



Palm tree leaves usage for biosorption and recovery of heavy metals from wastewater

Manal Kaakani^a, Md. Maruf Mortula^{a,*}, Mohamed Yehia Abouleish^b

^aCivil Engineering Department, American University of Sharjah, P.O. Box 26666, Sharjah, United Arab Emirates, emails: mmortula@aus.edu (M. Mortula), manal.kaakani@gmail.com (M. Kaakani)

^bDepartment of Biology, Chemistry, and Environmental Sciences, American University of Sharjah, P.O. Box 26666, Sharjah, United Arab Emirates, email: mabouleish@aus.edu

Received 1 November 2016; Accepted 13 May 2017

ABSTRACT

Biosorption can be a sustainable water treatment option. However, selection of biosorbent can be challenging and local availability plays an important role. This research investigates the effectiveness of palm tree leaves for biosorption of Cr(VI), Cu(II) and Zn(II), from synthetic wastewater. Batch tests were conducted to assess the effectiveness of metal removal; to identify optimal operating conditions and assess the competition among the metals. Column tests were conducted to assess the applicability of the biosorption process in a dynamic environment. Desorption tests were conducted to assess the recovery of the metals. Batch experimental results indicated high (67.5%–99.5%) removal of individual metals and all the metals together for different initial concentrations (2–10 mg/L) and pH levels (3–9). Isotherm models were applied successfully. The results from column experiments indicated high ($\geq 90\%$) capability of metal removal for long period (200–2,800 pore volumes processed). Desorption results indicated a high ($\geq 50\%$) recovery of the metals.

Keywords: Biosorption; Recovery; Heavy metals; Wastewater; Palm tree leaves

1. Introduction

Industrial wastewater contains high (93.25 mg/L of Cr(VI), 36.16 mg/L of Cu(II), 50.94 mg/L of nickel(III), and 196.72 mg/L of Zn(II)) levels of heavy metals that may pollute waterbodies such as rivers, lakes and groundwater, if not properly treated before being discharged into the environment [1]. Examples of metals include Al(III), Cd(II), Cr(VI), Cu(II), Fe(III), Pb(II), Hg(II), Ag(I), and Zn(II). At least 20 heavy metals are considered to be toxic, and approximately half of those metals are released in quantities that are hazardous to the environment, and human health [2]. Water treatment for heavy metals includes precipitation (with coagulation and flocculation), ion-exchange, complexation of dry biomass, adsorption, magnetic fields, fluidized bed reactor, iron flotation, and flue gas purification [3–8].

The adsorption process is used for wastewater treatment, due to high efficiency and ease of operation for large-scale treatments. The adsorption process, typically involves using activated carbon that adsorbs dissolved organic substances, metals and color, during the water treatment [9,10]. The cost of activated carbon production and reactivation is high [11], as a result, more focus is placed on testing other adsorbents [12]. Other studied adsorbents, include synthetic polymers, chitosan, zeolite, biomass, and silica-based substances [13–16]. Locally available materials are often preferred, due to commercial viability of the technology. Other concerns involve the biodegradability of the adsorbents; as a result, biosorption with living and non-living organisms gained credibility in recent years [14,17,18].

There is a growing interest in finding biological materials that are cost-effective, easily available, and have few limitations. Therefore, finding suitable materials and appropriate operating conditions are essential to addressing the concerns of heavy metal pollution using biosorption. Prior

* Corresponding author.

research investigated the use of cashew nut shells [19], olive cake [20], date pits and fruits [2,21], tea factory waste [22], maize cobs [23], algae [24], tree leaves [25–28], tree bark [29], wood saw dust [30], and other biomass [31–34]. Waste products and other natural products are readily used as sorbents, hence, allowing for an inexpensive and feasible method for removing pollutants from wastewater [30]. Tree leaves are one of the most widely generated organic waste materials in municipalities where there are large amount of green spaces. The ability to use dried tree leaves for the treatment of wastewater can add advantage to the organic waste management. However, the properties of the tree leaves can vary widely among the different trees. Palm tree is one of the mostly widely grown trees in the Middle East, hence, the leaves are one of the widely generated biological waste materials in the region. Earlier research demonstrated that palm tree leaves (PTL) can be successful as an adsorbent for removal of Cu(II) and Zn(II) [35,36]. PTL is known to have hydroxyl, carboxylic, and phenolic functional groups and they are expected to be good metal adsorbents. However, the use of those leaves for removal of multiple heavy metals was not investigated. As a result, this research assess the effectiveness of using PTL for biosorption of Cu(II), Cr(VI), and Zn(II) from wastewater, identify the suitable operating conditions for the treatment, and assess the recovery of the removed metals. These metals were chosen since they are available in large quantities in the industrial wastewaters [1]. This novel research not only develops treatment option for different heavy metals, but also provides an environmentally sustainable reuse option for dried PTL.

2. Materials and methodology

2.1. Materials

2.1.1. Adsorbent

PTL were used as the adsorbent material. The leaves were picked from the end of palm tree branches located at the American University of Sharjah (AUS) campus, Sharjah, United Arab Emirates. In this research, only the leaves were used, as the biological components of it were expected to be uniform, and accordingly can provide reliable results. The leaves were thoroughly washed in tap water, washed in distilled water, and then dried in an oven at 90°C for about 12 h. After drying, the leaves were crushed and grounded (to a sieve size no larger than 0.03 mm in size), and stored in a desiccator in a temperature (24°C) controlled room.

The scanning electron microscope (SEM) analysis (TESCAN VEGA III-LMU) was used for the physical morphology of the surface of the adsorbent material. The elemental composition of the adsorbent material was performed by SEM/energy dispersive X-ray spectrometry (EDS) analysis, using the energy dispersive X-ray spectroscopy detector (Oxford instruments XACT).

2.1.2. Adsorbate

The wastewater that was used in this research was prepared in the laboratory, by spiking 1 L of deionized water with the following metal salts: $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ for Cu(II), $\text{K}_2\text{Cr}_2\text{O}_7$ for Cr(VI), and $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ for Zn(II) solution, to

prepare different solutions with the metal concentrations of 2, 6, and 10 mg/L. The pH of the wastewater solution was adjusted using 0.1 M NaOH or 0.1 M HCl, after the adsorbent has been added.

2.2. Experiments

2.2.1. Batch experiments

Two sets of batch experiments were conducted in this research. The first set of batch experiments were conducted on individual metals only. In this set, pH levels of 3, 5, 7, and 9 were maintained to assess the effectiveness of pH control. The experiments were conducted in 250 mL bottles with a 0–10 g/L PTL, in a 2.5 g/L increment with the blank sample containing no tree leaves in 2, 6, and 10 g/L of Cu(II), Cr(VI), and Zn(II) solutions individually. The samples were shaken at 175 rpm for 2 h (equilibrium reached), and then filtered through 0.45 μm , and the filtrate was used for water quality analysis. During the biosorption process, the pH levels of the samples were maintained.

The second set of batch experiments investigated competitive biosorption processes. In this set, Cu(II), Zn(II), and Cr(VI) were mixed together during the preparation of synthetic wastewater, where the initial metal concentration of 2 mg/L was used with similar PTL dosage to that of the first set. These experiments were conducted at pH 5, 7, and 9. The procedure of conducting the experiments was similar to the previous set of batch experiments.

2.2.2. Fixed bed column experiments

The column experiment represented the dynamic biosorption process to assess the applicability of the technology. A glass column (2.25 cm diameter and 20 cm depth) was washed with distilled and acidic water, and then dried. The glass column was filled with the PTL. The column experiments were performed on a mixture of Cu(II), Zn(II), and Cr(VI) in synthetic wastewater. Experiments were conducted three times for three different pH levels (5, 7, and 9). The pH values were chosen based on high degree of biosorption from batch experiments. Column experiments were performed with the initial concentrations of the metals at 2 mg/L. During the experiment, synthetic wastewater was pumped in a thin tube at the bottom of the column, and it traveled through the PTL up the column, and discharged through a thin tube at the top. The pH was monitored at both the influent and effluent. The flow of the pump was predetermined and set constant during the course of the experiment. At different time intervals, aliquots of the treated effluent were collected and tested for the concentration of each metal that was leached from the column. The concentrations were plotted against the time to determine the breakthrough and saturation times. The breakthrough time was considered as the time at which 10% of the metal concentration (fraction leaching of 0.1) in the effluent has leached. The saturation time was when the effluent concentrations reach the level of influent concentrations (fraction leaching of 1.0). The effluent concentrations (fraction leaching) were plotted against pore volume processed, for dimensionless representation of the results. The pore volume processed, represents the number pore volumes

of the column treated during biosorption of the metals, and is represented by Eq. (1):

$$\text{Number of pore volumes} = \frac{Qt}{V_c \mu} \quad (1)$$

where Q represents the inlet flow rate of the influent to the column (mL/min); t is the time for each measurement (min); V_c is the volume of the column (mL); and μ is the porosity of the adsorbents in the column (dimensionless).

2.2.3. Desorption experiments

The PTL were collected after the column tests reached saturation, and dried to remove any moisture. Batch desorption tests were conducted, that involved mixing 2 mg of PTL with 100 mL deionized water, at pH 2.94 (acidic) and 12.9 (basic). The samples were agitated at 175 rpm for 2 h, filtered through 0.45 μm membrane, and then tested for water quality parameters.

2.3. Analytical technique

The analysis of heavy metals was performed using the HACH DR 5000 Spectrophotometer, following specific standard methods. The concentration of Cu(II) was measured using the USEPA Bicinchoninate method that was approved by the USEPA and Standard Method 3500 Cu C or E [37]. The concentration of Cr(VI) was measured using the USEPA 1,5-diphenylcarbohydrazide method that was accepted by the USEPA and Standard Method 3500 Cr B [37]. The concentration of Zn(II) was measured using the USEPA Zincon method that was approved by the USEPA for wastewater analyses and adapted from Standard Methods 3500 Zn B [37]. The metal concentrations were correlated with the results obtained from atomic absorption spectrometer (AAS). Forty samples of batch experiments were used to develop the correlation between results from HACH DR 5000 Spectrophotometer against the AAS. The correlation coefficients were 0.9301 for Zn(II), 0.9775 for Cr(VI), and 0.9961 for Cu(II).

2.4. Adsorption isotherms

Results obtained from the batch tests were fitted with the Langmuir and Freundlich isotherm models [38,39]. Langmuir's isotherm uses the following equation:

$$Q = \frac{abC_e}{1 + bC_e} \quad (2)$$

where Q represents the adsorption density (mg/g); C_e the concentration of the adsorbate at equilibrium (mg/L), and the variables a (mg/g) and b (L/mg) are characteristics of the materials used.

The Freundlich's isotherm uses the following equation:

$$Q = K_d C_e^{1/n} \quad (3)$$

where K_d (mg/g (L/mg)^{1/n}) and n (dimensionless) are characteristics of the materials used.

2.5. Statistical analysis

Individual batch test results were used to assess the statistical significance of the experimental variables. Statistical analysis was conducted using two-way analysis of variance (ANOVA) on percentage metal removal at different initial metal and PTL concentrations and also at different pH and PTL concentrations separately. Different ANOVA analysis was done for all different initial metal concentrations. All the tests were conducted based on 5% level of significance.

3. Results and discussion

3.1. Surface structure and elemental composition

The SEM image (Fig. 1) displays cavities which increase the surface area, and as a result increase the adsorption ability of the adsorbent. EDS analysis did not show any signals for the metals tested in this research, therefore, no contribution from the adsorbent material to the final results. The EDS analysis indicates the presence of carbon and oxygen as the major elements present in the adsorbent material.

3.2. Individual batch experimental results

The relationship between the amount of heavy metal (Cu(II), Cr(VI), or Zn (II)) remaining in solution and the different PTL dosage, at different initial concentration for the different heavy metals, is displayed in Figs. 2–4. The results and constants of the Freundlich and Langmuir isotherm models are displayed in Tables 1–3, for Cu(II), Cr(VI), and Zn(II).

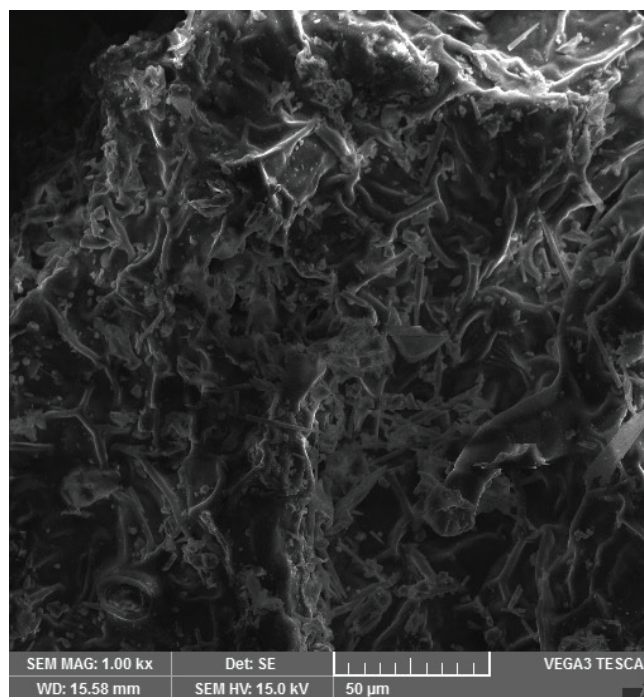


Fig. 1. Scanning electron microscope image of adsorbent.

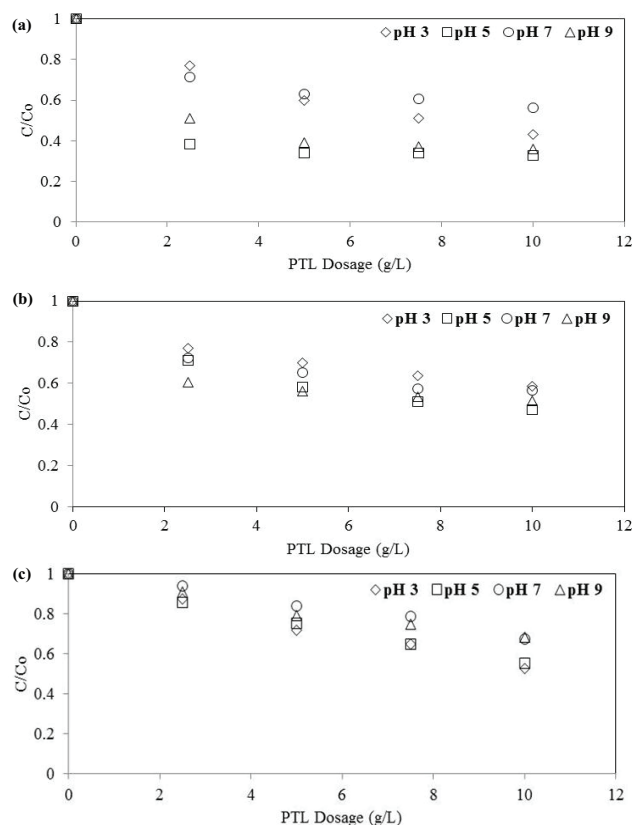


Fig. 2. The relationship between the amount of copper remaining in solution and different PTL dosage, at different initial copper concentrations: (a) 2 mg/L, (b) 6 mg/L, and (c) 10 mg/L.

3.2.1. Copper(II)

The percentage removal of Cu(II) increased as the PTL dosage increased for all the three initial concentrations. It indicated that the PTL was the reason for the decrease in Cu(II) concentrations. Based on the ANOVA test, the effect of PTL dosage on the percentage removal was statistically significant. Cu(II) removal from the solution decreased as the initial concentration increased, allowing for greater removal efficiency to occur at 2 mg/L, and the least efficiency at 10 mg/L of initial Cu(II) concentration. This was due to the fact that at high initial concentrations, the sorption sites are more competitive, leading to less percentage removal. ANOVA test results indicated that the effect of initial concentration on the percentage Cu(II) removal was statistically significant.

For all the three initial Cu(II) concentrations, the highest percentage efficiency was obtained at pH 5, and the lowest at pH 9, such results are consistent with other previous studies [26,40]. It could be due to the fact that at pH 3, hydrogen ions started competing with the Cu(II). The results also demonstrated that varying pH values have considerable effect on the removal efficiency for 2 mg/L, however, this was not observed with the other initial Cu(II) concentrations. It could be due to the fact that at low concentration, the presence of hydrogen ions could compete with the copper. However, at higher initial concentrations, the levels of hydrogen ions due to the change in pH could not affect the percentage removal

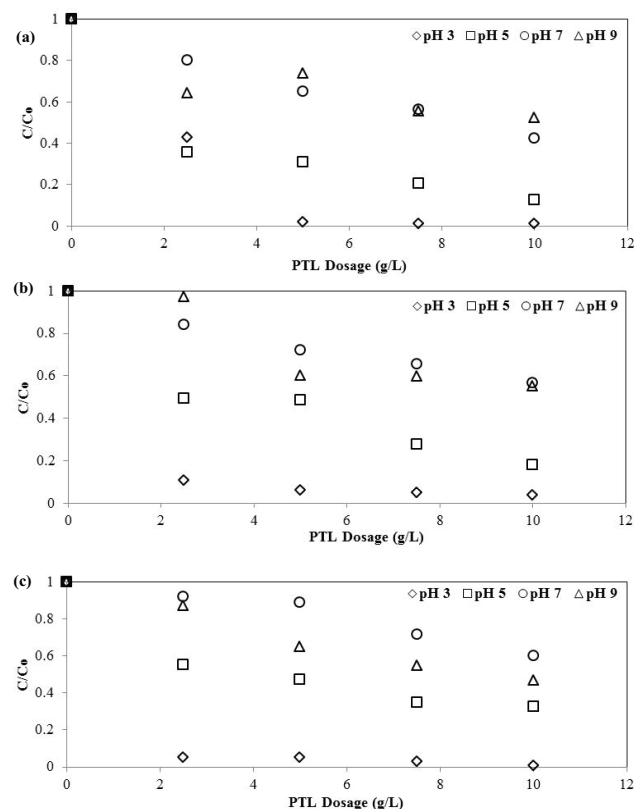


Fig. 3. The relationship between the amount of chromium remaining in solution and different PTL dosage, at different initial copper concentrations: (a) 2 mg/L, (b) 6 mg/L, and (c) 10 mg/L.

significantly. ANOVA test results revealed that the effect of pH on the percentage removal was statistically significant. In regard, to the isotherm models (Table 1), the Freundlich isotherms represented much higher regression coefficients than that illustrated by the Langmuir isotherms. The biosorption capacity ranged from 0.19 to 0.86 mg/g. This result is lower than that observed by a previous study [35], which could be due to the use of different tree leaves and high (100 ppm) initial copper concentrations used.

3.2.2. Chromium(VI)

The percentage removal of Cr(VI) increased with the increase in PTL dosage for all the initial concentrations. It could be due to the fact that Cr(II) was adsorbed onto the PTL. Based on the ANOVA test, the effect of PTL dosage on the percentage removal was statistically significant, except for the tests conducted at a pH 3. Since at pH 3, the competition for adsorption sites increased with the availability of high amount of hydrogen ions, the effect of PTL dosage was not significant. The high Cr(VI) removal was maintained for all initial concentrations. For all the initial concentrations of Cr(VI), the highest percentage efficiency was obtained at pH 3 and the lowest at pH 9, which was attributed to the presence and affinity of carboxylic and phenolic groups in PTL toward Cr(VI), and as a result affected the biosorption of Cr(VI) [3]. These functional groups are active at low pH

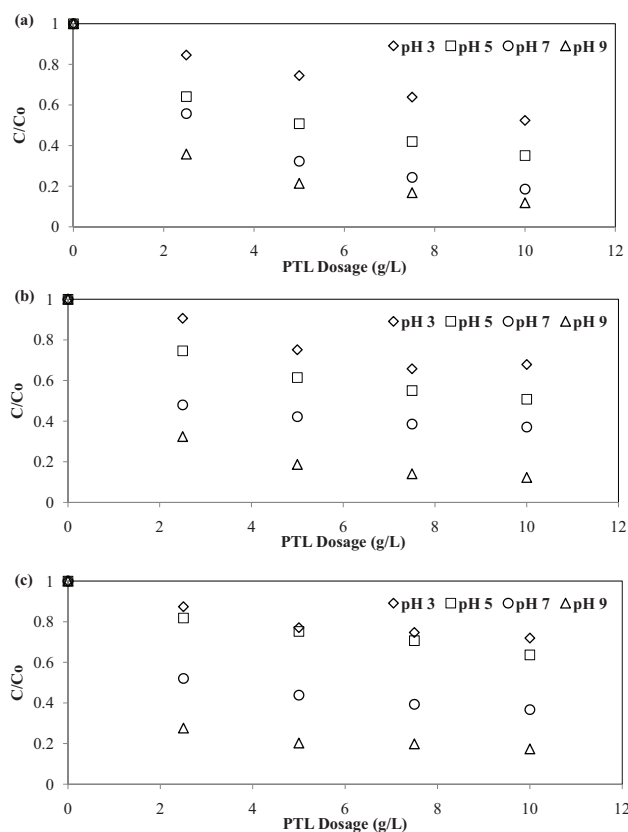


Fig. 4. The relationship between amount of zinc remaining in solution and different PTL dosage, at different initial copper concentrations: (a) 2 mg/L, (b) 6 mg/L, and (c) 10 mg/L.

levels as opposed to the high pH. ANOVA test results indicated that the effect of initial concentration on the percentage Cr(VI) removal was statistically significant for pH 5, 7, and 9. However, the effect was not significant for pH 3.

In regard, to the isotherm models (Table 2), both models did not predict the experimental results consistently. The results at acidic pH were better correlated than at other pH levels. ANOVA test results revealed that the effect of pH on the percentage removal is statistically significant. At the initial concentrations of 6 and 10 mg/L, the Freundlich isotherm was better correlated than the Langmuir isotherm. Biosorption capacity ranged from 0.07 to 4.152 mg/g, which was higher than the ones observed during the Cu(II) sorption.

3.2.3. Zinc(II)

Similar to Cu(II) and Cr(VI), the percentage removal of Zn(II) increased with the increase in the PTL dosage, for all the three initial concentrations. It indicated that Zn(II) was adsorbed on the PTL. Based on the ANOVA test, the effect of PTL dosage on the percentage removal was statistically significant. Consistent with the other metals, high percentage removals were observed at low initial concentrations. It indicated similar adsorption behavior to both Cu(II) and Cr(II). For all the three initial concentrations of Zn(II), the highest removal efficiency was 86% at pH 9, and the lowest was 28%

Table 1
Isotherm parameters and constants for copper

| Isotherm | C_0 (mg/L) | pH | Constants | | Regression coefficient |
|------------|-----------------|----|-----------|----------|---------------------------|
| | | | a | b | |
| Langmuir | 2 | 3 | 0.9766 | 6.4235 | 0.5466 |
| | | 5 | -0.5072 | -10.4057 | 0.7884 |
| | | 7 | -0.0620 | -2.4177 | 0.9307 |
| | | 9 | -0.1433 | -1.6122 | 0.6754 |
| Freundlich | 2 | | K_f | n | |
| | | 3 | 0.8508 | 0.4141 | 0.9677 |
| | | 5 | 7.4672 | 0.9070 | 0.9041 |
| | | 7 | 4.273 | 0.1632 | 0.9672 |
| Langmuir | 6 | 3 | -0.1722 | -5.6177 | 0.9534 |
| | | 5 | -0.4992 | -6.7762 | 0.9169 |
| | | 7 | -0.1493 | -4.5409 | 0.8462 |
| | | 9 | -0.0874 | -3.6269 | 0.9538 |
| Freundlich | 6 | | K_f | n | |
| | | 3 | 2.8697 | 0.1229 | 0.9547 |
| | | 5 | 1.8739 | 0.2760 | 0.9928 |
| | | 7 | 3.2859 | 0.1237 | 0.9392 |
| Langmuir | 10 | 3 | 0.1473 | 0.7169 | 0.838 |
| | | 5 | 0.3126 | 0.5224 | 0.7729 |
| | | 7 | 0.0395 | 1.7158 | 0.8750 |
| | | 9 | 0.2307 | 6.3299 | 0.2415 |
| Freundlich | 10 | | K_f | n | |
| | | 3 | 0.2107 | 0.4543 | 0.2502 |
| | | 5 | 0.5801 | 0.3355 | 0.8981 |
| | | 7 | -0.7166 | 0.8134 | 0.5895 |
| | | 9 | 0.6528 | 0.2626 | 0.4527 |

at pH 3. It could be due to the effect of hydroxyl group present in the PTL in addition to some probable precipitation at high pH levels. ANOVA test results indicated that the effect of initial concentration on the percentage Zn(II) removal was statistically insignificant, except for the case of pH 5. The acidic pH provided the lowest uptake of the metals, due to the cation competition effects with H_3O^+ ion [41]. The results showed that varying the pH has considerable effect on the removal efficiency, for all the initial concentrations of Zn(II). High pH levels observed to provide favorable biosorption capacity. ANOVA test results revealed that the effect of pH on the percentage removal is statistically significant. The results demonstrate that the Freundlich model represented a slightly higher advantage than the Langmuir model, due to the higher correlation coefficients (Table 3). Biosorption capacity ranged from 0.14 to 2.77 mg/g. This result was similar to the Cr(VI) sorption capacity and Zn(II) sorption observed in a previous study [36].

Table 2
Isotherm parameters and constants for chromium

| Isotherm | C_o (mg/L) | pH | Constants | | Regression coefficient |
|------------|-----------------|----|-----------|----------|---------------------------|
| Langmuir | 2 | | a | b | |
| | | 3 | 0.4513 | 0.0181 | 0.9995 |
| | | 5 | 4.0371 | 6.5822 | 0.0158 |
| | | 7 | 0.0777 | -0.3467 | 0.5392 |
| | | 9 | -0.3634 | -3.6040 | 0.2377 |
| Freundlich | 2 | | K_f | n | |
| | | 3 | 0.1672 | 0.7256 | 0.5842 |
| | | 5 | 0.9033 | 0.7646 | 0.7820 |
| | | 7 | 0.0023 | 0.3905 | 0.0000 |
| | | 9 | 1.6173 | 0.4238 | 0.7100 |
| Langmuir | 6 | | a | b | |
| | | 3 | -4.3011 | -1.8972 | 0.7441 |
| | | 5 | 1.9331 | 3.1458 | 0.2976 |
| | | 7 | -0.5286 | -75.2630 | 0.0613 |
| | | 9 | 0.0216 | -3.8850 | 0.8466 |
| Freundlich | 6 | | K_f | n | |
| | | 3 | 1.3054 | 1.8103 | 0.9901 |
| | | 5 | 0.6025 | 0.7376 | 0.5257 |
| | | 7 | 1.0616 | 0.3313 | 0.9398 |
| | | 9 | -3.4589 | 0.0500 | 0.6281 |
| Langmuir | 10 | | a | b | |
| | | 3 | 4.1186 | 0.3245 | 0.4019 |
| | | 5 | -2.2467 | -14.1773 | 0.5505 |
| | | 7 | 0.0081 | -4.2816 | 0.7571 |
| | | 9 | 0.5224 | 2.1047 | 0.5230 |
| Freundlich | 10 | | K_f | n | |
| | | 3 | 0.4317 | 1.6842 | 0.6163 |
| | | 5 | 1.5672 | 0.3694 | 0.8958 |
| | | 7 | -1.0733 | 0.4621 | 0.6078 |
| | | 9 | 0.2134 | 0.1532 | 0.1022 |

3.3. Competitive biosorption

The relationship between the amount of heavy metal remaining in solution and different PTL dosage, in competing batch tests, is displayed in Fig. 5. The behavior of the metals did not significantly change due to competition. The removal of the metals was higher than that observed with individual metals (section 3.1).

The removal efficiency of Cu(II) was higher, when competing with Cr(VI) and Zn(II), than that observed in individual experiments. The Cu(II) did not compete with the other metals, for the active sites. The presence of other ions excited the active sites for the Cu(II), and enhanced the biosorption capacity. The highest removal efficiency was observed at neutral pH.

Cr(VI) was the most competitive of all metals, as the removal efficiency was 98.4% at acidic pH. The rate of Cr(VI) removal was higher than that observed during individual

Table 3
Isotherm parameters and constants for zinc

| Isotherm | C_o (mg/L) | pH | Constants | | Regression coefficient |
|------------|-----------------|----|-----------|----------|---------------------------|
| Langmuir | 2 | | a | b | |
| | | 3 | 0.2538 | 1.7733 | 0.6658 |
| | | 5 | -0.7681 | -5.1868 | 0.9020 |
| | | 7 | 0.9615 | 1.7192 | 0.9270 |
| | | 9 | -1.4035 | -2.8647 | 0.4613 |
| Freundlich | 2 | | K_f | n | |
| | | 3 | 0.4987 | 0.3597 | 0.7343 |
| | | 5 | 1.3228 | 0.4789 | 0.9883 |
| | | 7 | 0.7122 | 0.6360 | 0.9727 |
| | | 9 | 1.1976 | 0.8527 | 0.9527 |
| Langmuir | 6 | | a | b | |
| | | 3 | 0.1178 | -0.5353 | 0.4479 |
| | | 5 | -0.5577 | -8.8099 | 0.8629 |
| | | 7 | -0.1800 | -3.0250 | 0.9450 |
| | | 9 | -1.1211 | -2.9705 | 0.9321 |
| Freundlich | 6 | | K_f | n | |
| | | 3 | -0.0993 | 0.4477 | 0.0053 |
| | | 5 | -1.0293 | 3.6208 | 0.9265 |
| | | 7 | 4.4972 | 0.1594 | 0.9946 |
| | | 9 | 1.6567 | 0.7919 | 0.9798 |
| Langmuir | 10 | | a | b | |
| | | 3 | -0.0541 | -12.3013 | 0.5578 |
| | | 5 | -0.2702 | -11.2375 | 0.7845 |
| | | 7 | -0.5542 | -6.9833 | 0.9643 |
| | | 9 | 0.8685 | 3.4092 | 0.7742 |
| Freundlich | 10 | | K_f | n | |
| | | 3 | 2.8306 | 0.0289 | 0.7647 |
| | | 5 | 2.7628 | 0.0689 | 0.8780 |
| | | 7 | 3.1457 | 0.1313 | 0.9994 |
| | | 9 | 2.7692 | 0.4896 | 0.9310 |

experiments. Some of the removals could be attributed to the precipitation process, independent of the competition with other metal ions. The pattern observed was similar to that observed for Cu(II).

Regarding removal of Zn(II), the highest efficiency was 83.7% at basic pH among all the competitive tests. The values were similar to the removal efficiencies observed during individual experiments. This indicated that the pattern of Zn(II) removal was not impacted by the competition, and that it was due to the different types of active sites for the biosorption, among the different metals.

3.4. Fixed bed column tests

Investigating the relation between the fraction of metal leaching in the effluent against the number of pore volumes of water processed revealed high effluent concentrations initially, and this could be attributed to the water seeping through the pores out of the column without any significant sorption (Fig. 6).

At pH 5, Cr(VI) did not reach exhaustion until processing 2,500 pore volumes (about 287 h; Fig. 6). The high rate of Cr(VI) removal was consistent with that of the batch test results. Cu(II) reached exhaustion after processing approximately 1,800 pore volumes (about 260 h). Zn(II) reached exhaustion after processing 200 pore volumes (about 52 h). The acidic influent showed no signs of precipitation of the metals, unlike what was previously observed at neutral pH.

The effect of pH on the treatment of metals was consistent to what was observed during the batch experiments. At pH 7, Cr(VI) reached exhaustion very quickly (within 500 pore volume processed; Fig. 6). However, 2,400 pore volumes (267 h of experiment) of water were processed before Zn(II) reached exhaustion. Cu(II) did not reach exhaustion until 2,800 pore volumes were processed. The pattern of removal for the different metals was consistent with the batch experimental results.

At pH 9, Cr(VI) reached exhaustion within 1,100 pore volume processed (Fig. 6). This was consistent with the results from the batch experiments. However, Zn(II) and Cu(II)

precipitated throughout this experiment, and as a result, the experiments were stopped after 4 d. At this pH, biosorption and precipitation occurred simultaneously. Therefore, removal of the metals was not solely caused by biosorption by the PTL, but also due to them precipitating in the influent tank.

3.5. Desorption tests

Desorption experimental results demonstrated that Cu(II) biosorption on the PTL was not strong, and that it was not difficult to be removed and recovered from the sorbed phase from the PTL (Fig. 7). It was consistent with another previous study on different tree leaves [26]. Zn(II)

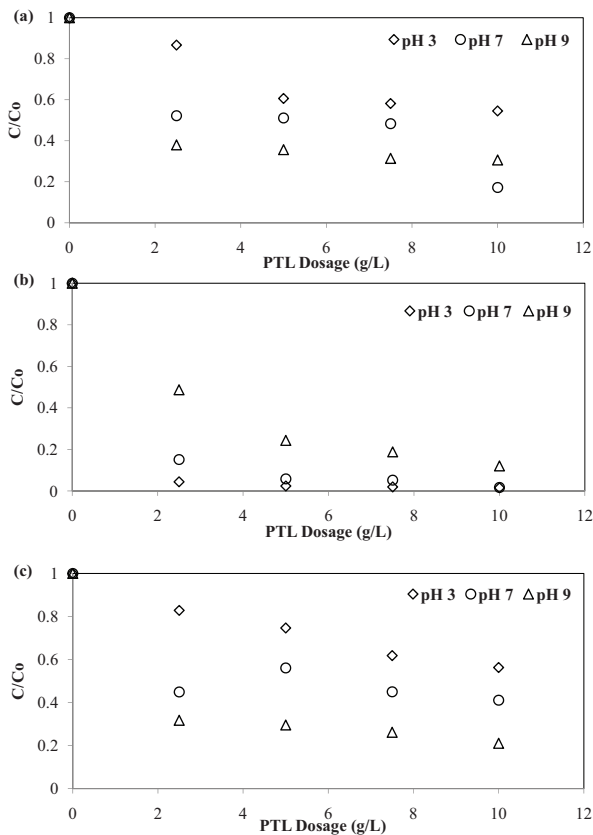


Fig. 5. The relationship between the amount of heavy metal remaining in solution and different PTL dosage, in competing batch tests, for (a) copper, (b) chromium, and (c) zinc.

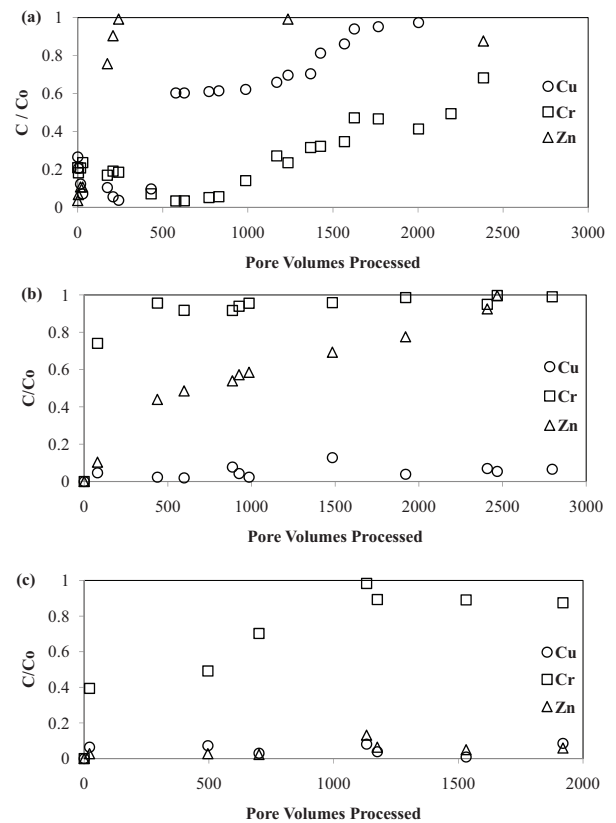


Fig. 6. The relationship between the amount of heavy metal leaching, and different pore volumes processed in column tests, at different pH (a) pH = 5, (b) pH = 7, and (c) pH = 9.

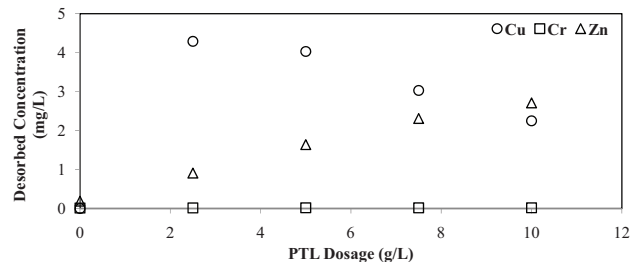


Fig. 7. The relationship between the amount of heavy metal desorbed and different PTL dosage.

was also recovered at a reasonable rate. Cr(VI), unlike other heavy metals, did not display a good recovery capacity; however, it could still be significant when treated in large volumes. The results also indicated that the acidic pH was more successful at recovering the heavy metals, compared with basic pH. Since, both Cu(II) and Zn(II) can be recovered at high levels, sorption sites are expected to be freed and reused again.

4. Conclusions

The study revealed that PTL can be a good biosorbent in removing metals at different operating conditions. Batch test results revealed a maximum removal of 67.5%, 99.5%, and 86% for Cu(II), Cr(VI), and Zn(II), respectively. During competitive batch tests, a maximum removal of 98.5% for Cr(VI), 83.7% for Zn(II), and 82.7% for Cu(II) was obtained with insignificant competition. In most cases the isotherm models were capable of predicting the data. Column tests revealed that PTL was capable of removing all the three metals consistently. All the metals were able to be recovered.

Acknowledgments

The authors would like to thank the American University of Sharjah for providing the facilities, and materials for this research. The authors also want to acknowledge the contribution of Gulf Environmental Research Center (GERC) and Bee'ah for providing the funding support through the project, GER-14-10.

References

- [1] C. Lee, M. Song, J.C. Ryu, C. Park, J. Choi, S. Lee, Application of carbon foam for heavy metal removal from industrial plating wastewater and toxicity evaluation of the adsorbent, *Chemosphere*, 153 (2016) 1–9.
- [2] A. El Nemr, A. Khaled, O. Abdelwahab, A. El-Sikaily, Treatment of wastewater containing toxic chromium using new activated carbon developed from date palm seed, *J. Hazard. Mater.*, 152 (2008) 263–275.
- [3] D.H.K. Reddy, K. Vijayaraghavan, J.A. Kim, Y. Yun, Valorisation of post-sorption materials: opportunities, strategies, and challenges, *Adv. Colloid Interface Sci.*, 242 (2017) 35–58.
- [4] Y. Chen, X. Hong, H. He, H. Luo, T. Qian, R. Li, H. Jiang, H. Yu, Biosorption of Cr(VI) by *Typha angustifolia*: mechanism and responses to heavy metal stress, *Bioresour. Technol.*, 160 (2014) 89–92.
- [5] G. Markou, D. Mitrogiannis, A. Celekli, H. Bozkurt, D. Georgakakis, C.V. Chrysikopoulos, Biosorption of Cu²⁺ and Ni²⁺ by *Arthrospira platensis* with different biochemical compositions, *Chem. Eng. J.*, 259 (2015) 806–813.
- [6] Metcalf & Eddy, Inc., *Wastewater Engineering, Treatment and Reuse*, McGraw-Hill, 2004.
- [7] S. Senel, L. Uzun, A. Kara, A. Denizli, Heavy metal removal from synthetic solutions with magnetic beads under magnetic field, *J. Macromol. Sci., Pure Appl. Chem.*, 45 (2008) 635–642.
- [8] A. Dabrowski, Z. Hubicki, P. Podkoscielny, E. Robens, Selective removal of the heavy metal ions from waters and industrial wastewaters by ion-exchange method, *Chemosphere*, 56 (2004) 91–106.
- [9] K. Muthukumar, N. Balasubramanian, T.V. Ramakrishna, Removal and recovery of chromium from plating waste using chemically activated carbon, *Met. Finish.*, 93 (1995) 46–53.
- [10] K. Ranganathan, Chromium removal by activated carbons prepared from *Casuarina equisetifolia* leaves, *Bioresour. Technol.*, 73 (2000) 99–103.
- [11] L. Dong, W. Liu, R. Jiang, Z. Wang, Study on reactivation cycle of biological activated carbon (BAC) in water treatment, *Int. Biodeterior. Biodegrad.*, 102 (2015) 209–213.
- [12] K. Srinivasan, N. Balasubramanian, T.V. Ramakrishna, Studies on chromium removal by rice husk carbon, *Indian J. Environ. Health*, 30 (1988) 376–387.
- [13] S. Babel, T.A. Kurniawan, Low-cost adsorbents for heavy metals uptake from contaminated water: a review, *J. Hazard. Mater.*, 97 (2003) 219–243.
- [14] J. Febrianto, A.N. Kosasih, J. Sunarso, Y. Ju, N. Indraswati, S. Ismadji, Equilibrium and kinetic studies in adsorption of heavy metals using biosorbent: a summary of recent studies, *J. Hazard. Mater.*, 162 (2009) 616–645.
- [15] H. Park, L.L. Tavlarides, Adsorption of neodymium (III) from aqueous solutions using a phosphorus functionalized adsorbent, *Ind. Eng. Chem. Res.*, 49 (2010) 12567–12575.
- [16] K. Yang, D. Kim, C. Lee, J. Choi, Adsorption of zinc and toluene by alginate complex impregnated with zeolite and activated carbon, *Curr. Appl. Phys.*, 9 (2009) 694–697.
- [17] Z. Filipovic-Kovacevic, L. Sipos, F. Briski, Biosorption of chromium, copper, nickel and zinc ions onto fungal pellets of *Aspergillus niger* 405 from aqueous solutions, *Food Technol. Biotechnol.*, 38 (2000) 211–216.
- [18] X. Ma, W. Cui, L. Yang, Y. Yang, H. Chen, K. Wang, Efficient biosorption of lead(II) and cadmium(II) ions from aqueous solutions by functionalized cell with intracellular CaCO₃ mineral scaffolds, *Bioresour. Technol.*, 185 (2015) 70–78.
- [19] S.P. Kumar, R. Subramaniam, S.D. Kirupha, A. Murugesan, T. Vidhyadevic, S. Sivanesan, Adsorption behavior of nickel(II) onto cashew nut shell: equilibrium, thermodynamics, kinetics, mechanism and process design, *Chem. Eng. J.*, 167 (2011) 122–131.
- [20] M. Abu Dayeh, M. Zaid, A. Al-Anber, Batch adsorption of cadmium ions from aqueous solution by means of olive cake, *J. Hazard. Mater.*, 151 (2008) 194–201.
- [21] A.A.M. Daifullah, M.M.S. Ali, N.S. Awwad, Removal of Pb²⁺, Cd²⁺, Fe³⁺, and Sr²⁺ from aqueous solution by selected activated carbons derived from date pits, *Solvent Extr. Ion Exch.*, 26 (2008) 764–782.
- [22] K.L. Wasewar, M. Atif, B. Prasad, I.M. Mishra, Batch adsorption of zinc on tea factory waste, *Desalination*, 244 (2009) 66–71.
- [23] M. Nassar, Adsorption of Fe⁺³ and Mn⁺² from ground water onto maize cobs using batch adsorber and fixed bed column, *Sep. Sci. Technol.*, 41 (2006) 943–959.
- [24] J. He, J.P. Chen, A comprehensive review on biosorption of heavy metals by algal biomass: materials, performance, chemistry, and modeling simulation tools, *Bioresour. Technol.*, 160 (2014) 67–78.
- [25] M. Gouamid, M.R. Ouahrani, M.B. Besaci, Adsorption equilibrium, kinetics and thermodynamics of methylene blue from aqueous solutions using date palm leaves, *Energy Procedia*, 36 (2013) 898–907.
- [26] M.R. Sangi, A. Shahmoradi, J. Zolgharnein, G.H. Azimi, M. Ghorbandoost, Removal and recovery of heavy metals from aqueous solution using *Ulmus carpinifolia* and *Fraxinus excelsior* tree leaves, *J. Hazard. Mater.*, 155 (2008) 513–522.
- [27] D.H.K. Reddy, Y. Harinath, K. Seshiah, A.V.R. Reddy, Biosorption of Pb(II) from aqueous solutions using chemically modified *Moringa oleifera* tree leaves, *Chem. Eng. J.*, 162 (2010) 626–634.
- [28] U. Shafique, A. Ijaz, M. Salman, W. Zaman, N. Jamil, R. Rehman, A. Javid, Removal of arsenic from water using pine leaves, *J. Taiwan Inst. Chem. Eng.*, 43 (2012) 256–263.
- [29] D.H.K. Reddy, K. Seshiah, A.V.R. Reddy, M.M. Rao, M.C. Wang, Biosorption of Pb²⁺ from aqueous solutions by *Moringa oleifera* bark: equilibrium and kinetic studies, *J. Hazard. Mater.*, 174 (2010) 831–838.
- [30] B. Radetic, Z. Kevresan, M. Klasnja, M., Sciban, Adsorption of heavy metals from electroplating wastewater by wood sawdust, *Bioresour. Technol.*, 98 (2007) 402–409.
- [31] R. Rehman, U. Shafique, J. Anwar, S. Ghafoor, Kinetic and isothermal biosorption studies of Co(II), Cu(II) and Ni(II), *Asian J. Chem.*, 25 (2013) 8285–8288.

- [32] J. Anwar, U. Shafique, W. Zaman, A. Nisa, M.A. Munawar, N. Jamil, M. Salman, A. Dar, R. Rehman, J. Saif, H. Gul, T. Iqbal, Removal of chromium of *Polyalthia longifolia* leaves biomass, *Int. J. Phytorem.*, 13 (2011) 410–420.
- [33] R. Rehman, J. Anwar, T. Mahmud, Adsorptive elimination of chromium(III) and nickel(II) from water by spent *Eugenia jambolana* leaves: isothermal and thermodynamical studies, *Asian J. Chem.*, 26 (2014) 644–648.
- [34] R. Rehman, J. Anwar, T. Mahmud, M. Salman, M. Saleem, Evaluation of batch biosorption of chromium (VI) from aqueous solution by chemically modified *Polyalthia longifolia* leaves, *J. Chem. Soc. Pak.*, 33 (2011) 846–852.
- [35] N. Hamdi, F.A.A. Al-Rub, M. Kandah, H. Allaboun, J. Hamdi, Decontamination of Cu^{2+} - tained water through biosorption onto palm tree leaf particles, *Jordan J. Civil Eng.*, 4 (2010) 222–230.
- [36] F. Al-Rub, Biosorption of zinc on palm tree leaves: equilibrium, kinetics, and thermodynamics studies, *Sep. Sci. Technol.*, 41 (2006) 3499–3515.
- [37] A.D. Eaton, *Standard Methods for the Examination of Water and Wastewater*, 21st ed., APHA, AWWA, WEF Publication, USA, 2005.
- [38] I. Langmuir, The adsorption of gases on plane surface of glass, mica and platinum, *J. Am. Chem. Soc.*, 40 (1918) 1361–1402.
- [39] H. Freundlich, *Kapillarchemie, eine darstellung der chemie der kolloide und verwanter gebiete*, *Academische Bibliothek*, (1909).
- [40] S.P. Kumar, R. Subramaniam, V. Sathyaselvabala, S.D. Kirupha, S. Sivanesan, Removal of copper(II) ions from aqueous solution by adsorption using cashew nut shell, *Desalination*, 266 (2011) 63–71.
- [41] R. Yavuz, I. Orbak, N. Karatepe, Factors affecting the adsorption of chromium (VI) on activated carbon, *J. Environ. Sci. Health, Part A*, 41 (2006) 1967–1980.