Treatment of electronics industry effluent using low-cost and commercial adsorbents: A comparative study

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Abstract. In the present study, the potential of two low-cost adsorbents namely kenaf (Hibiscus cannabinus L.) bast fiber and golden apple snail (Pomacea canaliculata) shell to treat heavy metals concentration in electronics industry effluent has been investigated. The physicochemical properties and adsorption mechanisms were determined using several analytical instruments such as Fourier Transform Infrared (FTIR) Spectrometer, Scanning Electron Microscope (SEM) and Energy Dispersive X-ray (EDX) Spectrometer. With an initial metal ion concentration of 50 mg/L, the adsorption of Cd(II), Cr(VI), Cu(II), Ni(II), Pb(II) and Zn(II) was optimized at acidic media (solution pH of 4.0-6.0), 60 minutes of contact time and 0.5 g of adsorbent dosage. The equilibrium data of metal ions adsorption onto kenaf bast fiber and golden apple snail shell followed the Langmuir isotherm model. Based on Langmuir isotherm model, the adsorption capacity of adsorbents for metal ions was in the order of Pb(II) > Cu(II) > Zn(II) > Ni(II) > Cd(II) > Cr(VI). Golden apple snail shell was able to remove Cr(VI), Ni(II) and Zn(II) ions from the electronics industry effluent at a higher capacity as compared to kenaf bast fiber and commercial mangrove stem derived activated carbon. The presence of carbonate functional group in green apple snail shell favored the adsorption of metal ions. Overall, results from this study suggest that kenaf bast fiber and golden apple snail shell have great potential to be used as alternative adsorbents to treat industrial effluents.

1. Introduction

Industrial activities such as mining, smelting, electroplating, electronics, and battery manufacturing have caused significant water pollution, worldwide. It is known that effluents from aforementioned industries are normally contained high level of heavy metals such as Cd, Cr, Cu, Ni, Pb and Zn [1]. The amount of heavy metals discharged into water environment is continue to increase, year by year [2]. In fact, in many cases, the concentration of toxic metals exceeds the permissible limits set by World Health Organization (WHO) [2,3]. A high concentration of heavy metals in aquatic environment is of great concern. Heavy metals can easily enter the food web and therefore may create serious problems and as well as adverse effects to human [4]. For instance, excessive intake of Pb may cause toxic effects to human kidney and nervous system. According to WHO, the safe blood level of Pb is 0.1 g/m³ [5]. In addition, anemia begins to occur when Pb level in blood greater than 0.3 g/m³ (children) and 0.6 g/m³ (adults) [5], respectively. At blood Pb concentration as low as 5 µg/dL, the human intelligent quotient (IQ) will be affected [6]. In this context, children are at high risk.
The remediation of water polluted by heavy metals remains a great challenge to environmental scientists. Although modern treatment techniques such as ion exchange, flocculation, electrodialysis, and electrodeposition are reported to be effective to treat contaminated water, their operational costs are expensive [7]. Adsorption has been regarded as an economical method for lowering heavy metals concentration in contaminated water [8]. Activated carbon is the most widely used adsorbent for this purpose. In spite of its high porosity and capacity to remove pollutants, activated carbon is known costly [7,9]. Great efforts have been directed towards the development of cost-effective adsorbent for adsorption technique particularly for application in developing countries such as Malaysia, Indonesia, and Thailand. The ultimate aim of this study was to evaluate the feasibility of kenaf bast fiber and golden apple snail shell as low-cost adsorbents for water treatment.

2. Materials and methods

2.1. Preparation of adsorbents
The kenaf bast fiber was kindly supplied by Malaysian National Kenaf and Tobacco Board, Kubang Kerian, Kelantan. The golden apple snail shell was obtained from a paddy farmer in Pendang, Kedah. Both materials were soaked in tap water overnight and rinsed several times with deionized water. The materials were then dried in an oven at 70 °C for 24 hours and ground to a fine powder (150-250 μm) using a laboratory mill. To avoid moisture effect, the adsorbents were kept in self-sealing bags until ready for characterization and adsorption experiments.

2.2. Characterization studies
In this study, Fourier Transform Infrared (FTIR) spectra, Scanning Electron Microscope (SEM) images, and Energy Dispersive X-ray (EDX) spectra were obtained before and after the interaction of adsorbents with heavy metals. A Thermo Nicolet 6700 ATR-FTIR Spectrometer and a Hitachi SU 8020 UHR SEM were used in characterization studies. For FTIR analysis, the scanning range was from 4000 to 400 cm⁻¹ with 35 cumulative scans. Meanwhile, for SEM and EDX analyses the samples were coated with a thin layer of platinum. This procedure is important in order to avoid electron charging which might reduce the quality of SEM image and EDX spectra. The adsorbents were observed at several magnifications.

2.3. Adsorption studies
The 250 mL stock solutions of 1000 mg/L were prepared by dissolving the exact amount of metal salts (Cd(NO₃)₂,4H₂O, K₂Cr₂O₇, Cu(NO₃)₂.3H₂O, Ni(NO₃)₂.6H₂O, Pb(NO₃)₂ and Zn(NO₃)₂.6H₂O) in deionized water, separately. The stock solutions were then diluted to the required concentrations. Metal salts used in this study were of analytical grade and used as received.

Prior to application on real electronics effluent, the ability of both kenaf bast fiber and golden apple snail shell to remove heavy metals was tested in batch adsorption studies. The effects of several experimental parameters such as solution pH, contact time and adsorbent dosage on adsorption of heavy metals by both adsorbents were studied in details. The effect of solution pH was conducted in the pH range of 1.0 to 6.0. The initial solution pH of 50 mL of 50 mg/L metal ion solution was adjusted using 0.1 mol/L HCl and 0.1 mol/L NaOH solutions. The pH was measured using a Thermo Scientific Orion 2-Star pH meter. The effect of contact time was performed at 15, 30, 45, 60, 75 and 90 minutes, while the effect of dosage was carried out using 0.125, 0.250, 0.500 and 0.750 g of adsorbent.

Adsorption experiments were conducted by shaking an amount of adsorbent with 50 mL of metal ion solution in 250 mL conical flasks by using a Protech Orbital shaker (model 720) set at 100 rpm. Following equilibration, the samples were then separated through filter paper (Advantec 231, 0.18 mm). The concentration of heavy metals in the supernatant was measured using a PerkinElmer AAAnalyst 400 Atomic Absorption Spectrometer (AAS). Calibration curve was plotted ($R^2 = 0.9989$)
prior to AAS measurement. All experiments were carried out in triplicates. The equilibrium adsorption capacity and the removal percentage were calculated using Equations (1) and (2), respectively [4,5]:

\[ q_e = \frac{C_i - C_f}{M} \times V \]  

(1)

\[ \text{Removal} \% = \frac{C_i - C_f}{C_i} \times 100 \]  

(2)

where \( q_e \) is the amount of metal ion adsorbed by adsorbent at equilibrium (mg/g), \( C_i \) and \( C_f \) are the initial and final concentrations of metal ions (mg/L), \( M \) is the mass of adsorbent (g) and \( V \) is the volume of metal ion solution (L).

2.4. Effectiveness and comparative studies

The effectiveness of kenaf bast fiber and golden apple snail shell to treat metal laden contaminated water was examined using an electronics industrial effluent. The effluent sample was obtained from an electronics factory in Shah Alam, Selangor. The industrial effluent was brought to the research lab, filtered through a filter paper for dirt and suspended solid removal. The concentrations of heavy metals in the effluent sample were then measured using AAS.

In this study, the applicability of kenaf bast fiber and golden apple snail shell to adsorb heavy metals from industrial effluent was compared with commercial mangrove stem derived activated carbon. The industrial effluent was treated using three adsorbents at optimum experimental conditions determined earlier in Section 2.3.

3. Results and discussion

3.1. Characterization studies

The Brunauer–Emmett–Teller (BET) surface area of kenaf bast fiber and golden apple snail shell were determined as 4.73 and 2.64 m²/g, while the average pore diameter of kenaf bast fiber and golden apple snail shell were measured as 1.53 and 2.38 Å, respectively. Based on porosity classification set by International Union of Pure and Applied Chemistry (IUPAC), both adsorbents are micropores.

![FTIR spectra](image)

FTIR spectra of kenaf bast fiber before (a¹) and after Ni(II) adsorption (a³), and FTIR spectra of golden apple snail shell before (b¹) and after Ni(II) adsorption (b³).

The presence of functional groups in both adsorbents was confirmed by FTIR analysis. Figure 1 presents the FTIR spectra of kenaf bast fiber and golden apple snail shell, before and after Ni(II) adsorption, as an example. Figure 1(a¹) shows the main characteristics of kenaf bast fiber at 3344, 1725 and 1645 cm⁻¹ which correspond to hydroxyl (OH) group, C-O stretching vibration and N-H
bending vibration of amine group, respectively. Following interaction with Ni(II), the wavenumber of these bands shifted to 3342, 1731 and 1642 cm\(^{-1}\) (Figure 1(a ii)). This phenomenon suggests the involvement of O-H, C-O and N-H in binding metal ions which might be through the formation of dative bond via sharing of valence electron [10,11].

From Figure 1(b'), discernible absorption bands at 1786, 1456, 1082, 855 and 712 cm\(^{-1}\) represent the properties of the carbonate (CO\(_3^{2-}\)) group [12]. After adsorption of Ni(II), a new absorption peak appeared at 3320 cm\(^{-1}\) was due to OH group. Meanwhile, the prominent band at 1456 cm\(^{-1}\) split into two bands at wavenumbers of 1474 and 1380 cm\(^{-1}\) (Figure 1(b ii)). Another set of new bands were observed at 1043 and 948 cm\(^{-1}\). These findings indicate that carbonate groups play an important role as binding site for metal ions mainly through electrostatic attraction [13].

The change in surface morphology following interaction with metal ions was studied using SEM analysis. Figure 2 shows the SEM images of kenaf bast fiber and golden apple snail shell, before and after interaction with Pb(II), as an example. From Figures 2(a i) and 2(b i), it is apparent that both adsorbents have dense and uneven surface morphology with no porous texture. Adsorption of Pb(II) onto both adsorbents changed their surface morphology significantly. After Pb(II) adsorption, it was observed that there were deposits on the surface of fiber (Figure 2(a ii)), meanwhile rod-like crystals with sharp and oval shape were clearly seen on the surface of snail shell (Figure 2(b ii)). These deposits and crystals could represent metal ion precipitates.

![Figure 2. SEM images of kenaf bast fiber before (a') and after Pb(II) adsorption (a'ii), and SEM images of golden apple snail shell before (b') and after Pb(II) adsorption (b'ii) at 10,000x magnification.](image)

In order to confirm the successful of heavy metals adsorption onto the surface of adsorbents, EDX analysis was performed. EDX analysis enables the determination of the elemental composition of adsorbents, particularly after the adsorption process. From Figure 3, C, O and K are the main elements in kenaf bast fiber, meanwhile Ca and O are the dominant elements in snail shell. The features of Cd
Lα₁ and Cd Lβ₁ were observed at 3.13 and 3.32 keV of EDX spectrum of fiber after interaction with Cd (Figure 3(a)). In the case of snail shell, the features of Cu Kα₁, Cu Kβ₁, Cu Lα₁ and Cu Lβ₁ were appeared at 8.05, 8.90, 0.93 and 0.95 keV following adsorption of Cu (Figure 3(b)). These findings support speculation made earlier in SEM analysis, of which deposits and crystals observed on the surface of adsorbents belong to metal ion precipitates.

3.2. Adsorption studies

The solution pH greatly affects the surface charge of the adsorbent and the degree of ionization and speciation of adsorbate in aqueous solutions [13,14]. Therefore, it is imperative to study such effect on the adsorption capacity of both kenaf bast fiber and golden apple snail shell. As stated in Section 2.3, the effect of solution pH was performed in the pH range of 1.0 to 6.0. Based on our preliminary studies, it was found that several metal ions started to form hydroxide precipitates at pH above than 6.0. To avoid any possible interference from hydroxide precipitates, we have set pH 6.0 as the maximum solution pH.

Figure 4(a) depicts the amount of Cd(II), Cu(II) and Pb(II) adsorbed onto snail shell as a function of solution pH, as an example. From Figure 4(a), it is clear that the adsorption of metal ions increased with an increase in solution pH and optimum pH was obtained at pH 6.0. A similar trend was obtained for kenaf bast fiber. In the case of snail shell, a lower amount of metal ions adsorbed at acidic media particularly at pH 1.0 and 2.0 can be related to a high amount of H⁺ or H₂O⁺ ions available, which has caused a competitive scenario with metal ions for adsorption sites (CO₂⁻). In contrast, at a higher pH values less H⁺ or H₂O⁺ ions were available. Therefore, metal ions were able to interact well with adsorption sites causing adsorption capacity to increase.

Of metal ions studied, Cr(VI) ions showed a unique adsorption behavior of which the adsorption capacity was initially increased from solution pH of 1.0 to 3.0 and decreased from pH 4.0 to 6.0 particularly onto kenaf bast fiber. Depending on the concentration of chromium and the pH of the solution, Cr(VI) normally exists in anionic forms in aqueous solution as Cr₂O₇⁻², HCrO₄⁻, CrO₄²⁻ and HCr₂O₇⁻ [15,16]. These anions can interact effectively with protonated amine functional groups available in kenaf bast fiber.

From the environmental engineering point of view, an ideal adsorption process should not take much time to treat contaminated water. In this study, the effect of contact time was studied up to 90 minutes. The adsorption of metal ions onto both adsorbents increased with contact time and attained equilibrium at about 60 minutes for an initial concentration of 50 mg/L of metal ions.

Figure 4(b) shows the effect of the adsorbent dosage on the amount of Pb(II) ions adsorbed by snail shell, as an example. As can be seen from Figure 4(b), the adsorption of Pb(II) decreased significantly from 39.25 mg/g to 7.11 mg/g when the amount of dosage was increased from 0.125 to 0.750 g. This
scenario can be explained by the fact that at the lower dosage, the ratio of adsorption sites of adsorbent to adsorbate was low. Therefore, all adsorption sites were occupied by adsorbate. In contrast, at higher dosage the aforementioned ratio was high. In other words, more adsorption sites were available than adsorbate, causing many of these sites were unoccupied. Therefore, the amount of metal ions adsorbed was decreased. Sessarego et al. [17] and Sharma et al. [18] have also obtained and discussed similar explanation.

![Figure 4](https://via.placeholder.com/150)

Figure 4. Effect of solution pH (a) and adsorbent dosage (b) on the adsorption of metal ions onto golden apple snail shell.

### 3.3. Adsorption isotherms

In such adsorption study, the interaction and distribution of metal ions on the surface of adsorbents can be described using adsorption isotherm models [18,19]. In this study, the adsorption equilibrium data were fitted to the Freundlich and Langmuir isotherm models. Freundlich isotherm is an empirical model and was developed to describe adsorption process that occurs at multilayer heterogeneous surface which involve interaction between molecules of adsorbates and active sites of adsorbents [20]. The linear form of the Freundlich isotherm can be represented by Equation (3) [21]:

$$\log q_e = \log K_f + \frac{1}{n} \log C_e$$

where $q_e$ is the amount of metal ion adsorbed per unit weight of adsorbent (mg/g), $K_f$ (mg/g) and $n$ (g/L) are the Freundlich constants. $C_e$ is the equilibrium concentration of metal ions (mg/L). Meanwhile, Langmuir isotherm is a theoretical model for monolayer adsorption with the homogenous surface without interaction between adsorbed molecules [22]. The linear form of the Langmuir isotherm can be expressed in Equation (4) [23]:

$$\frac{C_e}{q_e} = \frac{C_s}{Q} + \frac{1}{Qb}$$

where $Q$ is the maximum adsorption capacity at monolayer surface (mg/g) and $b$ is the Langmuir constant (mL/mg). The validity of both isotherm models was checked and depicted in Figures 5(a) and 5(b). Table 1 lists the Freundlich and Langmuir constants for metal ions adsorption by the golden apple snail shell. Based on the correlation coefficient ($R^2$) values, the adsorption equilibrium data were well fitted to the Langmuir isotherm model. Based on $Q$ value determined from Langmuir isotherm model, the affinity of snail shell towards metal ions was in order of Pb(II) (120.47 mg/g) > Cu(II) (94.18 mg/g) > Zn(II) (85.09 mg/g) > Ni(II) (78.34 mg/g) > Cd(II) (52.99 mg/g) > Cr(VI) (31.62 mg/g).
Table 1. Freundlich and Langmuir constants for metal ions adsorption by golden apple snail shell.

| Metal ion | Freundlich | Langmuir |
|-----------|------------|----------|
|           | $K_f$ (mg/g) | $1/n$ (g/L) | $R^2$ | $Q$ (mg/g) | $b$ (L/mg) | $R^2$ |
| Cd(II)    | 6.17       | 0.63     | 0.8015 | 52.99      | 0.06       | 0.9978 |
| Cr(VI)    | 34.94      | 0.28     | 0.7399 | 31.62      | 0.24       | 0.9880 |
| Cu(II)    | 10.93      | 0.49     | 0.9028 | 94.18      | 0.47       | 0.9762 |
| Ni(II)    | 22.95      | 0.82     | 0.7430 | 78.34      | 0.15       | 0.9598 |
| Pb(II)    | 40.80      | 0.60     | 0.8127 | 120.47     | 0.29       | 0.9761 |
| Zn(II)    | 25.36      | 0.17     | 0.8305 | 85.09      | 0.08       | 0.9905 |

Figure 5. Test of linearized Freundlich equation (a) and linearized Langmuir equation (b) for adsorption of Cd(II), Cu(II) and Pb(II) onto golden apple snail shell.

3.4 Effectiveness and comparative studies

The feasibility of kenaf bast fiber and golden apple snail shell to treat metal contaminated water was further evaluated using an electronics industry effluent. The adsorption performance of both low-cost adsorbents was compared with mangrove stem derived activated carbon (MSDAC). MSDAC is a commercial adsorbent and has been widely used for water treatment in Malaysia. The removal of metal ions from electronics industry effluent is given in Table 2.

From Table 2, it is clear that the adsorption capacity of kenaf bast fiber and golden apple snail shell was comparable to that of MSDAC. In fact, the snail shell was able to adsorb Cr(VI), Ni(II) and Zn(II) at a higher capacity than MSDAC and kenaf bast fiber under experimental conditions studied. It is also important to note that the three adsorbents studied were successfully reduced Pb(II) and Cu(II) concentration from 8.72 and 5.25 mg/L to less than 0.10 and 0.20 mg/L, respectively, and thereby meeting the Malaysian Environmental Quality Act 1974 maximum limit of 0.10 mg/L and 0.20 mg/L for Pb and Cu in industrial effluent to be discharged into inland surface water [24].

Table 2. Removal of metal ions from electronics industry effluent.

| Adsorbent          | Metal ion | Concentration of metal ion (mg/L) | Removal (%) |
|--------------------|-----------|----------------------------------|-------------|
|                    | Before adsorption | After adsorption |
| Kenaf bast fiber   | Cd(II)    | 0.41                             | 0.32        | 21.95   |
|                    | Cr(VI)    | 0.64                             | 0.18        | 71.88   |
|                    | Cu(II)    | 5.25                             | 0.18        | 88.38   |
|                    | Ni(II)    | 1.86                             | 0.67        | 63.98   |
|                    | Pb(II)    | 8.72                             | 0.09        | 96.22   |
|                    | Zn(II)    | 3.25                             | 0.88        | 72.92   |
| Golden apple snail shell | Cd(II)    | 0.41                             | 0.29        | 29.27   |
|                    | Cr(VI)    | 0.64                             | 0.09        | 85.94   |

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Cu(II) 5.25 0.16 96.95
Ni(II) 1.86 0.38 79.57
Pb(II) 8.72 0.04 99.54
Zn(II) 3.25 0.39 88.00

Mangrove stem derived activated carbon
Cd(II) 0.41 0.20 51.22
Cr(VI) 0.64 0.17 73.44
Cu(II) 5.25 0.10 98.10
Ni(II) 1.86 0.47 74.73
Pb(II) 8.72 0.06 99.31
Zn(II) 3.25 0.44 86.46

4. Conclusion
In the present work, the efficacy of kenaf bast fiber and golden apple snail shell to reduce heavy metals concentration in electronics industry effluent has been successfully evaluated. The physicochemical properties and adsorption mechanism were studied using several analytical instruments. Results obtained from this study highlight the applicability of both materials as alternative low-cost and environmentally friendly adsorbents for water treatment, particularly to be used in developing countries such as Malaysia, Indonesia, and Thailand, where similar resources are available at a huge amount. In order to evaluate the versatility of kenaf bast fiber and golden apple snail shell to be used as universal adsorbents for water treatment, it is therefore worth to investigate their performance using different type of industrial effluents. There is ready supply of kenaf bast fiber and golden apple snail shell. Their utilisation in water treatment as adsorbents will not only solve water pollution issue, but also reduce the risk of solid waste disposal from agricultural activity.

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