Characterization of coffee grounds as biosorbent for removal dyes from aqueous solutions

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Abstract. Low cost and effective biomass wastes may have ample applications in water decontamination procedures. Coffee waste is one of the most popular used as low cost adsorbents for the removal of dyes from aqueous solutions. The aim of this research is to study the effect of washing the coffee residue for dyes adsorption. The characterization functional group of adsorbents was characterized with FTIR, and proximate analysis. The experimental data obtained in the present study indicate that coffee grounds are suitable for use as biosorbents in the removal of dyes.

1. Introduction
Indonesia is one of the largest coffee producing country in the world. In the last five years coffee production in Indonesia reached 650,000 tons/year, still below Brazil, Vietnam and Colombia [11, 22]. From the production of coffee, it will also produce solid waste of coffee grounds. In Yogyakarta itself many emerging coffee shops in recent years. So coffee grounds also increased in the region of Yogyakarta. So far, a small percentage of coffee grounds is used only as compost and animal feed, most of which are simply thrown away or burned away. The burning of these coffee grounds products contributes substantially to the production of carbon dioxide that can cause the greenhouse effect [23]. Therefore, it needs further handling in this coffee grounds for useful purposes and converting this waste into a new resource material.

Coffee grounds has a lignocellulosic composition of cellulose and hemicellulose is high enough. From some studies mentioned that coffee ground contain 51.5% cellulose and 40.55% hemicellulose [1]. From the composition of this coffee ground can be used as a raw material of adsorbent. Utilization of coffee grounds as a decontamination agent of chemical substances in wastewater has been developed. Coffee grounds pulp is widely used as an adsorbent because of its high adsorption capacity [13, 14]. One of them can be used as adsorbent to absorb the textile/batik dye from the wastewater waste of the textile/batik factory.

Adsorption is considered to be quite attractive in terms of its efficiency of dyes removal. Although the use of common materials (activated carbon, zeolite, clay) is still popular due to the high adsorption capacity, they are expensive, too. Thus there is a growing demand to find relatively efficient, low cost and easily available adsorbents for the adsorption of dyes. Some of the reported adsorbents include orange bagasse, palm fruit bunch, chitosan, etc [21, 7, 13]. Many literatures had studied about the possible application of coffee grounds as heavy metal adsorbents [13,10] and in particular as dye
adsorbents [8,10, 15, 16]. Coffee grounds are generally called the solid wastes discarded from the extraction process of coffee beans.

In the current work, coffee grounds were collected from local cafe in Yogyakarta, Indonesia. The adsorption was performed in batch process and studying the effect of washing process of coffee grounds. The coffee grounds were also fully characterized.

2. Experiment

2.1. Materials
Coffee grounds were collected from local cafe (Hype Kulture and Kedai Rukun Lokal Cuisine & Brew, Yogyakarta, Indonesia). Remazol Yellow RG from Bratchem (Yogyakarta, Indonesia).

2.2. Preparation of biosorbent
The sample of coffee grounds were collected from local cafe (Hype Kulture and Kedai Rukun Lokal Cuisine & Brew, Yogyakarta, Indonesia) were washed with hot water to remove the brown color and residual organics and then dried at 80°C for approximately 8 h. Coffee grounds were also washed with metanol and n-hexane for comparing the effect of washing with the characteristic of adsorbent and the maximum uptake of the dyes. Fresh coffee grounds, Coffee grounds prepared by metanol and coffee grounds prepared by n-hexane are noted as CG, CGM, and CGH, respectively.

2.3. Characterization of biosorbent
Coffee grounds were characterized by lignocellulose content analysis using Chesson Method (Datta, 1981). Proximate analysis carried out by GB/T12496. Chemical characterization was carried out by FTIR spectroscopy in order to identify the functional groups at the surface of carbon materials. The FTIR measurement was carried out by FTIR Spectrophotometer (Shimadzu 8400S) using the KBr technique with wavenumber range of 500-4000 cm⁻¹.

2.4. Analysis of the sample
The dye concentration in aqueous solution was measured using absorption in a UV/Vis spectrophotometer at a characteristic wavelength. The amount of adsorption at the time, qₜ (mg/g) was calculated from the following equation:

\[ qₜ = \frac{(C₀ - Cₜ)V}{W} \]  

Where \( C₀ \) and \( Cₜ \) are the initial and final (equilibrium) concentrations of dye (mg/L), respectively, \( V \) the volume of dye solution (L) and \( W \) is the weight of the adsorbent (g).

3. Results and discussions

3.1. Biosorbent characterization
The proximate analysis for coffee grounds is shown in Table 1. From the results show the composition of coffee grounds is mostly carbohydrates of 62.14%.

Typical FTIR spectra obtained for CG, CGM, and CGH are shown in Figure 1. A comparative study of these spectra indicates that there was a slight difference in the results of FTIR analysis for CG, CGM and CGH. Two peaks at 2920 and 2850 cm⁻¹ were identified in previous roasted Arabica and Robusta coffee samples (Kemsley et al., 1995) and also on Arabica green coffee samples (Craig et al., 2011, 2012), in relation to stretching bonds C–H is asymmetrical and symmetrical. Studies of FTIR analysis of caffeine on soft drinks have investigated peaks at 2882 and 2829 cm⁻¹, with the latter being due to the asymmetric stretching of C–H bonds of methyl (–CH₃) group in the caffeine molecule (Paradkar & Irudayaraj, 2002). Other FTIR studies also reported two peaks at 2927-2925 and 2855 cm⁻¹, being respectively attributed to asymmetric and symmetric C–H stretching in lipids (Cremer &
Kaletunç, 2003). Thus, the peaks at 2920 and 2850 cm\(^{-1}\) observed in the spectra presented for all samples (CG, CGM and CGH) in Figure 1 can be attributed to combination peaks to which both caffeine and lipids contribute. From Figure 1, it can be seen that at the wavelengths of 2920 and 2850 cm\(^{-1}\) for coffee treated with methanol and n-hexane deformed. It shows that the caffeine and lipid content in coffee grounds dissolves in solvents. In the wavelength area of 2850 cm\(^{-1}\), a new peak appeared in the treatment using methanol and n-hexane which showed the addition of the \(-\text{CH}_3\) group attached to the surface of the coffee grounds.

### Table 1. Proximate Analysis of Coffee Grounds

| Component | Composition, % |
|-----------|----------------|
| Carbohydrate | 62.14 |
| Protein | 16.34 |
| lipid | 10.47 |
| Ash | 4.67 |
| Water content | 6.38 |

The peak at 1740 cm\(^{-1}\) was also investigated in the previous FTIR study in roasted coffee, related to carbonyl vibration (C=O) of the ester group in triglycerides (Kemsley et al., 1995) or aliphatic esters (Lyman et al., 2003), show lipid bonds. The combination of absorption at 1740 cm\(^{-1}\) (stretching C=O) and at 2360-2260 cm\(^{-1}\) (stretching H–C=O) can be interpreted as a group of aldehydes (Miller et al., 2003), which are easily found in roasted coffee as a degradation of unsaturated fatty acids, such as linoleic acid, which is quite abundant in coffee lipid fraction (Oliveira et al., 2006). The results of this study, illustrate that the aldehyde group is also soluble in the solvents which are indicated by decreasing peaks in this area. The wavelength of 1650 cm\(^{-1}\) has been supported by Garrigues et al. (2000) because of the presence of carbonyl groups in their FTIR analysis of trichloromethane extracts from roasted coffee and then using quantitative analysis of caffeine procedures in samples of roasted coffee. In this study, it was seen that the peak of 1650 cm\(^{-1}\) was deformed. This shows that the solvent used can dissolve caffeine in coffee.

![Figure 1. FTIR Analysis for CG, CGM and CGH](image-url)
3.2. Biosorbent testing

The results of dyes (remazol yellow RG) adsorption on coffee grounds (CG, CGM and CGH) can be seen in Figure 2. From Figure 2, it can be seen that untreated coffee grounds (CG) is able to adsorb dyes better than coffee grounds treated (CGM and CGH). It is possible for the number of groups on the surface of the coffee grounds dissolves in the solvent so that the surface of the coffee can no longer adsorb the dyes.

![Figure 2. Adsorption of Dyes](image)

4. Conclusions

Coffee grounds undergoes changes in functional groups on its surface after being treated using methanol and n-hexane. The functional group that showed caffeine, fat and aldehyde decreased in peak after treatment with methanol and n-hexane. The adsorption results showed that coffee without treatment was able to adsorb dyes better than coffee by treatment (CGM and CGH).

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