mg/g)	5.28	12.73	25.88	34.23	49.75	7.17	21.27	27.77	38.91	52.63
h (mg/g min)	6.81	5.29	4.84	17.71	13.02	28.65	19.23	18.24	10.47	8.46
r	0.999	0.998	0.996	0.999	0.997	0.999	0.999	0.999	0.999	0.996
Elovich kinetics										
ά (mg/g min)	3.985	4.953	6.061	11.833	17.341	3.360	8.363	11.032	19.339	10.901
β (g/mg)	0.398	0.269	0.157	0.116	0.057	0.572	0.138	0.088	0.087	0.060
r	0.996	0.964	0.999	0.985	0.978	1	0.987	0.999	0.991	0.991
Natarajan and Khalaf										
$K_{\text{N-K}}$ (min^{-1}) × 10^3	13.7	8.6	9.3	3.6	3.2	30.2	28.2	17.2	5.8	4.3
r	0.991	0.991	0.983	0.981	0.933	0.939	0.995	0.955	0.955	0.946
Intraparticle diffusion										
k_d (mg/g min$^{1/2}$)	2.32	3.44	5.78	7.06	12.05	1.94	8.59	10.19	10.51	11.31
C_d (mg/g)	0.27	1.06	2.88	3.69	7.96	0.90	1.09	1.10	1.47	1.76
r	0.999	0.994	0.990	0.994	0.990	1	1	0.990	0.990	0.990

(figure not shown). The results of the pseudo-second-order model, k_2, $q_{e,\text{exp}}$, $q_{e,\text{cal}}$ and r, are reported in Table 4. It can be seen that at all initial metal concentrations and for the entire biosorption period, the linear regression correlation coefficient values were found to be higher ($r \geq 0.996$) and it has been shown that a good agreement between calculated q_e ($q_{e,\text{cal}}$) and experimental ($q_{e,\text{exp}}$) values for both metals. Consequently, the pseudo-second-order kinetics equation is adequate to describe the experimental data for the biosorption of both metal ions on CL. Similar kinetic results were already reported by some authors for the sorption of pollutants (heavy metals and dyes) on various sorbents [11,12,19,33,49–52].

The Elovich model has been used for the description of the biosorption of pollutants from aqueous solutions on materials [47,53,54]. The differential form of this equation is written as follows:

$$\frac{dq_t}{dt} = \alpha \exp(-\beta q_t) \tag{5}$$

This equation can be linearized in the following form:

$$q_t = \frac{1}{\beta}\ln(\alpha \cdot \beta) + \frac{1}{\beta}\ln(t) \tag{6}$$

where q_t is the biosorption capacity at time t (mg/g), α is the initial biosorption rate (mg/g min) and β is the desorption constant (g/mg).

The values of Elovich parameters were given in Table 4. It was observed that Elovich equation represents a good fit with the experimental data for cadmium only, because for all the studied concentrations (25–300 mg/L), the linear regression correlation coefficients values, r, were found to be higher, and varying between 0.987 and 1.

The biosorption kinetics data can be described by Natarajan–Khalaf equation, which is described by the following differential equation:

$$\frac{dC}{dt} = K_{\text{N-K}} C \tag{7}$$

Integrating Eq. (7) for the boundary conditions of $t = 0$ up to t and of $C = C_0$ up to $C = C_t$, Eq. (7) became Eq. (8):

$$\ln\frac{C_0}{C_t} = K_{\text{N-K}} t \tag{8}$$

where C_0 (mg/L) and C_t (mg/L) represent the concentration of metal ions at initial and at any time t, respectively, and $K_{\text{N-K}}$ (min^{-1}) represents the biosorption rate constant.

The value of the biosorption rate constant, $K_{\text{N-K}}$, was determined from the plot of $\ln(C_0/C_t)$ vs. t. The kinetic parameters of Natarajan–Khalaf equation are regrouped in Table 4. From this, it can be shown that Natarajan–Khalaf equation is unsuitable to describe the experimental data for the biosorption of both metals and for all initial concentrations, because the correlation coefficients obtained were low ($r \geq 0.933$ for copper and $r \geq 0.939$ for cadmium).

Biosorption kinetics is usually controlled by different mechanisms of which the most general were the diffusion mechanisms which can be explained by intraparticle diffusion model proposed by Weber–Morris. Weber-Morris plots related to intraparticle diffusion have the same general features: initial curved portion, linear portion and plateau portion. The initial curved portion is the bulk diffusion stage. The linear portion is the gradual biosorption stage where intra-particle diffusion is rate-controlled. The plateau portion is the final equilibrium stage where intra-particle diffusion starts to slow down due to extremely low solute concentrations in the solution [55]. The rate constant for intraparticle diffusion is determined using equation given by Weber–Morris:

$$q_t = k_d \cdot t^{1/2} + C_d \tag{9}$$

where q_t is the biosorbed amount at any time, k_d is the intraparticle diffusion rate constant (mg/g min$^{1/2}$) and C_d is the intercept, which represents the thickness of the boundary layer. A larger intercept means a greater effect of the boundary layer [11].

If intraparticle diffusion is rate-limited, then plots of adsorbate uptake q_t vs. $t^{1/2}$ would result in a linear relationship, k_d and C_d values can be obtained from these plots (Fig. 11 and Table 4). The plots are multilinear and there are two different portions, indicating the different stages in biosorption of both metals. The first portion represents the metal ions were biosorbed within a $t^{1/2}$ value of about first minute; this can be attributed to the rapid use of the most readily available sorbing sites on the biosorbent surface. This portion is the gradual biosorption stage. The second portion is the final equilibrium stage. The values of k_d were determined from the slopes of the first linear portion and it was observed that these values (intraparticle diffusion rate constant) of both metal ions increasing with the initial concentrations. Furthermore, it was observed that the values of C_d for both metals increasing with the initial concentrations, which indicates an increase in the thickness and the effect of the boundary layer. The plots of intraparticle diffusion model shown in Fig. 11 were not linear over the whole time range for both metals, implying that more than one process affected the biosorption. A similar phenomenon was observed for the biosorption of copper by potato peel [11].

In brief, these results indicate that the biosorption system of both metals on CL (*Typha angustifolia*) at all initial concentrations and for entire biosorption period obeyed the pseudo-second-order kinetics model and intraparticle diffusion is not the only rate limiting step, but other processes might implicate in controlling the rate of biosorption. Additionally, only the biosorption cadmium kinetic data were best described by Elovich kinetic model.

3.3. Equilibrium isotherm studies

The examination of the equilibrium isotherms is a condition for predicting the biosorption uptake of the biosorbent, which is one of the main parameters required for designing an optimized system. Various isotherm models have been used to describe the equilibrium data nature of biosorption. For this purpose, the biosorption equilibrium data for both metal ions on CL were modeled by Langmuir [56], Freundlich [31], Harkins–Jura [57] and Flory–Huggins [31] equations. The linear forms of these four isotherm models were represented as follows:

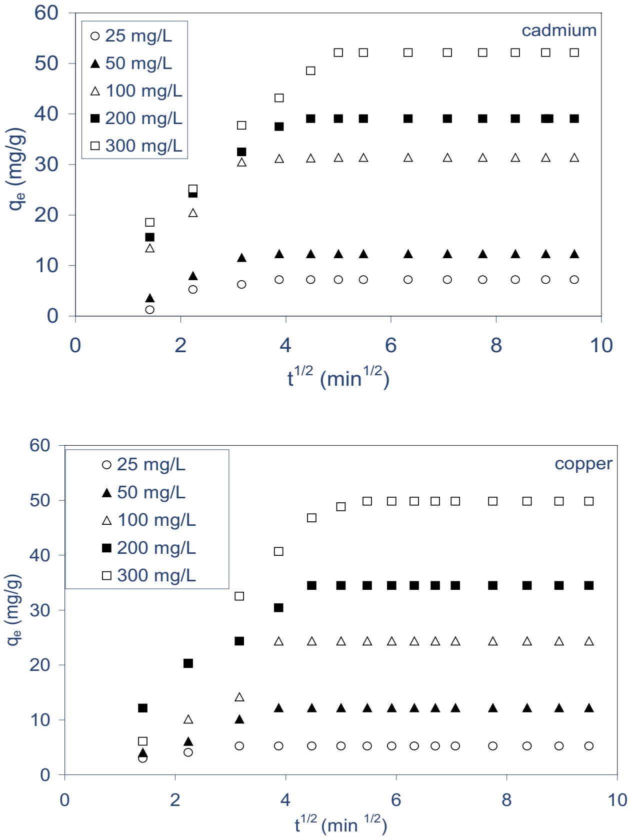

Fig. 11. Intraparticle diffusion plots for the biosorption of cadmium and copper on CL (C_0: 25–300 mg/L; biosorbent dosage: 0.3 g; stirring speed: 400 rpm; T: 25°C).

Langmuir: $$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{bq_m} \times \frac{1}{C_e} \tag{10}$$

Freundlich: $$\ln q_e = \ln K_F + \frac{1}{n_F} \ln C_e \tag{11}$$

Harkins–Jura: $$\frac{1}{q_e^2} = \frac{B_{\text{H-J}}}{A_{\text{H-J}}} - \frac{1}{A} \log C_e \tag{12}$$

Flory–Huggins: $$\ln\left(\frac{\theta}{C_0}\right) = \ln K_{\text{FH}} + n_{\text{FH}} \ln(1-\theta) \tag{13}$$

where q_m is maximum biosorption capacity (mg/g), b is Langmuir constant (L/mg), K_F mg$^{1\text{-}1/n}$ L$^{1/n}$/g) is Freundlich biosorbent capacity, $1/n_F$ is heterogeneity factor (if $n_F > 1$, the biosorption is a favorable physical process), $A_{\text{H-J}}$ and $B_{\text{H-J}}$ were

Harkins–Jura constants, q is the degree of surface coverage, K_{FH} is the indication of Flory–Huggins equilibrium constant and n_{FH} is constant model exponent.

Fig. 12 shows the plotted models including the fitted models at 25°C and the result parameters isotherm studies were summarized in Table 5. Relying upon the obtained correlation coefficient values (r), it was clear that Langmuir model provided a good fit ($r \geq 0.998$) for the experimental equilibrium biosorption data for both metal ions, which attest that the system involves a homogeneous surface with equal energy and equally available sites for biosorption [58]. Such finding is similar to that made in previous works on sorption of heavy metals by different sorbents [6,41,51,59–62]. The maximum biosorption capacity (q_m) of Langmuir were 97.80 and 113.46 mg/g, respectively, for copper and cadmium. As $n_F > 1$, biosorption of both metal ions on CL is a favorable physical process.

The interaction of metal ions and biosorbent was further evaluated by separation factor (R_L), which demonstrates the favorability of the biosorption [11]. R_L value ($R_L = 1/(1 + bC_0)$) is a dimensionless constant separation factor, an equilibrium parameter derived from the Langmuir model. The R_L values indicate whether the isotherm is favorable ($0 < R_L < 1$), unfavorable ($R_L > 1$), irreversible ($R_L = 0$) or linear ($R_L = 1$). The R_L values for both metals biosorption on CL were in the range of 0–1 (Table 5), suggesting that the biosorption of both metal ions is favorable.

The thermodynamic parameters that must be considered to determine the process as changes in enthalpy ($\Delta H°$), entropy ($\Delta S°$) and free energy ($\Delta G°$) are calculated using the following equations [47]:

$$\Delta G° = -R_g T \ln b \tag{14}$$

$$\Delta G° = \Delta H° - T\Delta S° \tag{15}$$

where (K) is the absolute temperature and R_g is the gas constant, and b (L/mol) is the Langmuir equilibrium constant.

The values of $\Delta G°$ were obtained according to Eq. (14) at different temperatures (25°C–55°C). From the slope and the intercept of the plot of $\Delta G°$ vs. T (Figure not shown), $\Delta H°$ and $\Delta S°$ values were estimated. The calculated parameters by using the above equations were collected in Table 6. The negative values of $\Delta G°$ for both metals reveal the feasibility of the process and the spontaneous nature for the biosorption on CL and with a high preference of cadmium to CL at lower temperatures. The lower and positive value of $\Delta S°$ (32.39 and 41.43 J mol^{-1} K^{-1}), respectively, for copper and cadmium indicates that may imply that no remarkable change in entropy occurred during the biosorption of ion metals. The negative values of enthalpy change (−17.7 kJ/mol) indicated the exothermic nature of the biosorption and the positive

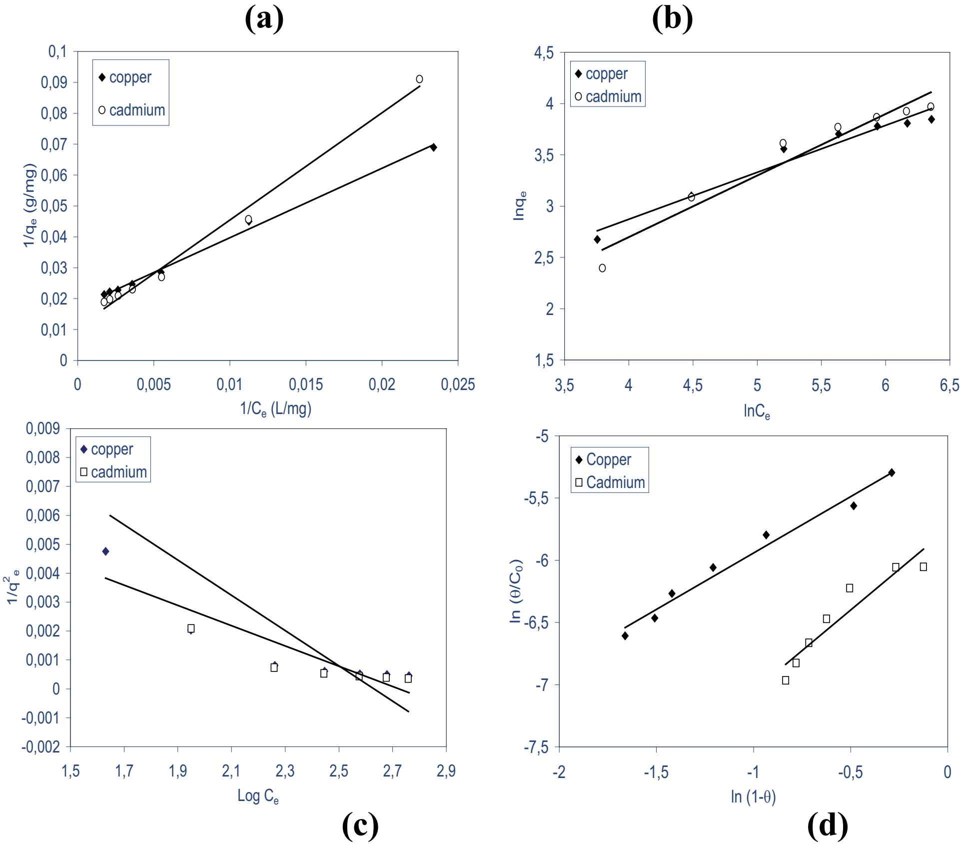

Fig. 12. Linear plots of isotherm models for the biosorption of cadmium and copper on CL: (a) Langmuir (form 1), (b) Freundlich, (c) Harkins–Jura and (d) Flory–Huggins.

Table 5
Fitted isotherm models for copper and cadmium biosorption on CL at 25°C

Isotherm	Parameters	Metal ions	
		Copper	Cadmium
Langmuir	q_m (mg/g)	97.80	113.46
	$b \times 10^3$ (L/mg)	10.2	8.8
	r	0.999	0.998
	R_L (50–400 mg/L)	0.072–0.024	0.086–0.044
Freundlich	K_F (mg$^{1-1/n}$ L$^{1/n}$/g)	2.84	1.34
	n_F	2.19	1.66
	r	0.978	0.971
Harkins–Jura	$A_{\text{H-J}}$ (mg^2/g^2)	163.93	285.71
	$B_{\text{H-J}}$	0.132	0.123
	r	0.851	0.911
Flory–Huggins	$K_{\text{F-H}} \times 10^3$ (L/mg)	6.5	3.1
	$n_{\text{F-H}}$	0.92	1.30
	r	0.988	0.947

Table 6
Thermodynamic parameters for the biosorption of ion metals on CL

Ion metals	T (°C)	$\Delta H°$ (kJ/mol)	$-\Delta G°$ (kJ/mol)	$\Delta S°$ (J/mol K)
Copper	25	–17.7	11.00	32.39
	35		11.87	
	45		12.26	
	55		12.51	
Cadmium	25	23.99	11.91	41.43
	35		11.53	
	45		10.59	
	55		9.99	

value of enthalpy change (23.99 kJ/mol) indicated the endothermic nature of the biosorption interaction, respectively, for copper and cadmium. These results prove what we found above in effect of temperature. Similarly, the thermodynamic parameters were reported for the removal of copper by potato peel [11] and for the removal of cadmium by fiber fruit luffa [21] and by custard apple fruit (*Annona squamosa*) shell [64] (Table 7).

3.4. Desorption of metal from CL

In order to assess the practical utility of the CL (*Typha angustifolia*) biosorbent, desorption experiments were conducted to regenerate the biosorbent. After biosorption of the metal ion, desorption and regeneration potential of CL was evaluated for three cycles (or times) using HCl (0.1 N) solution as desorbing agent. This is because at low pH, positive charges developed on the surface of CL due to which electrostatic repulsion occurs between the cationic metal ions and the biosorbent, resulting in the detachment of cationic ions from the biosorbent surface.

The percentage of each metal ion desorbed (or desorption efficiency) was computed using the equation:

$$\%\text{Desorption} = \frac{q_{\text{desorbed}}}{q_{\text{biosorbed}}} \times 100 \tag{16}$$

where q_{desorbed} and $q_{\text{biosorbed}}$ represents the amounts of metal ion desorbed and biosorbed, respectively.

Three consecutive cycles of biosorption–desorption experiments were performed for both metal ions. Desorption of each metal ion was almost complete during three cycles, with a desorption efficiency for first cycle of 92.8% and 95.3% for copper and cadmium, respectively.

4. Evaluation of CL as biosorbent

The maximum biosorption capacities (q_m) of CL (*Typha angustifolia*) for the removal of copper and cadmium have been compared with those of other biosorbents reported in literature (Table 7). It was clear that the leaves of *Typha angustifolia* used in the present study have a relatively suitable biosorption capacity of 97.80 and 113.46 mg/g, respectively, for copper and cadmium. Therefore, it can be concluded that this solid waste can be used as an effective biosorbent material for the removal of copper and cadmium from aqueous media.

Table 7
Comparison of maximum biosorption capacity of some sorbents

Biosorbents	Initial concentration range (mg/L)	Equilibrium time (min)	q_m (mg/g)	Reference
Copper				
Meranti sawdust	1–200	120	32.05	[44]
Phanerochaete chrysosporium, immobilized	10–500	60	98.85	[63]
Potato peel	25–300	15–35	84.74	[11]
Sawdust	10–50	180	6.58	[17]
Modified peanut husk	10–50	180	10.15	[17]
Cedar sawdust	200	120	294.12	[33]
Crushed brick	200	120	153.84	[33]
AC of rubber wood sawdust (PAC)	5–40	240	5.62	[15]
Commercial activated carbon (CAC)	5–40	180	4.71	[15]
Nano-composite adsorbent	2–75	between 50 and 120	173.62	[6]
Cattail leaves (*Typha angustifolia*)	25–300	10–30	97.80	Present study
Cadmium				
Annona squamosa shell	50–200	30	71.0	[64]
Pristine biomass	5–80	20	19.01	[65]
Modified biomass	5–80	20	45.87	[65]
Phanerochaete chrysosporium, immobilized	10–500	60	85.98	[66]
Phanerochaete chrysosporium free		60	70.38	[66]
Raphanus sativus peels	5–100	120	19.82	[67]
Banana peel	*	20	5.71	[68]
$YVO_4:Eu^{3+}$ nanoparticles	25–200	90	99.01	[62]
Curcumin formaldehyde resin	100–300	60	119.05 at 25°C	[30]
Composite cation exchanger	200–1,000	>40	250	[69]
Mango peel	*	60	68.98	[45]
Fiber fruit luffa	50–200	5–23	97.33 at 25 °C	[21]
Cattail leaves	25–300	5–25	113.46 at 25°C	Present study

5. Conclusion

The results of the present investigation showed that the cattail (*Typha angustifolia*) leaves can be promising biosorbents for the removal of heavy metals such as copper and cadmium from aqueous media. The characterization of *Typha angustifolia* leaves revealed that the heterogeneity, porous surface and functional groups made CL favorable and effective to remove heavy metals from wastewater. The optimum pH for biosorption was 5.0 for copper and 6.0 for cadmium. The presence of salt in solution reduced the biosorption of copper and cadmium on CL. The biosorption process was relatively faster, the contact time required to reach the equilibrium at initial concentrations ranging from 25 to 300 mg/L was from 10 to 30 min and from 5 to 25 for copper and cadmium, respectively. This shows their good kinetic properties. The kinetics data at different initial metal ions concentrations were fitted to Lagergren pseudo-first-order, Blanchard pseudo-second-order, Elovich, Natarajan–Khalaf and intraparticle diffusion models. The kinetics biosorption data for both metal ions were found to conform to pseudo-second-order kinetics with a good correlation, and for the diffusion mechanism studies, the obtained results reveal that intraparticle diffusion is not the only rate limiting step, but other processes may control the rate of biosorption for both metal ions on CL. Equilibrium data were fitted to Langmuir, Freundlich, Harkins–Jura and Flory–Huggins isotherm models, and the equilibrium data were best described by Langmuir isotherm model for both metal ions. The maximum monolayer biosorption capacity was 97.80 and 113.46 mg/g for copper and cadmium, respectively at 25°C. The negative values of $\Delta G°$ at different temperatures show that the biosorption process on CL (*Typha angustifolia*) is spontaneous for both metals. Enthalpy changes are negative which further confirm that the process is exothermic in nature for copper, in contrary for cadmium which is an endothermic process.

Complete desorption and regeneration of the biosorbent for three cycles and partial regeneration in the fourth cycle showed that the material is an effective biosorbent. Consequently, the results of this study will be useful for using this waste material *Typha angustifolia* leaves as an economic, effective and a nonhazardous bio-material for the removal of heavy metals in wastewater treatment.

Acknowledgment

The authors acknowledge the research grant provided by the Ministry of Higher Education and Scientific Research of Algeria.

Symbols

$A_{\text{H-J}}$ — Harkins–Jura model constant, mg^2/g^2
B — Langmuir model constant, L/mg
$B_{\text{H-J}}$ — Harkins–Jura model constant
C_0 — Liquid phase initial concentrations of metal ion, mg/L
C_d — Thickness of the boundary layer
C_e — Liquid phase concentrations of metal ion at equilibrium time, mg/L
C_t — Liquid phase concentrations of metal ion at any time, mg/L
d_m — Mean diameter, mm
k_1 — Rate constant of Lagergren pseudo-first-order model, min^{-1}
k_2 — Rate constant of pseudo-second-order model, g/mg min
k_d — Intraparticle diffusion rate constant, mg/g $\text{min}^{1/2}$
K_F — Freundlich biosorbent capacity, $\text{mg}^{1-1/n}$ $\text{L}^{1/n}/\text{g}$
K_{FH} — Equilibrium constant of Flory–Huggins model, L/mg
$K_{\text{N-K}}$ — Biosorption rate constant of Natarajan–Khalaf model, min^{-1}
n_F — Freundlich model constant
n_{FH} — Constant of Flory–Huggins model exponent
pH_{pzc} — Point of zero charge
q_e — Amount of biosorption at equilibrium, mg/g
q_m — Maximum monolayer biosorption capacity, mg/g
q_t — Amount of each metal ion biosorbed on CL at time t, mg/g
r — Correlation coefficient
R_g — Universal gas constant, J/mol K
R_L — Dimensionless constant separation factor of Hall
SSA — Specific surface area, m^2/g
t — Time, min
T — Absolute temperature, K
V — Volume of the solution, L
W — Mass of the used biosorbent, g
α — Initial biosorption rate of Elovich model, mg/g min
β — Desorption constant, g/mg
q — Degree of surface coverage of Flory–Huggins model
$\Delta G°$ — Free energy change, kJ/mol
$\Delta H°$ — Enthalpy change, kJ/mol
$\Delta S°$ — Entropy change, J/mol K

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