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Efficiency of Palm Oil Kernel Shell (OPS-Fe_3O_4) for Phenol Waste Degradation Routes

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Abstract: *Phenol is a hazardous waste that can irritate humans' skin, eyes, and mucous membranes. It has been found that the phenol content in wastewater generally ranges from 1-6800 ppm. Phenol removal applications such as adsorption separation are highly recommended, including the application of activated carbon. Activated carbon can be produced from natural biomass with a high content of lignin, carbon, and hemicellulose. OPS (Palm Oil Kernel Shell) is one of the most developed biomass. Textured OPS is a dark grey hard-textured endocarp. The application of magnetite (Fe3O4) effectively modified the adsorbent to increase waste degradation. The experimental results revealed variations in adsorbent dosage, particle size, and contact time. At various adsorbent doses, adding 1g/ml was more effective in producing up to 98.5% removal. Meanwhile, the size of 0.05 mm produces higher degradation when compared to 0.22 mm and 0.55 mm. The optimum contact time shows that it occurs in 50-60 minutes. The FTIR results showed that the most abundant O-H, C=C and N-H content was found to be adsorbed at each particle size.*

Keywords: *Fe_3O_4, OPS, Phenol, Size, Time*

INTRODUCTION

Phenol is a chemical compound with many applications in petrochemical, petroleum, textile, and pharmaceutical (Hao et al., 2000). However, the effect of phenol in the human body is harmful because it irritates the skin, eyes, and mucous membranes in humans. Animal effects have also reported reduced fetal weight, growth retardation, and abnormal development. The Environmental Protection Agency reports that the maximum phenol content in industrial effluent discharges is one ppm (Dutta et al., 1996). Moreover, the phenol content in wastewater generally ranges from 1-6800 ppm (Banat et al., 2000). Applications for phenol removal are being developed by various methods, such as adsorption, membrane separation, flocculation, solvent extraction, photodegradation, and oxidation (Garbellini et al., 2010; Lalhruaitluanga et al., 2010). Currently, the most widely used adsorption application utilises activated carbon from biomass. Biomass used as an adsorbent can generally be viewed in terms of surface area, porosity, and regeneration (Singha and Das, 2011). In addition, the content of biomass containing lignin and hemicellulose has been recommended. There are many reports on the development of activated carbon from materials such as corn cobs, bagasse, rubber seeds, coconut shells, bamboo, and agricultural waste materials. Rattan Sawdust Biomass (ACR) was reported in the application of phenol degradation with a concentration of up to 149.25 mg/g at a phenol content of 200 mg/L (Hameed et al., 2008). Coconut shell-based activated carbon (BAC-T) at an activation temperature of 800oC can have a high surface area of around 1069 m2g-1 and is 97.7% effective in phenol adsorption (Li et al., 2022).

Figure 1. Scheme of Fe_3O_4 on OPS particle sites.

The reported percentage is around 5.5 Empty Branches (EFB) of OPS products, accumulating to 4.56 million tons annually (Ho & Khan, 2020). The characteristics of the oil core-shell are the endocarp texture, which is hard, dark grey to black and smells sour. The surface texture of the shell is smooth, but the edges are rough and pointed. OPS specific gravity ranges from 1.19-1.37 SSD, 0.15-8 mm thickness, and 500-600 for bulk density (Shakir et al., 2019). Final tests proved that OPS contained carbon, hydrogen, oxygen, nitrogen, and sulfur with concentrations of 50.73, 5.97, 40.83, 0.36, and 0.06% respectively (Chang et al., 2016). OPS also has percentages of cellulose, hemicellulose, and lignin ranging between 20.5, 22.3, and 49.9% (Saka et al., 2008). The high content of lignocellulose and carbon in OPS makes it a source of biomass for waste adsorption applications. The application of magnetite is an effective modified adsorbent to increase waste degradation. Magnetic media can widely absorb magnetite to separate molecules in a solution. Applying magnetic palm kernel biochar in phenol removal achieved an efficiency of 93.39% at pH 8 (Hairuddin et al., 2019). This study aimed to determine the effect of adsorption on the oil palm shell OPS adsorbent with a combination of Fe3O4 magnetite on the decrease in Phenol levels. In addition, qualitative and quantitative analyses were carried out to determine the effect of several parameters, such as contact time, particle size, and adsorbent dosage, on the phenol removal performance. Freundlich and Langmuir's theory was used to identify the mechanisms inherent in phenol adsorption.

RESEARCH METHOD

Preparation and Synthesis

The oil palm shells are cleaned and dried in the sun. After that, the material was split based on its size variations, namely 0.05 mm, 0.22 mm, and 0.55 mm. Then, the shell powder is carried out by the combustion process by pyrolysis synthesis using operating conditions of heating rate 3.5^{o}C/min, 500^{o}C, 1 hour, and auto-pressure.

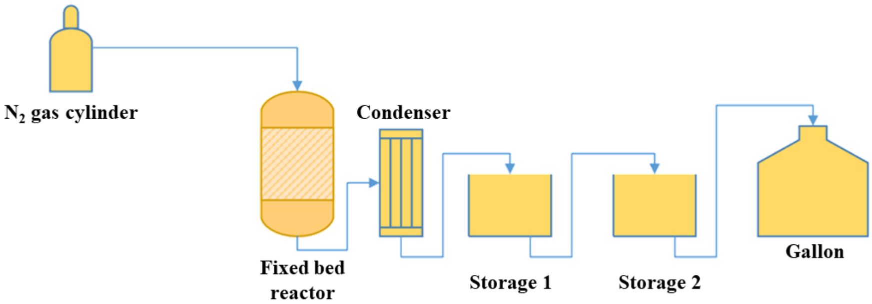

Figure 2. Illustration of a laboratory-scale pyrolysis reactor

Then, the resulting carbon from combustion was weighed as much as 4 g and dissolved in 200 mL of deionized water with stirring at 300 rpm and a temperature of 70oC. Magnetic preparation was done by combining 8g FeCl3.6H2O and 4g FeSO4.7H2O (mol ratio 2:1) in 200 mL deionized water. The iron oxide mixture was then added 10 ml/min into the carbon solution, stirring for 1 hour. Then, 100 mL of 5M NaOH was added using a pipette, and the pH was checked at 70°C for 2 hours. The precipitate is then filtered using deionized water and ethanol until the pH reaches neutral. The precipitate was then dried at 105°C for 2 hours.

Absorbent Testing

Phenol adsorption analysis used pH 8 with an adsorbent dose of 0.5 g/ml, 0.75g/ml, and 1 g/ml with a contact time of 60 minutes with an initial concentration of 25 ml. It was stirred using a magnetic stirrer and batch method. Then variations in size of 0.55 mm, 0.22 mm, and 0.05 mm were added to the solution. Variation of contact time is used to determine the level of adsorption at 10, 20, 30, 40, 50, and 60 minutes. The slurry was separated to obtain liquid filtrate for UV-Vis analysis at a wavelength of 750 nm and solid filtrate for FTIR analysis.

Characterization

FTIR analysis was used to determine the adsorbed components based on different types of size variables and impregnation effects. In comparison, SEM analysis aims to analyze the surface and the area of the solid pores before and after impregnation..

RESULTS AND DISCUSSION

Effect of Size Particle and Dosses Adsorbent

Figure 1. projects the variable dose of adsorbent and particle size on removal adsorption. The adsorbent doses used included 0.5g, 0.75g, and 1 g. The experimental results show that adding more adsorbents affects the removal of phenol levels. The highest optimum value was obtained at the addition of 1 g each. At the same time, the variation in particle size showed that 0.05 mm OPS-Fe3O4 particles could remove phenol levels with a value of 98.32%. Meanwhile, the 0.22 mm and 0.55 mm particle sizes show 89.54% and 78.36% respectively. The pore size distribution effect increases the accessibility and diffusion of the waste molecules. Smaller particle dimensions can increase the space capacity for increased adsorption performance (Saueprasearsit et al., 2010). So, in this case, the experiment supported the theory. Increasing the adsorbent dose and small particle size increases phenol removal efficiency at a concentration of 100 mg/L.

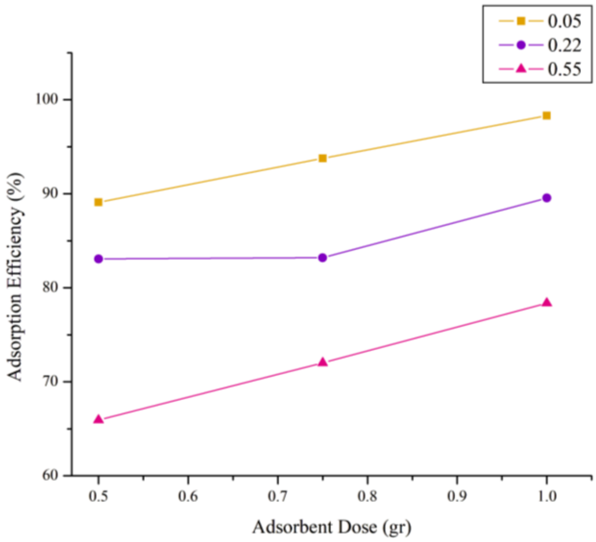

Figure 3. Size of particle and dosses adsorbent on adsorption efficiency.

Effect of Contact Time

The variables influencing contact time were set at 10, 20, 30, 40, 50, and 60 minutes, with a pore size of 0.05mm for OKS-Fe3O4. The adsorption method employed was a batch type, conducted at a speed of 80 rpm using a 25 ml phenol solution. Stirring was implemented to enhance film diffusion toward the pore diffusion point. The experimental results indicated that contact times of 50-60 minutes achieved a high removal efficiency of 98.19% and 98.32%, respectively. In contrast, 10 minutes of stirring resulted in a phenol absorption rate of 81.2%. During the initial contact period, the active sites of the adsorbent facilitated the adsorption of phenol into the adsorbent's pores, typically occurring within the first 0-10 minutes. At 50-60 minutes, a dynamic equilibrium between adsorption and desorption rates was observed, leading to a reduction in the number of adsorbed molecules within the pores, indicative of a saturated condition.

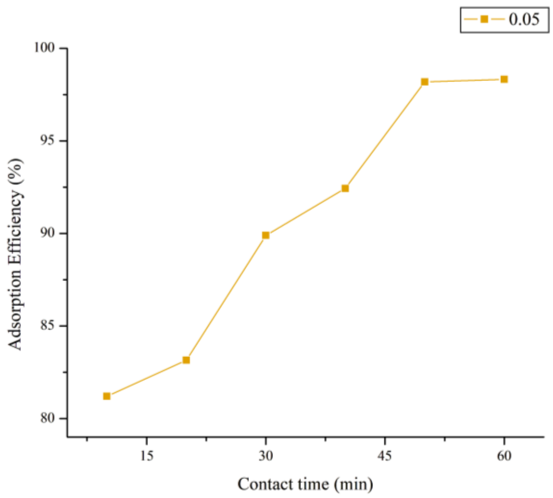

Figure 4. Effect of contact time

Review on Magnetic Biosorbent for Phenol Application

Several researchers have developed phenol adsorption capacity experiments. The results of this experimental work utilized operating conditions at pH 8 with an agitation speed of 160 rpm and the batch method. Several variables were incorporated to investigate the effects of adsorbent dosage, particle size, and contact time on the removal of phenolic waste. The adsorbent doses were 0.5 mg/L, 0.75 mg/L, and 1 mg/L. The particle sizes provided were 0.55 mm, 0.22 mm, and 0.05 mm. Meanwhile, the contact times used were 10, 20, 30, 40, 50, and 60 minutes.

Table 1 presents several literature studies examining the elimination of phenol waste. Hairuddin et al. (2019) employed the same biomass with the addition of magnetite when applying ten mg/L phenol for 60 minutes. This study demonstrated that phenol waste removal could reach 93.39%; however, the particle size used was not specified. Alni et al. (2022) utilized Chinese cabbage impregnated with ethanol solvent under operating conditions of 20 minutes, a phenol concentration of 10 mg/L, and a particle size of 0.004 mm. This study achieved the highest phenol removal compared to other data, reaching 99.03%. Additionally, green tea and foundry sand were used as adsorbents, achieving 92% and 97% phenol removal rates, respectively.

Table 1. Review on the effectiveness of magnetic biosorbent for phenol removal.

Type of adsorbent	Supports	Operation condition		Removal Efficiency (%)	Phenol concentration (mg/L)	References
		Time (min)	Size (mm)			
Palm Oil Kernel Shell (OPS)	Fe_3O_4	60	0.05	98.32%	100	This works
Palm Kernel Biochar	Fe_3O_4	60	-	93.39%	10	Hairuddin et al., 2019
Chinese Cabbage	Ethanol	20	0.004	99.03%	10	Alni et al., 2022
Green Tea	H_3PO_4	60	0.5	92.00%	25	Ali et al., 2022
Foundry Sand	HNO_3, HCl, HF, H_3PO_4, and H_2SO_4	10800	0.05-2	97.00%	953	Rodrigues et al., 2021

FTIR and SEM Analysis

Functional groups on the OPS-Fe3O4 surface were analyzed using Fourier Transform Infrared Spectroscopy (FTIR). The graphical results depict the relationship between wavenumber and the percentage of transmitted adsorption. Figure 3 illustrates the surface functional groups based on variations in particle size (0.05 mm, 0.22 mm, and 0.55 mm). It was observed that the carboxylic acid (O-H) group exhibited increased absorption with smaller particle sizes. Specifically, the 0.05 mm particle size demonstrated the highest O-H absorption, peaking at 3196.16 cm^{-1}. In contrast, the 0.22 mm and 0.55 mm particle sizes showed O-H stretch components at 3169.90 cm^{-1} and 3176.47 cm^{-1}, respectively.

The N-O (Nitro Compound) functional group was also well-adsorbed on the surface of each particle size. The highest value was observed for the 0.55 mm particle size, peaking at 1554.79 cm^{-1}. Single C-H bonds were detected at particle sizes of 0.22 mm and 0.05 mm, with peaks at 2793.16 cm^{-1} and 2796.29 cm^{-1}, respectively. The N-H functional group absorption was lower in the 0.05 mm particles than the 0.22 mm particles. The alkene triple bond (C=C) exhibited the most significant absorption at 0.05 mm, with a value of 983.03 cm^{-1}, compared to the 0.22 mm and 0.55 mm particle sizes. Additionally, the alkyne group (C≡C) was detected only in the 0.05 mm particles, with a peak at 2161.57 cm^{-1} under low conditions.

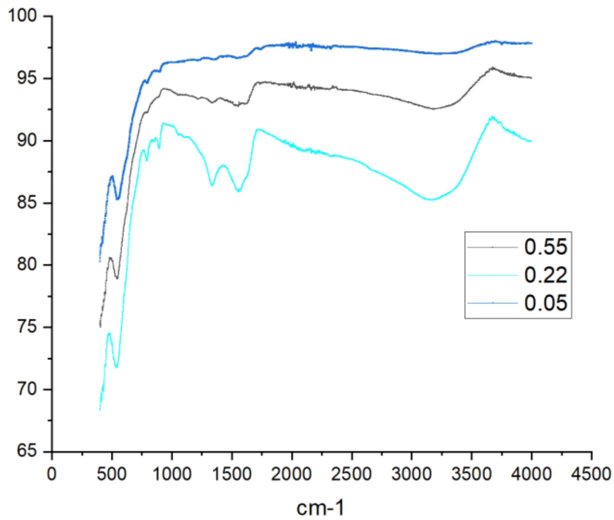

Figure 5. The wave number of different sizes on phenol adsorption.

The heating process at 500°C resulted in the formation of many pores prior to impregnation. Many of these porous surfaces remained unfilled to reduce the water content, although this had the opposite effect. The absence of pores on the surface after impregnation indicates that the initially empty pores on the adsorbent surface have been filled.

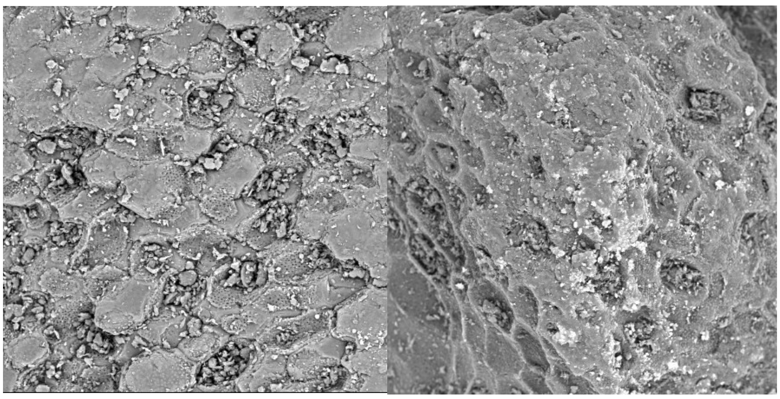

Figure 6. Before and After Impregnation

CONCLUSIONS

OPS-Fe3O4 demonstrated great adsorption activity for the removal of phenol waste. The adsorption experiments were conducted at pH 8 under batch conditions. The variation in adsorbent mass indicated that a 1 g/ml mass was more effective in adsorbing phenol waste than 0.75 g/ml and 0.5 g/ml. The particle size of 0.05 mm achieved a high removal efficiency of 98.32%. Contact time was used to determine the saturation point of the adsorbent surface, and the study found that a contact time of 50-60 minutes with a particle size of 0.05 mm resulted in efficiencies of 98.19% and 98.32%, indicating a tendency towards saturation. The functional group analysis revealed that O-H and C=C groups were well adsorbed at the smallest particle size of 0.05 mm. Other functional groups were also detected, including N-O, N-H, and C-H. These findings suggest that OPS-Fe3O4 is a promising adsorbent for removing phenol waste at a concentration of 100 ppm.

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