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Preparation and Characterisation of Biosorbent from Local Robusta Spent Coffee Grounds for Heavy Metal Adsorption

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In this study, the removal of lead heavy metal pollutants from artificially lead-contaminated water was carried out using biosorbent prepared from local Robusta spent coffee grounds. The effects of temperature of carbonisation and concentration of HCl solution as activating agent on biosorbent characteristics and lead-adsorption capabilities were investigated. Characterisation of the resulting biosorbent included functional groups by Fourier Transform Infra-Red Spectrophotometer (FTIR) and morphological properties by scanning electron microscope (SEM). Lead-adsorption capabilities were studied using a synthetic wastewater containing 50 ppm of lead. All adsorption processes were carried out for 30 min at room temperature with the ratio of spent coffee grounds biosorbent mass to lead solution volume of 1:10. Concentrations of lead solution before and after adsorption were measured using an atomic absorption spectrophotometer. Result showed that fixed carbon content of biosorbent prepared from spent local-coffee grounds was 97.1 %, it is fulfilled the requirement of Standar Industri Indonesia (SII) as potential activated carbon. Carbonisation and activation processes have altered the functional groups of spent coffee grounds. The prepared biosorbent showed a rougher and more porous surface morphology following the treatments. Adsorption process using spent coffee grounds biosorbent carbonised at 400 °C and activated using 0.2 M HCl solution gave the highest lead-removal percentage of 51.6 % and adsorption capacity of 8.6683 mg/g.

1. Introduction

Lead is considered as the most hazardous pollutants amongst all toxic metals. Lead-contaminated wastewater is mainly generated from accumulator/batteries industry, paint and dyes industry, electroplating, and ceramic/glass manufacturing (Momcilovic et al., 2011). Removal of heavy metal pollutants such as lead has been a great research interest due to the significant risks of pollutants to human health and environment.
Among the studied techniques, adsorption is considered as the most practical, inexpensive, and efficient method in reducing lead and other heavy metal pollutants (Azouaou et al., 2014). Many waste and waste biomass materials thus have been assessed and used as biosorbent precursor in attempt to eliminate lead-contaminant from water/wastewater. These include waste tire rubber ash (Mousavi et al., 2010), soybean oil cake (Erdem et al., 2013), rice husk (Abdel-Ghani et al., 2007), sesame husk (Surchi, 2011), pine cone (Momcilovic et al., 2011), walnut shell (Wolfova et al., 2013), banana stalk (Ogunleye et al., 2014), and spent tea leaves (Zuorro and Lavecchia, 2010). Even though the lead-adsorption capabilities reported were varied (from 5.44 to 200 mg/g), the evaluated waste and waste biomass materials have demonstrated as promising and effective biosorbent precursors.
Spent coffee ground may also be used as a potential alternative material for biosorbent due to its high carbon content (about 50.6 %) (Mussatto et al., 2011). Lavecchia et al. (2010) has compared the use of spent tea leaves and spent coffee grounds for eliminating lead from aqueous solution. The amount of lead removed per dry weight of spent coffee ground adsorbent was similar to that of spent black tea leaves, i.e. 11.1 mg/g and 11.3 mg/g. Azouaou et al. (2014) has also studied the use of untreated coffee ground in a packed-bed up-flow column to remove artificial lead-contaminated water. The highest lead-adsorption capacity obtained was

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78.95 mg/g. This may be optimised by treating the spent coffee ground using physical and/or chemical treatment(s) (Lamine et al., 2014).
Chemical activation requires lower carbonisation temperature compared to temperature on physical activation, which improves the pore structure development of carbon (Lamine et al., 2014) and thus its adsorption capacity. Jin et al. (2012) reported that the adsorption capacity of straw pulp prepared by K_2CO_3 increased with an increase in carbonisation temperature within 500 °C to 800 °C and then decreased with an increase in carbonisation temperature from 800 °C to 900 °C. Proper combination of activating agent and carbonisation temperature will determine specific surface areas of carbon (Hirunpraditkoon et al., 2011).A recent study by Imawati and Adhitiyawarman (2015) has employed a combination of physics and chemical treatments on spent coffee ground for lead removal adsorption. The spent coffee ground was carbonised at 600 °C for 4 h and chemically activated using 0.1 M HCl solution and 0.1 M H_3PO_4 solution. Carbonisation and activation processes were aimed to improve its adsorption capabilities. These processes develop pore structure and surface area of biosorbent (Ogunleye et al., 2014). The maximum adsorption capacities obtained by Imawati and Adhitiyawarman (2015) for HCl-activated and H_3PO_4-activated biosorbents were 3.3255 mg/g and 2.6090 mg/g, respectively. HCl solution showed a better performance as an activating agent compared to that of H_3PO_4. These results, were still much lower than the result obtained by Lavecchia et al. (2010) and Azouaou et al. (2014). This study also reported that carbonisation temperature gave insignificant effect on adsorption capacities. Further evaluation on potential application of spent coffee ground as activated biosorbent is therefore needed. The objective of this present study was to investigate the effects of temperature of carbonisation and concentration of HCl solution as activating agent on the characteristics and lead-adsorption capacities of biosorbent derived from local spent coffee grounds.

2. Materials and Method

2.1 Materials

A Robusta (Coffea canephora) coffee ground obtained from local market in Surabaya, Indonesia was used in this study. Its spent-coffee grounds were synthetically prepared following this procedure: 50 g of coffee grounds were brewed in 1.5 L of boiled water. The resulted spent coffee grounds were then repeatedly washed with water (coffee to water ratio of 1 : 5) until the filtrate was virtually colourless and neutralised, filtered, and oven-dried at 105 °C for 3 h. The average particle size of spent coffee grounds was -70/+100 mesh. All chemicals used in this study were of analytical grade.

2.2 Preparation of spent coffee ground biosorbent

Local Robusta spent coffee grounds were firstly washed with distilled water and oven-dried (Memmert UM-500) at 105 °C for 3 h. The spent coffee grounds were then introduced into a tube furnace (Barnstead Thermolyne 21100) at temperatures of 400 °C, 500 °C, and 600 °C for a 3 h carbonisation process. Nitrogen gas was used at carbonisation process at flow rate of 150 mL/min. The activation process was performed by soaking the carbonised spent coffee grounds in hydrochloric acid solution with desired concentrations (0.1 M, 0.2 M, and 0.3 M). After 24 h, the slurry was filtered and washed. The remaining activated coffee grounds were oven-dried at 105 °C for 3 h. Characterisation of the resulting biosorbent included functional groups by Fourier Transform Infra-Red Spectrophotometer/FTIR instrument (Shimadzu FTIR-8400S) and morphological properties by Scanning Electron Microscope/SEM (JEOL JSM-6510 LA) at an accelerating potential of 5.0 kV.

2.3 Adsorption of Lead using prepared biosorbent

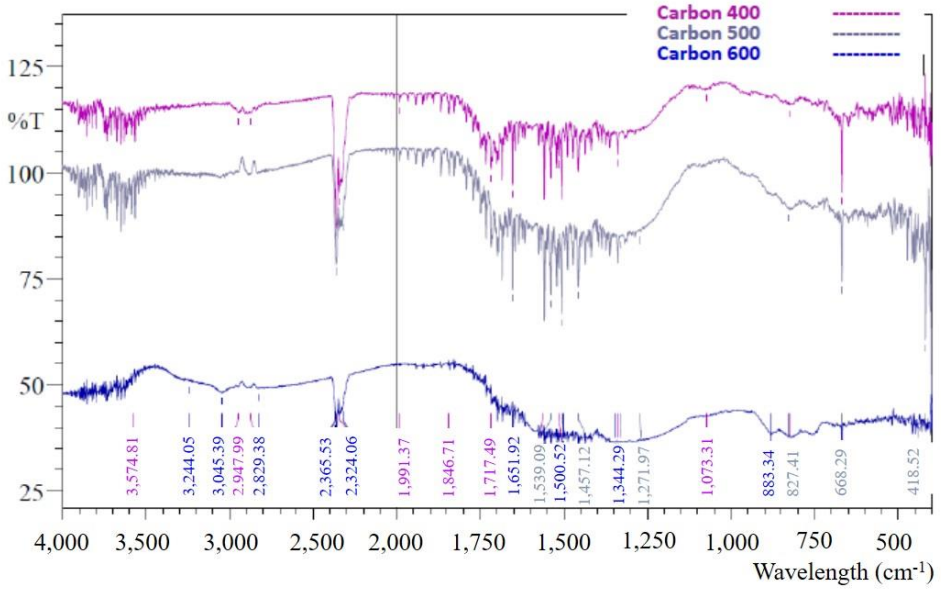
Lead-adsorption capabilities were studied using a synthetic wastewater containing 50 ppm of lead. The synthetic wastewater was prepared by dissolving lead nitrate ($Pb(NO_3)_2$) in distilled water. All adsorption processes were carried out in a shaking water bath (Memmert type WB 14-Germany) for 30 min at room temperature. Mass to volume ratio of spent coffee grounds biosorbent and lead solution of 1:10 was used throughout the adsorption experiments. Separation process was performed using Whatmann No. 42 filter paper. The concentrations of lead solution before and after adsorption were measured using an atomic absorption spectrometer/AAS instrument (Shimadzu AA-6200). The obtained data were then used to calculate lead-removal percentage and adsorption capacity.

3. Results and discussion

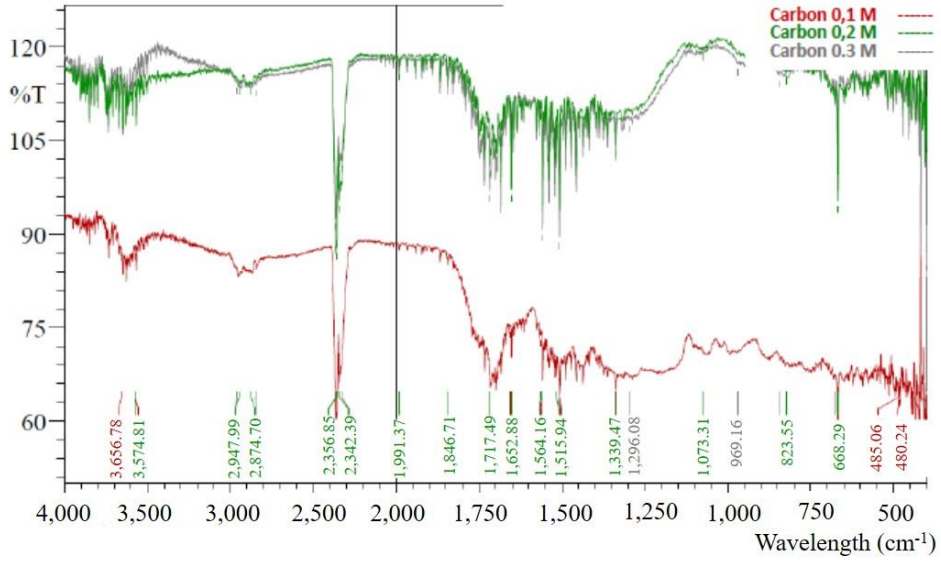
The result of proximate analysis of biosorbent derived from local spent coffee ground was as follows: moisture content of 4.95 %, ash content of 1.57 %, volatile matter content of 1.29 %, and fixed carbon content of 97.14 %. This composition has fulfilled the requirement of Standar Industri Indonesia (SII. 0258-88) for activated carbon (Ramdja et al., 2008).

3.1 Effect of carbonisation and activation processes on biosorbent characteristics

The effects of carbonisation temperatures and HCl concentrations on FTIR spectroscopic characteristics are shown in Figure 1(a) and 1(b). The analysis of bands and peaks with their corresponding surface functional groups for native, carbonised, and activated spent coffee grounds is presented in Table 1. Chemical transformation occurred following the treatments which are indicated by the shift in bands, alter in wavelength numbers, and difference in absorbance (Ogunleye et al., 2014). Some of the functional groups were enhanced and disappeared besides changing their wavelength numbers.



(a)



(b)

Figure 1: FTIR spectra for spent coffee grounds (a) carbonised at various temperatures with 0.2 M HCl and (b) activated with various HCl concentrations following carbonisation at 400 °C

Native spent coffee ground has C-H stretches, R-COH (aldehyde), and N-H stretch of amide. After carbonisation, there was an increase in aldehyde functional groups. The carbonised and activated spent coffee ground biosorbent showed C-H, R-COH, and C-Cl groups. By the appearance of C-Cl groups within the spent coffee ground biosorbent, the chemical activation process using HCl solution may be considered successful.
The SEM micrographs of spent coffee ground before and after modification (carbonisation-activation) are given in Figure 2. Some slight differences on its surface are observed at the micrographs. A rougher and more porous

surface morphology are noticeable following the carbonisation and activation processes. There appears to be no significant observable changes in appearance of the activated spent coffee ground following variation in HCl concentration, as illustrated in Figure 3.

Table 1: FTIR analysis of native, carbonised (at 400 °C), and activated spent coffee ground

Functional Groups	Native (cm^{-1})	Carbonised (cm^{-1})	Activated (cm^{-1})
C-H	1,374.66	2,852.03	1,457.59
	2,923.39	2,922.43	2,893.5
	-	-	2,937.86
N-H	3,325.52	3,314.91	-
H	1,750.75	1,688.07	1,717.49
I	-	1,703.5	-
R-C=O	-	1,733.39	-
C-Cl	-	-	668.29
	-	-	668.76
	-	-	823.55

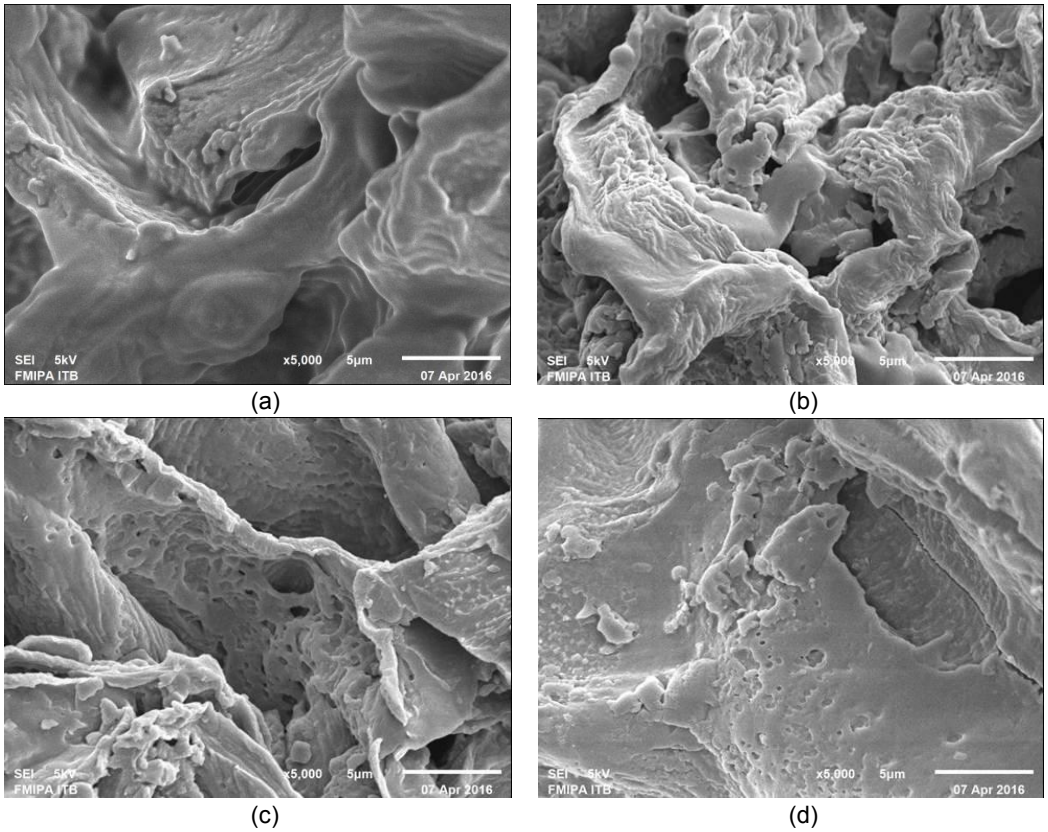
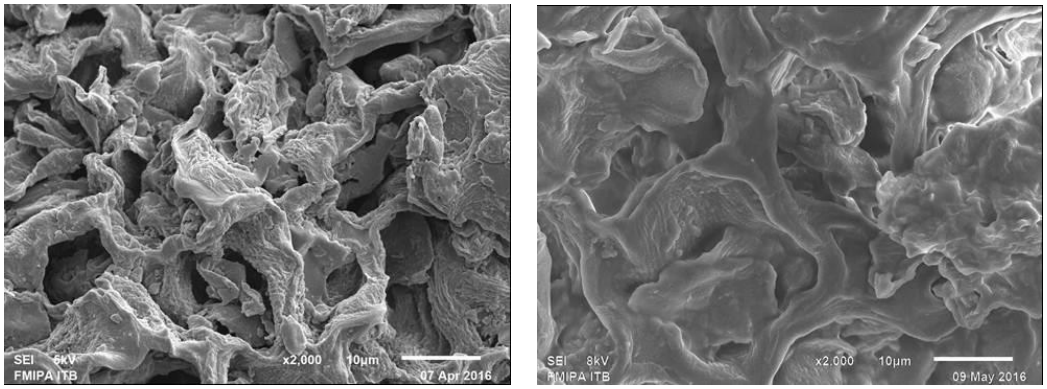


Figure 2: SEM micrographs of the spent coffee ground particles (a) native and carbonised at (b) 400 °C, (c) 500 °C, and (d) 600 °C (5,000× magnification, bars = 10 µm)



(a) (b)

Figure 3: Effect of HCl concentration on SEM micrographs of the spent coffee ground biosorbents (a) 400 °C, 0.1 M and (b) 400 °C, 0.2 M (2,000× magnification, bars = 10 µm)

3.2 Effect of process variables on lead-adsorption capacities

The effects of carbonisation temperature and HCl concentration on lead-adsorption capacities were also studied through adsorption process using synthetic lead-contaminated wastewater with initial concentration of 50 ppm. The ratio of mass of biosorbent to the volume of synthetic wastewater was 1 to 10 for all adsorption experiments. The results are presented in Figure 4. The highest lead-adsorption capacity is shown by the lowest amount of lead concentration after adsorption. The increase in carbonisation temperature from 400 °C to 600 °C has decreased lead removal percentage on different biosorbents under investigation. The higher the temperature of carbonisation, the more ash will be formed thus reducing its surface area (Rasdiansyah et al., 2014). Among all concentration studied, HCl concentration of 0.2 M gave the best results. Any concentration higher than 0.2 M will destroy the pore structure of biosorbent leading to a reduction on its adsorption capacity. These results are in accordance with that of biosorbent characteristics.

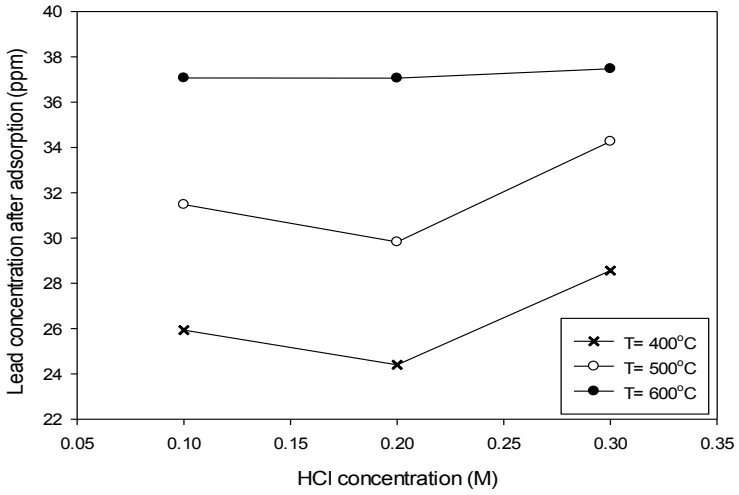


Figure 4: Effects of carbonisation temperature and HCl concentration on lead concentration after adsorption

Spent coffee ground biosorbent carbonised at 400 °C and activated using 0.2 M HCl solution gave the highest lead-removal percentage of 51.6 % and lead-adsorption capacity of 8.6683 mg/g. This present study gives better result compared to that of previous study conducted by Imawati and Adhitiyawarman (2015), i.e. 3.2555 mg/g, and slightly lower than the result obtained by Lavecchia et al. (2010), i.e. 11.1 mg/g. This result is, however, much lower than the result obtained by Azouaou et al. (2014). Variances in method, type and coffee origin may contribute to these differences.

4. Conclusions

Spent coffee ground is proven to be a potential biosorbent precursor for lead-removal adsorption. All parameters studied gave effects on biosorbent characteristics and lead-adsorption capacity. The highest lead-removal percentage (51.6 %) was obtained on adsorption process using spent coffee ground carbonised at 400 °C and activated using 0.2 M HCl solution. The mass to volume ratio of spent coffee ground biosorbent to lead solution was 1 : 10. The adsorption was conducted at room temperature for 30 min. The best adsorption capacity obtained was 8.6683 mg/g.

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