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UNIVERSITI TEKNOLOGI PETRONAS

Studies on the Removal of Sulfides from Wastewater

By

Naveed Ahmad

A THESIS
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DEGREE OF MASTER IN
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PERAK

May 2009

DECLARATION

I hereby declare that the 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 UTP or other institutions.

Signature: _____

Name : _____NAVEED AHMAD _____

Date : _____

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ABSTRACT

In the present work a thorough and systematic study has been made on the removal of sulfides by oxidation and precipitation methods. Both synthetically prepared sulfide solution and industrial waste water sample containing sulfide were treated by this method in the present investigations.

Iodometric and spectrophotometeric methods were used for the analysis of sulfide and sulfur bearing other radicals. The treatment was carried out by aeration in the presence of UV light, oxidation by hydrogen peroxide in the presence of ferric oxide catalyst, precipitation using iron salts followed by aeration and aeration in the presence of ultrasonic vibration. Aeration in the presence of UV light was found to be very effective for the removal of sulfide. The effects of sulfide concentration and partial pressure of oxygen on the kinetics of oxidation of sulfide under specific UV light intensity was investigated. Sulfide oxidation was found to be faster at higher UV light intensity. The catalyst synthesized for the oxidation of sulfide was analyzed by XRD, FT-IR, SEM and EDX. The precipitate formed in the treatment process was also analyzed following the above mentioned techniques. SEM analysis of ferric oxide synthesized by sol-gel technique revealed that the average particle size of the sample was less than 200nm. The XRD picture of the catalyst reveals that the presence of non-stiochiometric ferric oxide appears as a major crystalline phase. In the FT-IR spectra of the catalyst sample stretching vibration of FE-O was observed in different regions. Oxidation of sulfide by hydrogen peroxide in the presence of synthesized ferric oxide catalyst was also found to be very effective.

The effects of sulfide concentration, catalyst loading, hydrogen peroxide dosing and temperature were investigated on the kinetics of sulfide oxidation. Sulfide oxidation by hydrogen peroxide in the presence of catalyst was found to be faster with the increase in temperature. Before oxidation initially the sulfide solution was highly alkaline (pH =11-12) and during oxidation the solution became almost neutral (pH=7-8). It was observed that by precipitation more than 70% of sulfide was removed from the wastewater. Complete removal of sulfide was achieved by aeration in the presence of precipitate formed. From the SEM picture of the precipitate formed no distinct or definite size of the particle was observed. Average particle size of the precipitate was found to be 500nm. From the EDX analysis of the precipitate, it was confirmed that

Fe and S were the major elements present in the sample. Some amount of Na and Cl were also observed in the sample.

Aeration in the presence of ultrasonic vibration has also been carried out for the removal of sulfide. The effects of air flow rate and sulfide concentration were investigated on the kinetics of sulfide oxidation.

Oxidation was carried out at different ultrasonic vibration frequencies. Rate of sulfide oxidation was found faster at higher air flow rate and sulfide concentration.

The results of this study are expected to be useful for the assessment of different alternatives for the removal of sulfide as well as for actual remediation of sulfidic wastewater in chemical and allied industries.

ABSTRAK

Sulfida selalunya ditemui di dalam air buangan yang dihasilkan dari industri – industri kimia dan petrokimia. Sulfida adalah bahan yang larut di dalam air, maka ia menjadi susah untuk diasingkan. Sekiranya kuantiti sulfida melebihi had yang dibenarkan, ia boleh menjadi bahan yang beracun untuk hidupan. Oleh itu, pengeluaran sulfida dalam air buangan industri adalah penting dengan mengubahnya menjadi bahan yang kurang beracun dan mudah dipisahkan iaitu sulfat.

Daripada kajian yang sedia ada, sulfida boleh teroksida dengan menggunakan agen-agen pengoksidaan seperti ozone, hidrogen peroksida dan udara. Proses pengoksidaan in boleh berlaku dengan atau tanpa pemangkin yang sesuai

Process "Wet Air Oxidation"pada suhu dan tekanan tinggi adalah saatu kaedah pengeluaran sulfida yang popular dengan mengubahnya menjadi sulfat.

Kajian yang terperinci dan sistematik telah dijalankan untuk pengeluaran sulfida menggunakan kaedah pengoksidaan dan pemendakan . Larutan sulfida yang disediakan secara sintetik dan air buangan dari industri yang mengandungi sulfida digunakan sebagai bahan eksperimen dalam kajian ini.

Kaedah 'Iodometric' dan 'Spectrophometric' adalah antara kaedah yang digunakan untuk menganalisis sulfida dan sulfur yang juga membawa radikal lain. Pengeluaran sulfida boleh dilakukan dengan mengguakan kaedah-kaedah berikut:

Pengudaraan menggunakan cahaya UV.

Pengoksidaan sulfida dengan Hidrogen Peroksida dan kehadiran pemangkin Ferik Oksida yang disediakan di makmal menggunakan kaedah 'Sol-Gel'.

Pengeluaran sulfida dengan kaedah pemendakan diikuti dengan proses pengudaraan mengunakan 'iron salts' dengan nisbah Fe^{+2}/Fe^{+3} yang berbeza.

Pengudaraan sulfida menggunakan 'Ultrasonic Vibrator'.

Proses pengudaraan sulfida menggunakan cahaya UV didapati sebagai kaedah yang sangat efektif. Kesan konsentrasi sulfida dan 'Oxygen Partial Pressure' ke atas kinetik pengoksidaan sulfida di bawah keamatan cahaya UV yang spesifik telah dikaji. Pengoksidaan sulfida didapati lebih cepat saat apabila menggunakan keamatan cahaya UV lebih tinggi .

Pemangkin yang disintesis untuk pengoksidaan sulfida telah dianalisis menggunakan alat XRD, FT-IR, SEM and EDX. Mendak yang terbentuk juga dianalisa menggunakan teknik – teknik di atas. Analisa SEM untuk Ferik Oksida yang

disintesasi dengan Teknik 'Sol-Gel' menunjukkan bahawa saiz partikel ferik oksida adalah kurang dari 200 nm. Gambar XRD pemangkin ferik oksida menunjukkan kehadiran Ferik Oksida yang tidak berstoikiometri sebagai fasa berhablur utama. Dalam spektra FT-IR sampel pemangkin, "stretching vibration" FE-O dapat dilihat di beberapa tempat yang berbeza.

Pengoksidaan sulfida dengan hidrogen peroksida dengan kehadiran pemangkin ferik oksida juga didapati sangat efektif. Kesan konsentrasi sulfide, muatan pemangkin, dos hidrogen peroksida dan suhu dikaji ke atas kinetik pengoksidaan sulfida.

Pengoksidaan sulfida menggunakan hidrogen peroksida dalam kehadiran pemangkin didapati berlaku dengan lebih cepat dengan peningkatan suhu.

Sebelum proses pengoksidaan, larutan sulfida adalah amat alkali (pH = 11-12) dan ketika proses pengoksidaan, larutan sulfida menjadi hampir neutral (pH=7-8). Didapati dengan proses pemendakan, lebih daripada 70% sulfida dapat dikeluarkan daripada air buangan. Pengeluaran sulfida secara sempurna dapat dicapai melalui pengudaraan ketika pembentukan mendak. Gambar SEM mendak yang terbentuk menunjukkan partikel mendak tidak mempunyai saiz yang berbeza atau tetap. Kebanyakan partikel didapati mepunyai saiz 500 nm.

Daripada analisa EDX mendak, Ferum dan Sulfur adalah elemen utama di dalam sampel . Sedikit natrium dan klorida juga ditemui di dalam sampel.

Pengudaraan menggunakan 'ultrasonic vibrator' juga turut dikaji sebagai salah satu kaedah pengeluaran sulfida. Kesan kadar kelajuan udara dan konsentrasi sulfida dikaji dalam kinetik pengoksidaan sulfida.

Proses pengoksidaan turut dilaksanakan menggunakan frekuensi 'ultrasonic vibrator' yang berbeza. Kadar pengoksidaan sulfida didapati lebih cepat dengan kadar kelajuaan udara dan konsentrasi sulfida yang lebih tinggi.

Hasil kajian ini diharapkan berguna dan menbantu dalam kajian alternatif lain untuk proses pengeluaran sulfida dan pemulihan air buangan bersulfidik dalam industri-industri kimia dan bersekutu.

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