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Utilization of Coffee Grounds and Fly Ash as Adsorbents to Reduce Phosphate Content in Laundry Wastewater

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ABSTRACT: Industrial laundry wastewater contains 70-80% phosphate which can cause environmental pollution and trigger the growth of algae blooms or eutrophication if it is discharged into the environment. The adsorption method was chosen to reduce the phosphate content in laundry waste because it is relatively simple and low cost. The adsorbent used can use coffee grounds and fly ash, where coffee grounds have 47.8-58.9%. The composition used for the adsorption process is a ratio of coffee grounds: fly ash (w/w) of 1:0 and 1:1. Contact time in the adsorption process varies between 30 minutes, 60 minutes, 90 minutes, 120 minutes, 150 minutes. Based on research results, the best reduction in phosphate levels from laundry waste was 45.88%, where the initial phosphate level in the waste was 10.2 mg/L. Apart from that, the efficiency of reducing COD levels with the best removal efficiency was 80.39% with the initial COD content in the waste being 4080 mg/L. The best composition for testing laundry waste is 1:1 coffee grounds and fly ash (w/w) and the best contact time for testing laundry waste is 150 minutes.

Keywords: adsorption; coffee grounds; fly ash; laundry wastewater; phosphate

1. Introduction

Laundry wastewater contains 70-80% phosphate originating from detergents. According to Abdoli et al. (2024), the discharge of large quantities of phosphate into the environment can result in algal blooms or eutrophication. One alternative and straightforward method to reduce laundry wastewater pollution is through the adsorption process. Adsorption is a mass transfer process in which molecules, ions, or atoms adhere to the surface of an adsorbent. The terms adsorption and adsorbate refer to the absorbent material and the substance being absorbed, respectively. Adsorption offers several advantages, including relatively low cost, a simple process, high effectiveness and efficiency, and the possibility of adsorbent regeneration for repeated use. In this study, coffee grounds and fly ash were utilized as adsorbents. According to Caetano et al. (2012), the raw spent coffee grounds contain 56.3% carbon, 7.7% hydrogen, 1.8% nitrogen, and 0.47% sulfur Campos et al. (2021). The high carbon content in coffee grounds can be exploited for producing activated carbon Campos et al. (2021). Activated carbon is a porous material produced from combustion, characterized by a high adsorption capacity Gorbounov et al. (2023).

In addition to coffee grounds, fly ash can also be used as an adsorbent material. Fly ash is a byproduct of coal combustion (Anggorowati & Lestari, 2022) that contains 40-60 % silica (SiO_2), 20-40 % alumina (Al_2O_3), and 5-15% iron oxide (Fe_2O_3) Gyambibi et al., (2023) Fly ash involves activating its silica and alumina content to form zeolitic structures. This process enhances the material's adsorption properties, making it suitable for use as an adsorbent Zhang et al. (2021).The production of activated carbon involves two stages: carbonization and activation. Carbonization is the process of incomplete combustion at high temperatures, where the material is carbonized without being oxidized. According to Abbasi et al., (2016), The carbonization temperature significantly influences the adsorption capacity of carbon-based adsorbents. Generally, increasing the carbonization temperature enhances the development of porous structures and surface area, leading to improved adsorption performance. However, this trend holds up to an optimal temperature, beyond which excessive heat may cause pore collapse and reduced adsorption capacity. After the carbonization process, residues may still cover the pore surface, and pore formation may be incomplete. To address this issue, chemical activation using 0.1 M HCl is carried out to enhance adsorption capacity by cleaning pollutants from the surface of activated carbon particles. According to

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Ganjoo et al. (2023), adsorption capacity can be further increased if carbon is heated at high temperatures and chemically activated. With a larger pore surface area, adsorbents made from coffee grounds and fly ash are capable of adsorbing more substances Zhang et al. (2024).

This research was conducted to evaluate the quality of adsorbents derived from coffee grounds and fly ash, including determining the best composition ratio. Thus, it aims to introduce a new innovation by combining coffee grounds and fly ash as adsorbents for the purification of laundry wastewater. The study also seeks to determine the effectiveness of the adsorbents in reducing phosphate, COD, turbidity, and pH levels in laundry wastewater.

2. Material and Methods

The equipment used in this research includes 60 mesh and 120 mesh sieves, 100 ml crucibles, a furnace, an oven, a turbidimeter, a pH meter, cuvettes, a graduated cylinder, a COD digester, a UV-Vis spectrophotometer, Fourier Transform Infrared (FTIR), and a Scanning Electron Microscope (SEM). The materials used in this study are coffee grounds, fly ash, and 0.1 M HCl. This research was conducted using variable compositions of coffee grounds and fly ash, namely 1 gram of coffee grounds : 0 grams of fly ash; and 0.5 grams of coffee grounds : 0.5 grams of fly ash. The adsorption process was performed with varying times of 30, 60, 90, 120, and 150 minutes.

2.1 Pretreatment

The coffee grounds were first dried under sunlight for 24 hours, then placed on a tray in batches of 100 grams to be further dried using an oven for 30 minutes at a temperature of 105-110°C. The carbonization process was then carried out at 600°C for 90 minutes. After the carbonization process, sieving was performed to obtain a homogeneous particle size of 60 mesh. The activation process followed, using 0.1 M HCl for 48 hours. The coffee grounds were washed with demineralized water until a neutral pH was achieved. Then, the coffee grounds were placed in the oven at 105-110°C for 30 minutes. As for the fly ash, it underwent activation through physical treatment, where it was heated at 600°C for 1 hour.

2.2 Adsorbent Testing

50 ml of laundry wastewater was contacted with coffee grounds and fly ash adsorbents for 30, 60, 90, 120, and 150 minutes at a stirring speed of 100 rpm. The mixture was then separated using filter paper to collect the adsorbate. Subsequently, tests were conducted on the laundry wastewater after the adsorption process.

2.3 Phosphate Content Test

The phosphate content can be determined by first creating a standard curve to obtain a correlation coefficient. To create a phosphate standard curve, a phosphate standard solution of 100 mg/L is prepared along with the phosphorus reagents: 25 ml of 5 N sulfuric acid, 2.5 ml of potassium antimonyl tartrate, 7.5 ml of ammonium molybdate, and 15 ml of ascorbic acid. The phosphate standard solution is diluted from 100 mg/L to 10 mg/L, and then further diluted to concentrations of 0.2, 0.4, 0.8, and 1 mg/L. Next, 10 ml of the diluted phosphate standard solution is placed in a beaker and mixed with 1.6 ml of the phosphorus solvent, and the mixture is left for 10-15 minutes until a blue color develops. A blank solution is prepared using 10 ml of distilled water and 1.6 ml of phosphorus solvent.

The phosphate content is measured using a UV-Vis spectrophotometer with an absorbance wavelength of 887.55 nm. The blank test is performed first, followed by testing the samples, allowing the phosphate content of the adsorbed laundry wastewater to be determined.

2.4 COD Content Test

A 2.5 ml sample is taken and placed into a Hach tube, then 1.5 ml of potassium dichromate oxidizer and 3.5 ml of sulfuric reagent are added. The sample is then placed in a COD reactor for 2 hours at 105°C. Afterward, 2 drops of ferroin indicator are added, and titration is performed using ammonium ferrous sulfate (FAS) until the color changes to orange. The COD content can be calculated using equation 1.

$$\text{COD (mg } O_2\text{/l)} = \frac{(a-b)c \times 1000 \times d \times p}{ml\ sample} \quad \text{.............................. (1)}$$

Explanation:
a = ml of FAS for blank
b = ml of FAS for sample
c = normality of FAS
d = oxygen equivalent weight (8)
p = dilution

2.5 Turbidity Test

The sample was placed into a cuvette up to the marked line and then inserted into the turbidimeter until the turbidity value (NTU) was displayed.

2.6 pH Test

The sample was tested using a pH meter by immersing the device into the sample and waiting until the reading appeared on the instrument's display.

2.7 pH Test

The percentage of efficieny is expressed in equation 2

$$\% \mathbf{E} = \frac{C_i - C_e}{C_i} \times \mathbf{100\%} \quad \text{.. (2)}$$

Explanation :
Ci = initial adsorbate concentration (mg/l)
Ce = Concentration after adsorption (mg/l)

3. Result and Disscussion

3.1 Phosphate Coontent Analysis Result

The data in Figure 1 shows that the phosphate content in laundry wastewater before undergoing the adsorption process was 10.20 mg/L. The phosphate content decreased

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after the adsorption process with variations in adsorbent composition, while maintaining constant stirring time and speed.

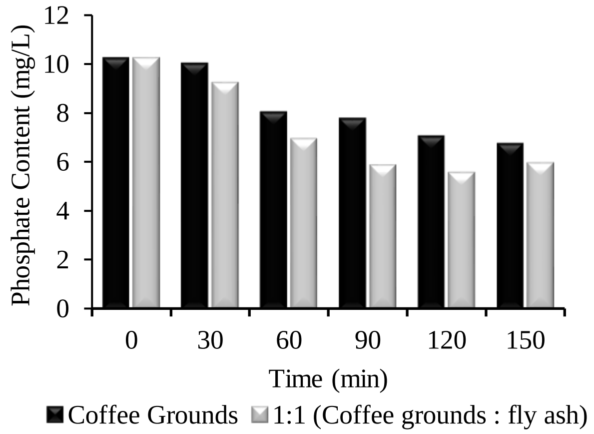

Figure 1. Phosphate Content Over Time

The highest phosphate concentration occurred at the 30th minute, with a value of 9.98 mg/L using 1 gram of coffee grounds as the adsorbent. In contrast, the lowest phosphate concentration was observed at the 120th minute, with a value of 5.52 mg/L using a 1:1 ratio of coffee grounds to fly ash. These findings indicate that the contact time of coffee grounds and fly ash with the laundry wastewater significantly influences the reduction of phosphate levels. According to Taufik et al. (2021), Increasing the contact time enabled the complete adsorption process to occur . Similarly, Mukherjee *et.al* (2022) reported that The optimum conditions for spent coffee grounds were used to produce activated carbon through physical activation in 90 minutes.

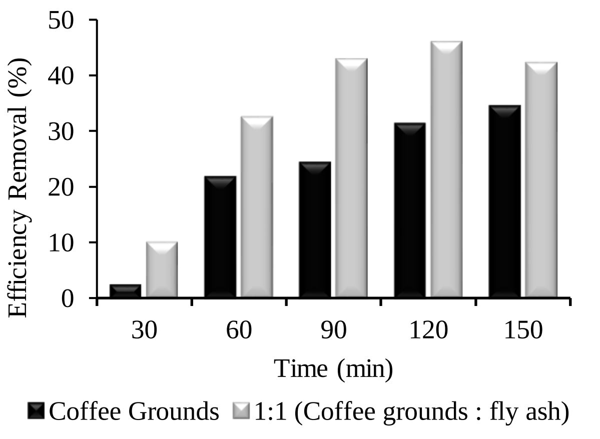

Figure 2. Phosphate Content Removal Efficiency

Figure 2 illustrates the pollutant removal efficiency (%) over time for coffee grounds and a 1:1 mixture of coffee grounds and fly ash. At 30 minutes, both adsorbents show low removal efficiency, but the mixture performs slightly better due to its enhanced surface area and adsorption sites. As contact time increases to 60 and 90 minutes, removal efficiency improves significantly, with the 1:1 mixture consistently outperforming coffee grounds. This superior performance can be attributed to the synergistic effect of fly ash, which increases porosity and adsorption capacity, According to Pan et al. (2017), the adsorption capacity of activated carbon increases as the particle size decreases, because smaller particles have more intermolecular forces, which enhance the adsorption process. At 120 and 150 minutes, both adsorbents approach equilibrium, where removal efficiency stabilizes. This reflects the saturation of the adsorbent's active sites, limiting further adsorption Söğüt and Gülcan (2023).

3.2 COD Content Analysis Result

Based on Figure 3, the initial COD concentration was 4080 mg/L. After the adsorption process, the COD concentration decreased at each time interval. The highest reduction occurred at the 120th minute, with a value of 160 mg/L using a variation of 1 gram of coffee grounds as the adsorbent. At this point, the COD level met the environmental quality standards set by the Indonesian Ministry of Environment Regulation No. 5 of 2014, which is 180 mg/L.

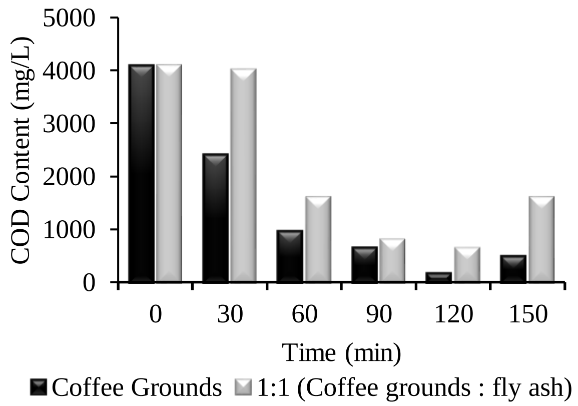

Figure 3. COD Content Over Time

The observed increase in COD concentration after 150 minutes is primarily due to the saturation of the adsorbent surface, where the active sites become fully occupied by the adsorbate. The removal efficiency improved as contact time increased, with the adsorption process consisting of two key phases: an initial rapid uptake phase followed by a slower uptake phase before reaching equilibrium. This behavior can be attributed to the abundance of vacant surface sites on the adsorbent at the beginning, facilitating efficient adsorption. However, as time progressed, the availability of free surface sites decreased, and the remaining sites became more challenging to occupy due to repulsive forces between the adsorbed organic pollutant molecules on the adsorbent's surface Khader et al. (2022). Over time, this phenomenon significantly reduces the adsorption capacity and efficiency of the adsorbent, making it less effective in pollutant removal. Optimal COD removal is generally achieved during the initial stages of the adsorption process, such as at the 30th minute, when the adsorbent's surface area and active sites are more abundant and available for adsorption, facilitating rapid removal of organic pollutants from the solution.surface area is more available for adsorption.

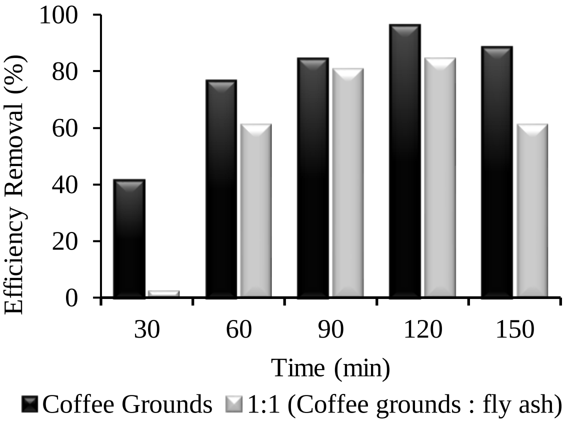

Figure 4. COD Content Removal Efficiency

Based on Figure 4, the highest efficiency in content reduction is 96.08% with the variation of 1 coffee grounds composition at the 120th minute. It can be concluded that the longer the contact time, the higher the absorption, but the absorption rate will decrease once equilibrium is reached.

3.3 Turbidity Analysis Result

As shown in Figure 5, the initial turbidity value of the laundry wastewater before contact with the adsorbent was 93.7 NTU. After contact with the adsorbent, the highest turbidity value was 25.1 NTU at the 30th minute, and the lowest was 9.1 NTU at the 150th minute.

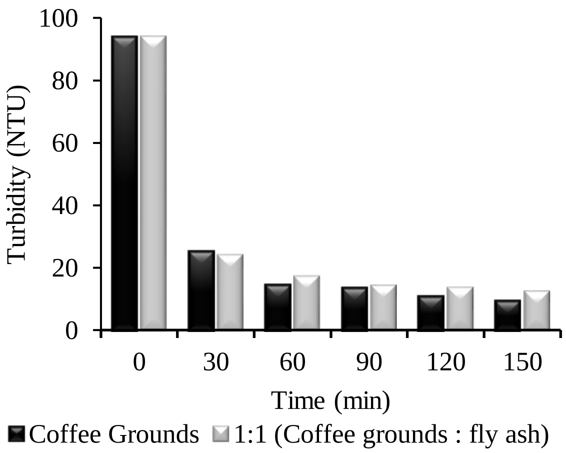

Figure 2. Turbidity Over Time

From the 60th to the 150th minute, the turbidity value of the laundry wastewater remained stable. This indicates that the system had reached saturation, meaning the coffee grounds and fly ash could no longer adsorb particles from the wastewater

In Figure 6, the highest turbidity removal efficiency of laundry wastewater was at the 150th minute, reaching 90.14%. This is due to the fact that with longer contact time, more collisions occur between particles and the adsorbent surface, leading to equilibrium. According to Söğüt and Gülcan (2023) , During adsorption, the concentration of the substance in the solution decreases until it balances with the concentration on the adsorbent, at which point the solution phase concentration stabilizes.

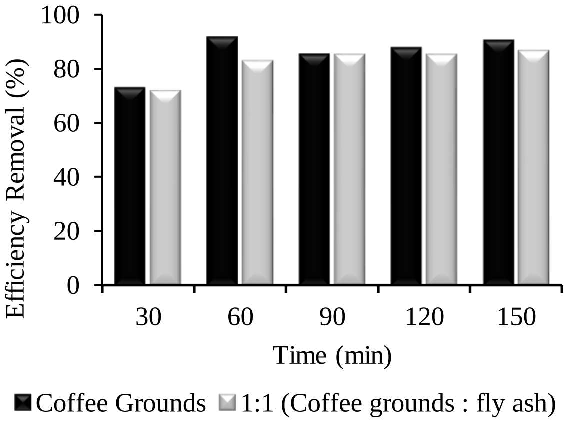

Figure 6. Turbidity Removal Efficiency

3.4 pH Analysis Result

Based on Figure 7, the pH value of the treated wastewater increased, with the initial pH of the laundry wastewater at 5.75, and at the 30th minute, it had risen to 8.12, using a 1:1 composition of coffee grounds and fly ash. The pH test was conducted to assess the water quality in the wastewater before and after treatment. The laundry wastewater used was initially acidic. After treatment, the pH of the laundry wastewater became neutral, which occurred due to the contact between the adsorbent and the wastewater. The adsorbent used was basic, with a pH of 8.12.

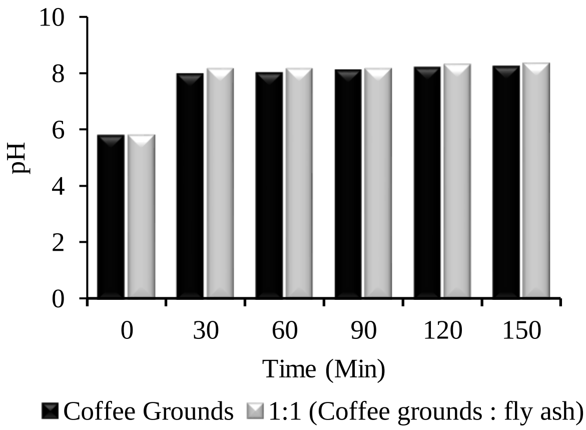

Figure 7. of pH Over Time

According to Wen et al. (2017), the presence of contaminants in wastewater can react with the residual HCl on the adsorbent, thereby removing H+ ions from the solution and increasing the pH. At the 120th minute, the pH of the laundry wastewater reached saturation, where the pH

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remained constant at 8.3, which met the established standard limits. Based on the research by Carnier et al. (2022) , it was demonstrated that spent coffee grounds have a greater sorption capacity for Pb and Cd at pH 10.

4. Conclusions

Based on the research conducted, several conclusions were drawn. The best composition in this study was a 1:1 ratio of coffee grounds to fly ash. The variation in adsorbent composition significantly influenced the adsorption process, with a smaller amount of adsorbent added resulting in a higher reduction of phosphate content in the laundry wastewater. Additionally, the optimal contact time of the adsorbent with the laundry wastewater was at the 150th minute. The best phosphate removal in the laundry wastewater was observed at the 120th minute, with a 1:1 ratio of coffee grounds to fly ash, achieving 5.91 mg/L. Furthermore, the highest turbidity removal efficiency was 90.14%, using 1 gram of coffee grounds at the 150th minute. The greatest reduction in COD content was at the 120th minute, reaching 160 mg/L. Additionally, the pH test results showed an increase, with the initial pH of the laundry wastewater at 5.75, which increased after contact with an adsorbent with a pH of 8.12.

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Statement
During the preparation of this manuscript, the authors used ChatGPT 4o to enhance the English language and proofread the text. Following the use of this tool, the authors thoroughly reviewed and revised the content to ensure accuracy and clarity. The authors take full responsibility for the final content of the publication.

CRediT authorship contribution statement
Yusmardhany Yusuf : Writing – review & editing. **Khalaida Fania Fatah :** Methodology, Data Curation, Formal analysis, Writing – original draft, Visualization. **Sinna Chaerunnabila Gunawan:** Investigation, Resources, Writing – original draft, Validation.
Bambang Soeswanto: Supervision, Resources, Writing – review & editing.
Rony Pasonang Sihombing : Methodology, Data Curation, Validation, Writing – review & editing.
Alfiana Adhitasari : Visualisation, Writing – original draft, Investigation, Formal analysis.

Declaration of competing interest
The authors declare that there are no known financial or personal conflicts of interest that could have influenced the research and findings presented in this paper.

Data availability
The data supporting the findings of this study are available upon reasonable request from the corresponding author.

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