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Heavy metal removal from aqueous solution by tannins immobilized on collagen

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ABSTRACT

Different recycled materials, which were derived from leather manufacturing processes, were used as adsorbents for the treatment of synthetic wastewater containing heavy metal ions. Three pelt scraps samples (P-M, P-Z and P-P), one shaving scrap (S) and one trimming scrap (T) were used as recycled adsorbents. Removal efficiency of Cu(II), Cd(II), Zn(II), Pb(II) and Cr(III) was evaluated by a laboratory-scale batch reactor at different solution pH. For all adsorbents except T sample, the adsorption of heavy metal ions begins between pH 2 and 4 and reaches near complete adsorption within the next 3–4 pH units, showing a typical cationic-type of adsorption. Removal trend of Cr(III) was quite similar without depending on the kind of adsorbents. From the kinetic experiments of Cu(II) by S adsorbent, adsorption of Cu(II) was better described by second-order reaction than first-order reaction. The initial removal rate of Cu(II) by S adsorbent was 7143 mg/kg·h. Adsorption isotherm of Cu(II) onto S adsorbent was well expressed by Langmuir equation and the maximum adsorption capacity of Cu(II) at pH 4 was calculated as 1667 mg/kg.

Keywords: Adsorption; Collagen; Heavy metal; Leather waste; Recycle; Tannin

1. Introduction

Contamination of toxic heavy metal ions in aqueous system causes a great concern in natural environment and in human health. For example, as cadmium accumulates mainly in the kidneys, it can easily reach a critical threshold at high levels and can lead to serious kidney failure. Copper is widely used in the several industrial purposes such as electroplating, transportation equipment and electrical industry. Whenever copper contamination occurs in the groundwater and surface water, human body will be contaminated with accumulated copper species through direct intake or food chains. Therefore, contamination of heavy metal ions in natural environments should be prevented before it can discharge into natural water systems.

Considerable progress has been made in the development of treatment methods such as electrochemical treatment, precipitation, adsorption, ion exchange, reverse osmosis and filtration. Among these treatment techniques, adsorption is generally preferred for the removal of heavy metal ions due to its high efficiency,

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easy handling, availability of different adsorbents and cost effectiveness. Adsorption is an efficient method in the removal of low concentrations of heavy metal ions.

Recently, many researchers have much attention in the recycle of solid wastes as alternative adsorbents from the viewpoint of waste recycling and re-utilization which have gained popularity. As reused or recycled adsorbents, fly ash, peat, activated sludge and waste sludge, have received much attention for the removal of heavy metal ions [1–6]. Lee and Davis [2] studied the removals of Cu(II) and Cd(II) with sludge produced from squid processing. Muzzarelli and Tubertini [4] have reported the use of chitin and chitosan extracted from crab, and their capability for the removal of heavy metal ions via ion exchange, adsorption and chelation. Several solid wastes such as fleshing scrap, pelt scrap, shaving scrap and trimming scrap have been generated from leather industry in Korea. The generated amount was approximately 220,000 ton/year on average. However, only a few fraction of total solid waste has been recycled as fertilizer, raw material of cosmetics and decorator material. Therefore solid wastes, a kind of bio-adsorbent, generated from leather industries were applied for the treatment of heavy metals from aqueous solution in this research. The objective of this work was to evaluate the adsorption capacity of heavy metal ions on the different recycled adsorbents in a batch reactor.

2. Methodology

2.1. Material

All chemicals were analytical grades. $Cu(NO_3)_2$, $Cd(NO_3)_2$, $Pb(NO_3)_2$, $Zn(NO_3)_2$ and $Cr(NO_3)_3$ were purchased from Sigma–Aldrich Company. $NaNO_3$ obtained from Fisher Scientific was used to fix ionic strength. All solutions were prepared with deionized water (18 MΩ cm) prepared using a Hydro-Service reverse osmosis/ion exchange apparatus (Model LPRO-20). All bottles and glassware were acid washed and rinsed with deionized water before use. Five different adsorbents obtained from leather industry in Korea were used in this study. The used adsorbents were trimming scrap (T), pelt scrap treated with phosphonium (P-P), zirconium (P-Z), mimosa (P-M) and shaving scrap immobilization with vegetable tannin.

2.2. Preparation of S adsorbent and characterization

Fig. 1 shows the process for the preparation of S adsorbent. After immobilization of tannin onto collagen, the S adsorbent was cut into 5–10 mesh size. As a pre-step, solid scrap of raw collagen matrix was washed with water and then it was cut into pieces having 1–5 mesh size with cutting machine. The raw collagen was treated with $Ca(OH)_2$ and Na_2S to increase alkalinity of the solid sample. Next step is a tannin process of the raw collagen matrix with vegetable tannin material. After removing ash and grease, immobilization of vegetable tannin onto collagen was performed with pickle solutions around pH 6. Depending on the structure, molecular weight and particle size, tannin material shows different complexing properties with collagen matrix. Generally it is well known that vegetable material, having low molecular weight and particle size, can easily penetrate into the collagen matrix while the larger one can precipitate in bulk solution. Therefore, in this work, a naphthalene-based penetrant was used to enhance penetration efficiency of tannin material into collagen matrix and binding efficiency of it with collagen matrix. Generally the basic structure of vegetable tannin material is aromatic polyphenol derivatives. In this study, mimosa, a kind of catechol tannin, was used as a vegetable tannin material. Fig. 2 shows chemical structure of the major component of mimosa tannin. Next step is fiber separation and drying process. Niagara beater was used to get disentangle of immobilized fiber with vegetable tannin in order to

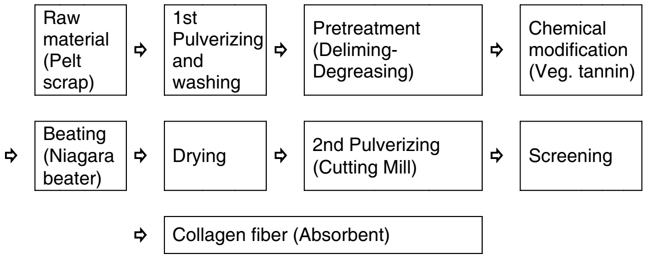


Fig. 1. Process for the preparation of S adsorbent.

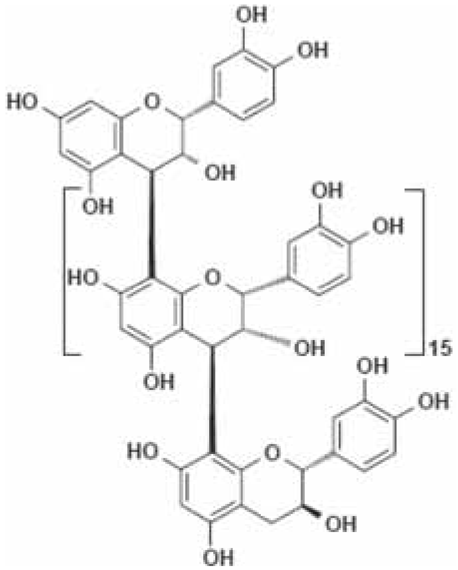


Fig. 2. The basic structure of mimosa.

enhance the recovery of fiber and to maximize specific surface area of fiber. And then the sample was dried at 70–80 °C. Final step is the secondary grinding and fragmentation process. Table 1 shows preparation conditions for the S adsorbent including the other four adsorbents.

Scanning electron microscopy was used to identify the morphology of the prepared S adsorbent. The SEM (Scanning Electron Micrograph, model JSM 5410LV, Japan) photographs were taken at three different magnifications to observe the surface morphologies of S adsorbent. Elemental analysis of S adsorbent was performed with Thermofinnigan (Model FlashEA1112, Italy). The surface area of S adsorbent was measured by low-temperature nitrogen adsorption and the data were interpreted using the Brunauer–Emmett–Teller (BET) equation. From the acidic and basic titrations of S adsorbent, surface acidity equilibrium constants (pK_{a1} and pK_{a2}) were determined. These values were used to calculate point of zero charge of S adsorbent (pH_{zpc}). Characteristics of the other adsorbents are also summarized in Table 1.

2.3. Adsorption experiments

The pH–edge adsorption experiments were carried out by mixing 0.1 g adsorbent with 50 mL of heavy metal solution (5×10^{-4} M) in 100 mL polypropylene conical tube (Falcon Co.). The used adsorbates were Cu(II), Cd(II), Zn(II), Pb(II) and Cr(III). At a fixed ionic strength of 0.01 M $NaNO_3$, the pH of the solutions was adjusted to between 2 and 9, using 0.1 M HNO_3 or 0.1 M NaOH, and equilibrated for an additional 24 h. After equilibration, the suspension pH was measured again and the removal results were plotted with this final pH value.

Effect of the contact time on the adsorption was examined with an initial adsorbate concentration of 5×10^{-4} M and an adsorbent dose of 2 g/L. In order to study the adsorption kinetics of Cu(II) onto the S adsorbent, 0.1 g of S adsorbent was mixed with 50 mL of 5×10^{-4} M Cu(II) solution, with a constant ionic strength (0.01 M $NaNO_3$). After adjusting the solution pH to 4 the bottles were placed in a shaker at constant temperature (25.0 ± 1.0 °C) and allowed to equilibrate for the specified time (10 min to 24 h). After the desired time, each sample was removed, filtered with 0.45 μm membrane filters, and then the dissolved copper concentration was measured using an inductively coupled plasma (ICP-OES, Perkin–Elmer Model Optima 2000 DV).

Table 1
Preparation conditions for five adsorbents used in this study

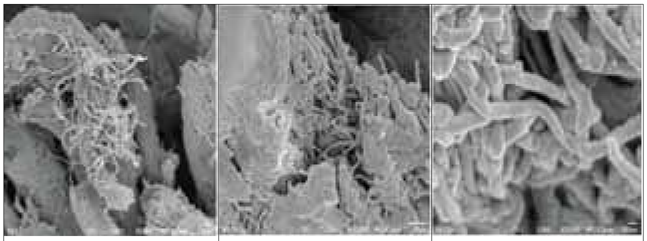
Sample	pH of the pickle solution	Tannin	Penetrant	Type
Pelt (P-M)	5.6	Mimosa 15%	GM 1.5%	Fiber
Pelt (P-Z)	5.6	Zirconium salt		Powder
Pelt (P-P)	5.6	Phosphonium salt		Powder
Shaving (S)	6.0	Mimosa 15%	GM 1.5%	Fiber
Trimming (T)	–	Chromium		Fiber

For the adsorption isotherm of copper ion, batch test was conducted. Each 0.1 g of S adsorbent was added with 50 mL of Cu(II) solution having different concentration (1×10^{-5}, 5×10^{-5}, 1×10^{-4}, 5×10^{-4}, 1×10^{-3} M), and then the mixture was shaken at 25.0 ± 1.0 °C for 24 h. After filtration the suspension using a 0.45 μm membrane filter, the dissolved copper concentration was measured using the ICP.

3. Results and discussion

3.1. Characteristics of S adsorbent

The SEM (Scanning Electron Micro-graph, model JSM 5410LV, Japan) photographs shown in Fig. 3 were taken at three different magnifications to observe the surface morphologies of S adsorbent. The surface of S adsorbent was much irregular due to the fiber bundle in the collagen fiber. The measured surface area of the S adsorbent was 49.87 m²/g. The surface acidity equilibrium constants (pK_{a1}, pK_{a2}) and point of zero charge (pH_{pzc}) of the S adsorbent measured from acid–base titrations was 5.47, 8.01 and 6.74, respectively. A result for the elemental analysis of S adsorbent is summarized in Table 2.



5,000 x magnification | 10,000 x magnification | 50,000 x magnification

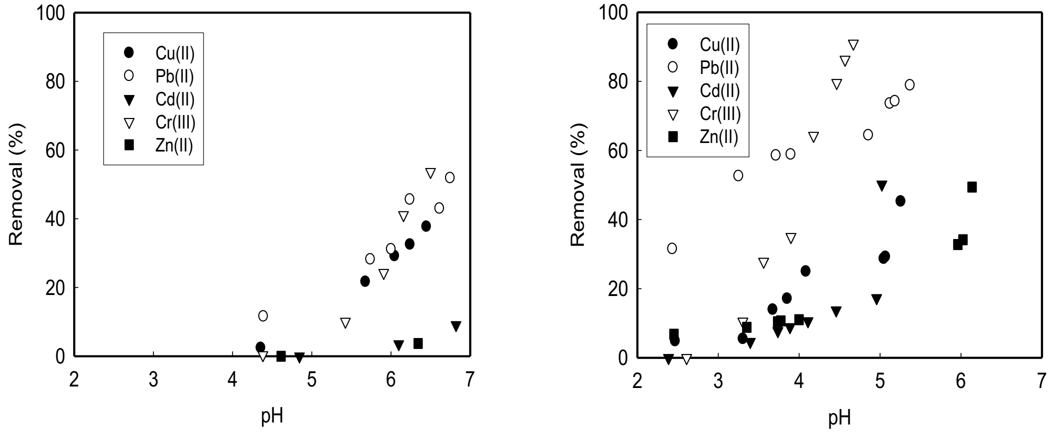
Fig. 3. SEM images of S adsorbent.

Table 2
Elemental analysis of S adsorbent

Adsorbent	Composition (%)				
	C	H	N	O	S
Shaving(S)	39.19	6.46	13.79	40.78	0.78

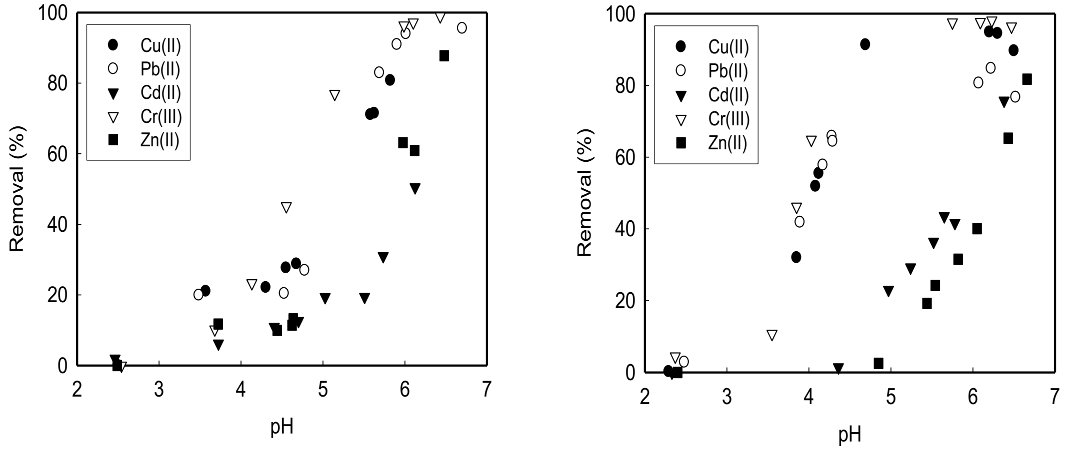
3.2. *pH–edge adsorption*

Fig. 4 shows the adsorption trends of five heavy metal ions onto the five different adsorbents. For all adsorbents except T, the adsorption of heavy metal ions by surface functional groups of the adsorbents begins between pH 2 and 4 and reaches near complete adsorption within the next 3–4 pH units, showing a typical cationic-type of adsorption [7]. In the absence of any complexing



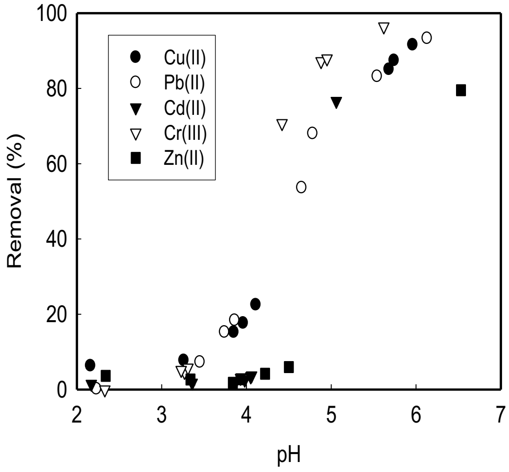
(a) Trimming (T)

(b) Pelt (P-P)



(c) Pelt (P-Z)

(d) Pelt (P-M)



(e) Shaving (S)

Fig. 4. pH–edge adsorption of five heavy metal ions on the different adsorbents.

species, the precipitation of metal ions depends only on the solution pH. Therefore MINEQL+ software was used to simulate precipitation of each metal ion (5×10^{-4} M). In this simulation, precipitation of Cr(III), Cu(II) and Pb(II) was predicted above pH 4.0, 5.4 and 5.6, respectively. However no precipitation of Zn(II), Cd(II) and Cr(III) was predicted over the pH range studied in this work. Removal trend of Cr(III) was quite similar without depending on the kind of adsorbents. Adsorption affinity for heavy metal ions of the adsorbents was the following order considering the pH–edge adsorption curves: Cr(III) > Pb(II) ~ Cu(II) >> Cd(II) ~ Zn(II). In general, major factors for the adsorption affinity of cationic heavy metal are known as ionic radius, electronegativity and degree of softness. And Sposito [18] reported that ionic radius and ionization energy are major controlling factors in the complex formation between heavy metal ions and ligands [8]. Ionic radius of Pb(II), Cd(II) and Cu(II) is 0.118 nm, 0.095 nm and 0.057 nm, respectively [9]. Electronegativity of Pb(II), Cd(II) and Cu(II) is 2.2, 1.7 and 1.0, respectively. And ionization potential of Pb(II), Cd(II) and Cu(II) is 70.18 eV, 33.90 eV and 42.11 eV, respectively. In this work, as the adsorption affinity of divalent heavy metal ions on adsorbents was Pb(II) ~ Cu(II) >> Cd(II), thus, it is regarded that heavy metal adsorption is not controlled by a single factor.

Among five adsorbents, P-M and S adsorbents immobilized with mimosa shows a greater removal capacity for Cu(II), Pb(II) and Cr(III). This result can be explained by the strong complexing ability of mimosa with metal ions. P-M adsorbent shows removal capacity for Cu(II) as 0.125 mmol/g and 0.225 mmol/g at pH 4 and pH 5, respectively. S adsorbent shows removal capacity for Cu(II) as 0.05 mmol/g and 0.225 mmol/g at pH 4 and pH 5, respectively. These removal capacities were slightly higher than that by immobilized black wattle tannin by Liao et al. [7]. Mimosa is composed of catechol structure as shown in Fig. 2. It is easily soluble in polar solutions and is traditionally used as tanning agents in leather manufacture because of its unique abilities to precipitate proteins and metal ions. Ii is generally known that the *ortho*-phenolic hydroxyl groups of tannins are responsible for chelating with metal ions to form a five-member-ring [10–14].

Compared to P-P and P-M adsorbents, S adsorbent shows a relatively constant removal capacity without depending on the type of metal ions. Even though the pH_{pzc} of S adsorbent is 6.74, most heavy metal adsorption begins between pH 2 and 4 and reaches near complete adsorption within the next 3–4 pH units. This result suggests that heavy metal removal on S adsorbent may occur through a strong chemical complexation. It is regarded as a promising adsorbent in the treatment of wastewater contaminated with mixture of heavy metal ions. Therefore S adsorbent was further used to investigate adsorption of copper at different reaction conditions. The adsorption efficiency of five heavy metals by five different adsorbents was summarized in Table 3.

3.3. Adsorption kinetics

The time dependent Cu(II) adsorption curves are shown in Fig. 5. The initial pH was 4 and then the final pH was ranged between 3.8 and 4.3. In this pH ranges, copper precipitation can be neglected. It was found that the uptake of Cu(II) increased with reaction time. The adsorption of Cu(II) was rapid in the first 2 h and then was slowed down as the equilibrium approached. The removed amounts of Cu(II) after 24 h were 10.76 g/kg. The results obtained from the variation of time were used to study the rate-limiting step in the adsorption process [5]. The rate constant (k_{ad}) for Cu(II) adsorption was determined from the following first-order rate expression.

Table 3
Removal amount of five heavy metals by adsorbents at pH 5

Adsorbent	Removal (g/kg)				
	Cu(II)	Pb(II)	Cd(II)	Cr(III)	Zn(II)
Pelt (P-Z)	6.89	17.06	5.6	7.8	4.9
Pelt (P-P)	4.82	29.85	5.1	12.0	3.6
Pelt (P-M)	13.30	18.41	6.5	10.4	0.8
Shaving (S)	8.67	18.93	16.9	11.7	6.4
Trimming (T)	3.02	8.33	0	0	0

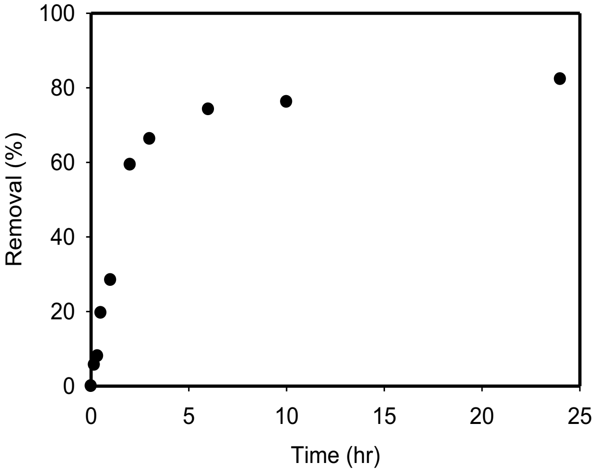


Fig. 5. Adsorption of Cu(II) on to S adsorbent as a function of time at pH 4.

$$\log(q_e - q_t) = \log(q_e) - \left(\frac{K_{\mathrm{ad}}}{2.303}\right)t \qquad (1)$$

where q_e and q_t (both mg/kg) are amount of copper adsorbed per unit mass of S adsorbent at equilibrium and time t, respectively, and k_{ad} is the rate constant (min^{-1}). The value of k_{ad} was calculated from the slope of the linear plot of log ($q_e - q$) versus time as shown in Fig. 6. The rate constant for Cu(II) adsorption was 4.6×10^{-3} min^{-1}. The correlation coefficient was 0.872. As the correlation coefficient was low, rate constant for the adsorption of Cu(II) was determined from the following second-order rate expression:

$$\frac{dq_t}{dt} = k(q_e - q_t)$$
$$\frac{t}{q_t} = \frac{1}{k_t q_e^2} + \frac{t}{q_e} \rightarrow \frac{t}{q_t} = \frac{1}{h} + \frac{t}{q_e} \qquad (2)$$

where, q_e and q_t (both mg/kg) are amount of copper adsorbed per unit mass of S adsorbent at equilibrium and time t, respectively, and k is the second-order rate constant. The value of k was calculated from the slope of the linear plot of t/q_t versus t as shown in Fig. 7. kq_e^2 in second-order equation can be expressed as initial removal rate (h). Initial removal rate (h) and second-order rate constant (k) were obtained from linear correlation between t/q_t and t. The k value was determined as 5.79 × 10^{-5} kg/mg·h. And h was 7,143 mg/kg·h. As the linear corelation coefficient was 0.984, the removal of Cu(II) by S adsorbent was well described by the second-order rate. Similar result was observed by Liao et al. [7] from the adsorption of Cu(II) onto collagen immobilized by tannins.

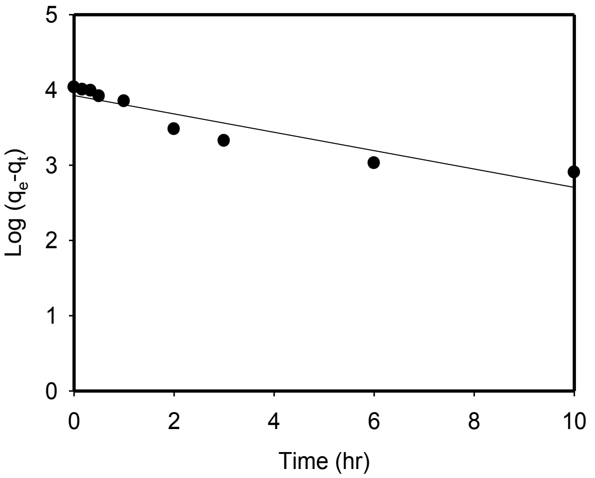


Fig. 6. The linear plot of log ($q_e - q$) versus time.

In order to investigate adsorption mechanism of heavy metal ion on S adsorent, an intra particle diffusion model expressed in Eq. (3) was applied [15].

$$q_t = k_1 \cdot t^{1/2} \qquad (3)$$

where q_t (mg/g) is the amount of Cu(II) adsorbed on S adsorbent, k_1 (mg/g/min$^{1/2}$) is a pore diffusion coefficient and $t^{1/2}$ is the square root of the reaction time. Fig. 8 shows a plot of the amount of sorbate adsorbed (q_t) and the square root of the time. A linear increase of q_t was observed at initial stage as increasing $t^{1/2}$ and then reached a plateau. The initial stage, showing a linear increase of adsorption, reflects pore diffusion of Cu(II) into the S adsorbent. The second stage showing fairly constant diffusion can be explained by exhaustion of the pore volumes.

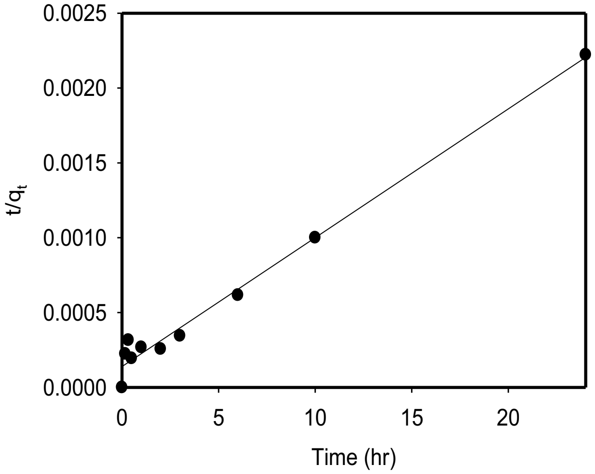


Fig. 7. The pseudo-second order plots for the removal of Cu(II) by S adsorbent.

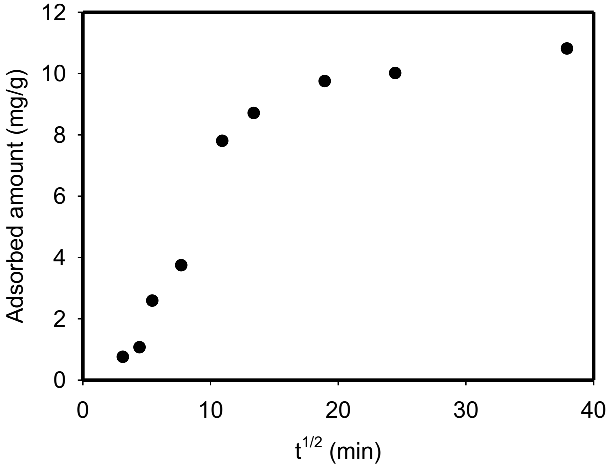


Fig. 8. A plot of the amount of sorbate adsorbed (q_t) versus square root of the time.

Removal of Cu(II) by S adsorbent can be described with the formation of metal–organic chelates because mimosa tannin has several phenolic hydroxyls. Jones (2000) reported the chemical structure of collagen fiber immobilized vegetable tannin [16]. In general, it is known that the ortho-phenolic hydroxyls of vegetable tannins can chelate with many metal ions to form five-member-ring [14].

3.4. Adsorption isotherm

Adsorption isotherm of Cu(II) on S adsorbent is shown in Fig. 9. When the experimental data were fitted with both the Langmuir and Freundlich equations, the experimental equilibrium relationships were described well by the Langmuir equation. Langmuir and Freundlich isotherm constants for Cu(II) adsorption on S adsorbent are summarized in Table 4. Langmuir isotherm is expressed by Eq. (4):

$$q = \frac{abC_e}{1 + aC_e} \tag{4}$$

where C_e is solute concentration (mg/L) at equilibrium and q is amount adsorbed (mg/kg), b and a the Langmuir constants representing adsorption capacity (mg/kg) and intensity of adsorption, respectively. The Langmuir plot of Cu(II) fitted well with a correlation coefficient (r^2) 0.996 as shown in Fig. 10. The values of b and a calculated from the slope and intercept of the linear plot of C_e/q versus C_e are shown in Table 4. Eq. (5) is a linear expression of Freundlich isotherm:

$$\log q = \log K + \log C_e \tag{5}$$

where q is adsorbed amount of Cu(II) on S adsorbent (mg/kg), C_e the equilibrium Cu(II) concentration in solu-

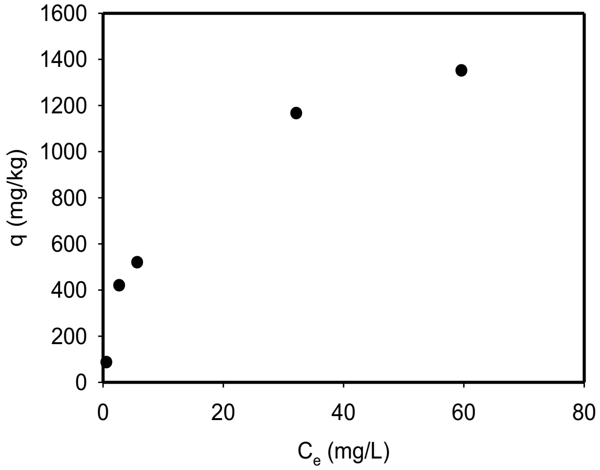
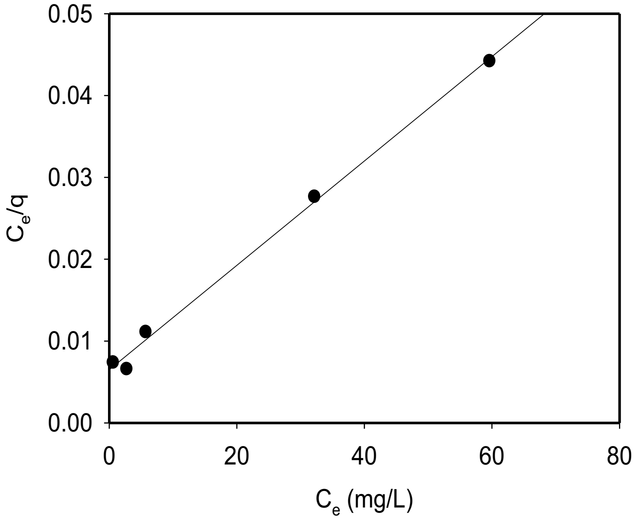


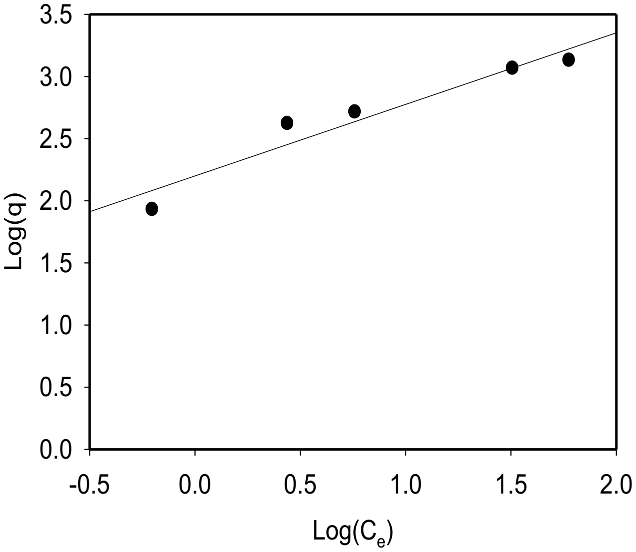
Fig. 9. Adsorption isotherm of Cu(II) on S adsorbent.

Table 4
Adsorption isotherm constants for Cu(II) onto the S adsorbent

Langmuir			Freundlich		
b (mg/kg)	*a*	r^2	*K*	*n*	r^2
1667	0.09	0.996	158	1.73	0.928



(a) Langmuir



(b) Freundlich

Fig. 10. Linear plot with (a) Langmuir and (b) Freundlich equations.

tion (mg/L), K and 1/n are the adsorption capacity and adsorption intensity, respectively. The Freundlich plot of Cu(II) showed a linear line with correlation coefficient (r^2) 0.928 as shown in Fig. 10. The value of n and K were calculated from the slope and intercept of the linear plot of log q versus log C_e and are shown in Table 4. From the adsorption isotherms of Cu(II) using immobilized tannins, Liao et al. [7] reported that Freundlich isotherm is better described the experimental data that than Langmuir isotherm.

4. Conclusions

Three pelt scraps samples (P-M, P-Z and P-P), one shaving scrap (S) and one trimming scrap (T) which were derived from leather manufacturing processing were selected as recycled adsorbents for the treatment of synthetic wastewater containing heavy metal ions. From the pH–edge adsorption test with Cu(II), Cd(II), Zn(II), Pb(II) and Cr(III) in a laboratory-scale batch reactor, the adsorption of heavy metal ions by surface functional groups of the adsorbents, except T adsorbent, begins between pH 2 and 4 and reaches near complete adsorption within the next 3–4 pH units, showing a typical cationic-type of adsorption. Removal trend of Cr(III) was quite similar without depending on the kind of adsorbents. From the kinetics experiments of Cu(II) by S adsorbent, removal of Cu(II) was better described by second-order reaction than first-order reaction. The initial removal rate of Cu(II) by S adsorbent was 7143 mg/kg·h. Removal isotherm of Cu(II) onto S adsorbent was well expressed by Langmuir equation and the maximum removal capacity of Cu(II) at pH 4 was calculated as 1667 mg/kg. From the adsorption test with the recycled leather wastes, it is possible to suggest that the recycled leather wastes are promising material in the treatment of waste water contaminated with heavy metal ions.

Acknowledgements

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