

SULFIDE REMOVAL FROM PETROLEUM  
REFINERY WASTEWATER USING  
HYDROGEN PEROXIDE AND CHEMICALLY  
MODIFIED ACTIVATED CARBON

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## **SUPERVISOR'S DECLARATION**

I hereby declare that I have checked this thesis, and, in my opinion, this thesis is adequate in terms of scope and quality for the award of the degree of Master of Science.

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I hereby declare that the work in this thesis is based on my original work except for quotations and citations which have been duly acknowledged. I also declare that it has not been previously or concurrently submitted for any other degree at Universiti Malaysia Pahang or any other institutions.

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HYDROGEN PEROXIDE AND CHEMICALLY MODIFIED ACTIVATED  
CARBON

MARIAH BINTI CHE MAMAT

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## ABSTRAK

Loji penapisan petroleum menjana air sisa, sisa pepejal dan enap cemar yang terdiri daripada sebatian organik, bukan organik termasuk logam berat. Rawatan lanjut diperlukan untuk sisa kilang penapisan petroleum kerana ia biasanya mempunyai kandungan sulfida yang tinggi yang dikenali sebagai bahan pencemar yang paling berbahaya. Ia dilepaskan ke persekitaran sebagai sulfida terlarut ( $S^{2-}$  dan  $HS^-$ ) dalam effluen dan  $H_2S$  dalam gas sisa. Oleh itu, penyingkiran sulfida dari kilang penapis minyak petroleum adalah sangat penting kerana ianya boleh mendatangkan bahaya kepada masalah manusia dan persekitaran disebabkan kealkalian dan tahap sulfida yang tinggi. Objektif dalam kajian ini adalah untuk mengetahui kemampuan hidrogen peroksida ( $H_2O_2$ ) dan karbon teraktif diubah suai secara kimia (AC-M) sebagai kajian pendekatan baru dalam penyingkiran sulfida dari sisa kilang penapisan petroleum. Kesan daripada pencemar berbahaya ini menjadi kebimbangan yang semakin meningkat terhadap isu-isu alam sekitar disebabkan pengaliran sulfida dari sisa kilang penapisan petroleum dengan melalui kaedah pengoksidaan dan kaedah penjerapan dalam kajian ini. Keputusan menunjukkan kepekatan sulfida dalam simulasi air sisa yang terbaik adalah 300 mg/L, dos  $H_2O_2$  adalah 1.5 ml dan masa tindak balas adalah 30 minit dalam proses pengoksidaan. Walau bagaimanapun, kepekatan sulfida dalam simulasi air sisa yang terbaik adalah 100 mg/L, jumlah berat AC-M adalah 0.5 g dan masa sentuh adalah 6 jam dalam proses penjerapan. Ciri-ciri AC-M yang disediakan akan dianalisis menggunakan SEM, EDX, BET, dan FTIR. Kajian kinetik mengenai keadaan penjerapan AC-M telah menunjukkan bahawa isotherm penjerapan Freundlich lebih sesuai dan proses penjerapan mengikuti model kinetik urutan Pseudo-kedua. Perbandingan antara kaedah pengoksidaan dan penjerapan dengan menggunakan parameter terbaik dalam pengurangan sulfida dari sisa kilang penapis petroleum sebenar telah ditentukan. Kecekapan kaedah pengoksidaan yang mampu mengurangkan kepekatan sulfida adalah 99.83% daripada 300 mg/L kepada 0.5 mg/L, kepekatan COD adalah 98.29% daripada 4100 mg/L kepada 70 mg/L dan pH adalah 29.08% daripada 11.86 kepada 8.41. Walau bagaimanapun, kecekapan kaedah penjerapan dalam pengurangan kepekatan sulfida adalah 95.70% daripada 100 mg/L kepada 4.3 mg/L, kepekatan COD adalah 98.29% daripada 4100 mg/L kepada 70 mg/L, dan pH adalah 3.0% daripada 12.00 kepada 11.65. Oleh itu, disimpulkan bahawa kaedah pengoksidaan lebih berkesan daripada kaedah penjerapan dalam penyingkiran sulfida daripada sisa air kaustik. Bagaimanapun, kedua-dua kaedah tersebut boleh meyingkirkan lebih daripada 90% terutamanya pada kepekatan sulfida dan COD. Ianya mencadangkan penggunaan kaedah pengoksidaan hibrid bersama kaedah penjerapan untuk mendapatkan lebih keberkesanan dalam penyingkiran sulfida. Maklumat yang diperolehi daripada kajian ini berguna untuk tujuan skala dalam industri penapisan petroleum.

## ABSTRACT

Petroleum refinery plants generate wastewater, solid waste and sludge composed of organic, inorganic compounds including heavy metals. Further treatment is needed for petroleum refinery wastewater because it typically has high concentration of sulfide which is known as the most hazardous pollutants. It is released to environment as dissolved sulfide ( $S^{2-}$  and  $HS^-$ ) in effluents and  $H_2S$  in waste gases. Thus, it is very important to remove sulfide from petroleum refinery wastewater that can bring harmful to human and environmental problems because of their alkalinity and high sulfide level. The objective in this study is to determine the ability of hydrogen peroxide ( $H_2O_2$ ) and chemically modified activated carbon (AC-M) as a new approach studies in sulfide removal from petroleum refinery wastewater. The effect caused by these hazardous pollutants and growing concern on environmental issues led to remove sulfide from petroleum refinery wastewater using oxidation method and adsorption method in this study. Result shows the best concentration of sulfide simulated wastewater is 300 mg/L,  $H_2O_2$  dosage is 1.5 ml and reaction time is 30 min in oxidation process. While, the best concentration of sulfide simulated wastewater is 100 mg/L, AC-M dosage is 0.5 g and contact time is 6 hr in adsorption process. The prepared AC-M was characterized using SEM, EDX, BET, and FTIR. The kinetic studies of the adsorption behaviour of AC-M have shown that Freundlich adsorption isotherm is fitted well and the adsorption process followed Pseudo-second order kinetic model. The comparative between oxidation and adsorption method using the best parameters on sulfide removal from actual petroleum refinery wastewater was determined. The efficiency of oxidation method which is able to remove sulfide concentration is 99.83% from 300 mg/L to 0.5 mg/L, COD concentration is 98.29% from 4100 mg/L to 70 mg/L, and pH is 29.08% from 11.86 to 8.41. While, the efficiency of adsorption method which is able to remove sulfide concentration is 95.70% from 100 mg/L to 4.3 mg/L, COD concentration is 98.29% from 4100 mg/L to 70 mg/L, and pH is 3.0% from 12.00 to 11.65. Thus, it is concluded that oxidation method more effective than adsorption method in sulfide removal from spent caustic. However, both methods were able to remove more than 90% removal especially on sulfide and COD concentration. It is recommended that oxidation method hybrid with adsorption method to provide more efficiency of sulfide removal. The information obtained from this study is useful for scale up purpose in the petroleum refining industry.

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