UNIVERSITI SAINS MALAYSIA

LAPORAN AKHIR PROJEK PENYELIDIKAN JANGKA *PENDEK*

FINAL REPORT OF SHORT TERM RESEARCH PROJECT

Sila kemukakan laporan akhir ini melalui Jawatankuasa Penyelidikan di Pusat Pengajian dan Dekan/Pengarah/Ketua Jabatan kepada Pejabat Pelantar Penyelidikan

RECEIVED
15 APR 2011
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ENTERP

1. **Nama Ketua Penyelidik:**
Name of Research Leader : **Prof. Bassim H. Hameed**

☑ Profesor Madya/ *Prof.* ☐ Dr./ *Dr.* ☐ Encik/Puan/Cik *Mr/Mrs/Ms*

2. **Pusat Tanggungjawab (PTJ):**
School/Department **School of Chemical Engineering**

3. **Nama Penyelidik Bersama:**
Name of Co-Researcher **Dr. Suhairi Abdul Sata**

4. **Tajuk Projek:**
Title of Project **DEVELOPMENT OF HETEROGENEOUS CATALYSTS FOR DEGRADATION OF DYE POLLUTANTS BY ADVANCED OXIDATION PROCESSES**

5. **Ringkasan Penilaian**/*Summary of Assessment*:	Tidak Mencukupi *Inadequate* 1	2	Boleh Diterima *Acceptable* 3	Sangat Baik *Very Good* 4	5
i) **Pencapaian objektif projek:** *Achievement of project objectives*	☐	☐	☐	☐	☑
ii) **Kualiti output:** *Quality of outputs*	☐	☐	☐	☐	☑
iii) **Kualiti impak:** *Quality of impacts*	☐	☐	☐	☑	☐
iv) **Pemindahan teknologi/potensi pengkomersialan:** *Technology transfer/commercialization potential*	☐	☐	☑	☐	☐
v) **Kualiti dan usahasama :** *Quality and intensity of collaboration*	☐	☐	☑	☐	☐
vi) **Penilaian kepentingan secara keseluruhan:** *Overall assessment of benefits*	☐	☐	☐	☑	☐

6. Abstrak Penyelidikan

(Perlu disediakan di antara 100 - 200 perkataan di dalam **Bahasa Malaysia dan juga Bahasa Inggeris.** Abstrak ini akan dimuatkan dalam Laporan Tahunan Bahagian Penyelidikan & Inovasi sebagai satu cara untuk menyampaikan dapatan projek tuan/puan kepada pihak Universiti & masyarakat luar).

Abstract of Research
(An abstract of between 100 and 200 words must be prepared in Bahasa Malaysia and in English). This abstract will be included in the Annual Report of the Research and Innovation Section at a later date as a means of presenting the project findings of the researcher/s to the University and the community at large)

Abstrak Penyelidikan (Bahasa Malaysia)

Tujuan kajian ini dijalankan adalah untuk mengkaji sistem pengunaan mangkin berlainan fasa untuk rawatan penyahwarnaan bagi dua jenis pencelup sebagai model air sisa daripada industri tekstil iaitu Acid Red 1 (AR1) dan Reactive Black 5 (RB5). Mangkin ini dihasilkan daripada bahan yang berkos rendah dan juga bahan sisa daripada pertanian yang senang didapati di Malaysia iaitu Montmorillonite K10, granite, kaolin dan juga abu daripada sekam padi dengan mengunakan teknik peranakan. Penjerapan/penyahjerapan Nitrogen, Penyerakan Tenaga X-ray (EDX), mikroskop elektron imbasan, Spektroskop pramerah jelmaan Fourier (FTIR) dan spektroskop pembelauan serbuk X-ray digunakan untuk pencirian mangkin. Kecekapan sistem/proses ini dipengaruhi oleh parameter seperti kesan muatan Fe(III) oksida di atas penyokong, dos mangkin, pH, kepekatan hidrogen peroksida, kepekatan awal pencelup yang digunakan dan suhu bagi tindak balas. Keadaan optimum bagi tindak balas yang diperolehi daripada proses penyahwarnaan bagi kedua□dua jenis pencelup ialah 0.070-0.14 wt.% bagi sokongan yang mengandungi Fe, 3.50-5.0 g L^{-1} bagi dos mangkin, pH 2.0-2.50 dan 8-20 mM kepekatan awal hidrogen peroksida dengan menggunakan 50 mg L^{-1} kepekatan awal pencelup pada suhu 30 °C tindak balas. Dibawah keadaan optimum, 96-99 % kecekapan penyahwarnaan dicapai bagi AR1 dan RB5 dicapai dalam masa 150 min dan 240 min bagi Fe-kaolin untuk penyahwarnaan AR1. Perubahan spektrum UV-Vis bagi sampel AR1 dan RB5 dalam larutan berair semasa perawatan jenis Fenton dikaji. Ikatan kumpulan azo (-N=N-) lebih senang untuk dimusnahkan dibandingkan dengan kumpulan cincin aromatik bagi kedua-dua jenis pencelup dengan menggunakan proses pengoksidaan jenis Fenton. Kajian bagi kestabilan jangka panjang bagi semua jenis mangkin (Fe-MK10, Fe-RHA, Fe-granite dan Fe-kaolin) menunjukkan terdapat penyusutan aktiviti selepas empat kali kitaran penggunaan. Ini adalah disebabkan oleh kehilangan jisim mangkin dan juga pengurangan tapak aktif mangkin semasa kajian dijalankan. Keputusan bagi kajian yang dijalankan ini menambahkan ilmu pengetahuan asas bagi perawatan air sisa yang mengandungi AR1 dan RB5 dan juga jenis□jenis pencelup azo yang lain dengan menggunakan proses pengoksidaan jenis Fenton ini.

Abstract of Research (English)

The primary aim of this study was to prepare Fe-based catalysts for the decolorization of two types of dye as a model of real textile wastewater, Acid Red 1 (AR1) and Reactive Black 5 (RB5). The catalysts were prepared from low-cost materials and agricultural by-product abundantly available in Malaysia, namely Montmorillonite K10, granite, kaolin and rice husk ash by impregnation method. Nitrogen adsorption/desorption, Scanning Electron Microscope (SEM), Fourier Transform Infrared spectroscopy (FTIR) and X-ray powder diffraction (XRD) were used to characterize the catalysts. The efficiency of the reaction system was explored as a function of the experimental parameters such as effect of iron (III) oxide loading on the supports, catalyst dosage, pH, hydrogen peroxide concentration, initial dye concentration and reaction temperature. The optimum conditions obtained for decolorization process for both dyes were 0.070-0.14 wt.% of Fe-contained supports, 3.50-5.0 g L^{-1} of catalyst dosage, 2.0-2.50 pH and 8.0-20 mM of initial concentration of hydrogen peroxide with 50 mg L^{-1} of initial dye concentration at 30 °C reaction temperature. Under the optimal condition, 96-99 % decolorization efficiency of AR1 and RB5 were achieved within 150 min of reaction and 240 min of time reaction was needed for Fe-Kaolin to decolorize AR1. The study of long-term stability revealed that Fe-MK10, Fe-RHA, Fe-granite and Fe-kaolin showed some activity decay after reuse for four consecutive cycles. This is due to the loss of catalysts (Fe-MK10, Fe-RHA, Fe-granite and Fe-kaolin) and active phase leaching during the experiments. The results can provide fundamental knowledge for the treatment of wastewater containing AR1 and RB5 and other azo dyes by Fenton-like oxidation process.

7. Sila sediakan laporan teknikal lengkap yang menerangkan keseluruhan projek ini.
[Sila gunakan kertas berasingan]
Applicant are required to prepare a Comprehensive Technical Report explaining the project.
(This report must be appended separately)

Attached is a comprehensive report.

Senaraikan kata kunci yang mencerminkan penyelidikan anda:
List the key words that reflects your research:

Bahasa Malaysia	*Bahasa Inggeris*
Penyahwarnaan	Decolorization
Sisa tekstil	Textile wastewater
Pemangkin berasakan ferum	Fe-based catalyst
Teknik peranakan	Impregnation method

8. Output dan Faedah Projek
Output and Benefits of Project

(a) * **Penerbitan Jurnal**
Publication of Journals
(Sila nyatakan jenis, tajuk, pengarang/editor, tahun terbitan dan di mana telah diterbit/diserahkan)
(State type, title, author/editor, publication year and where it has been published/submitted)

1. Daud, N.K. and Hameed, B.H. (2010). Decolorization of Acid Red 1 by heterogeneous Fenton-like process using rice husk ash-based catalyst. Journal of Hazardous Material, 176, 938–944. **(Impact Factor 2009: 4.144)**

2. Daud, N.K. and Hameed, B.H. (2010). Fenton-like oxidation of reactive black 5 solutions using iron exchanged Montmorillonite K10 as a catalyst. Journal of Hazardous Material, 176, 1118–1121. **(Impact Factor 2009: 4.144)**

3. Daud, N.K., Hameed, B.H. and Ahmad, M.A. (2010). Decolorization of Acid Red 1 dye solution by Fenton-like process using Fe-Montmorillonite K10 catalyst. Chem. Eng. Journal, 165, 111-116. **(Impact Factor 2009: 2.816).**

4. N.K. Daud, B.H. Hameed (2011), Acid Red 1 dye decolorization by heterogeneous Fenton-like reaction using Fe/kaolin catalyst, Desalination, 269, 291-293. **(Impact Factor 2009: 2.034)**

5. Ai Ni Soon, B.H. Hameed, Heterogeneous catalytic treatment of synthetic dyes in aqueous media using Fenton and photo-assisted Fenton process, Desalination 269 (2011) 1–16. **(Impact Factor 2009: 2.034)**

6. H. Hassan, B.H. Hameed, Oxidative decolorization of Acid Red 1 solutions by Fe–zeolite Y type catalyst, Desalination, Accepted manuscript, March 2011. **(Impact Factor 2009: 2.034)**

7. H. Hassan, B.H. Hameed, Fe-ball clay as effective heterogeneous Fenton type catalyst for the decolorization of Reactive Blue 4, Chemical Engineering Journal, Under major revision, (MS No: CEJ-D-10-02593) April 2011.

(b) **Faedah-faedah lain seperti perkembangan produk, pengkomersialan produk/pendaftaran paten atau impak kepada dasar dan masyarakat.**
State other benefits such as product development, product commercialisation/patent registration or impact on source and society.

/

* Sila berikan salinan/*Kindly provide copies*

(c) **Latihan Sumber Manusia**
Training in Human Resources

i) Pelajar Sarjana:
Graduates Students
(Provide names, degrees and status)

1. Nor Khonisah Binti Daud, **MSc** (by research), Fenton-like oxidation of acidic and reactive dyes using natural-materials supported catalysts, School of Chemical; Engineering, Completed 2010.
2. Hamizura Binti Hassan, **MSc** (by research), Decolorization of dye pollutants by Fenton-oxidation process using zeolite and natural based catalysts, School of Chemical; Engineering, Completed 2011.
3. Soon Ai Ni, (**PhD**), Development of Mesoporous Heterogeneous Catalysts for Wastewater Pollutants Abatement by Advanced Oxidation Process, School of Chemical Engineering, On going.

ii) Lain-lain:
Others

(2) Final year research project:

1. Nur Hidayah Bt. Mohmmad Azmi (2010) Degradation of reactive Red 120 using a heterogeneous Fenton Process Catalyzed by Fe-Activated Carbon, School of Chemical Engineering, Universiti Sains Malaysia.

(3) Research Assistant

9. **Peralatan yang Telah Dibeli:**
Equipment that has been purchased

None

11/4/2011

Tandatangan Penyelidik
Signature of Researcher

Tarikh
Date

Komen Jawatankuasa Penyelidikan Pusat Pengajian/Pusat
Comments by the Research Committees of Schools/Centres

Projek penyelidikan telah dijalankan dgn jaya.

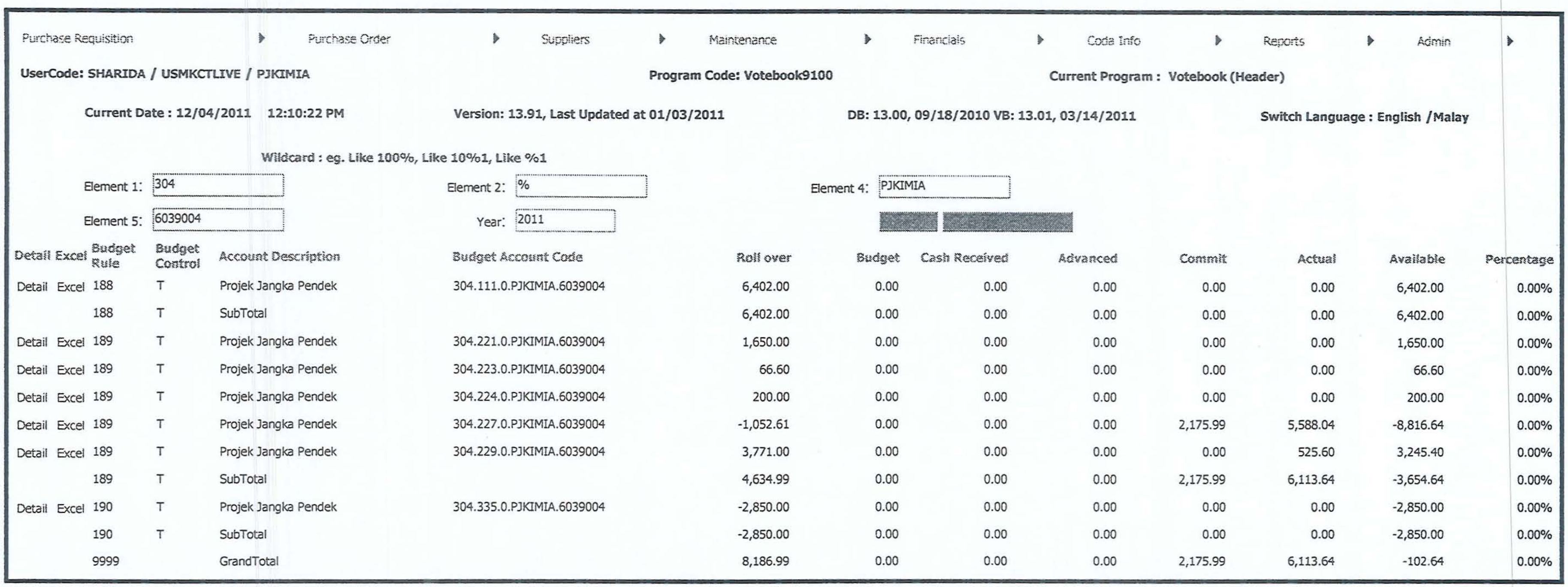
b/p

13/4/2011

TANDATANGAN PENGERUSI
JAWATANKUASA PENYELIDIKAN
PUSAT PENGAJIAN/PUSAT
Signature of Chairman
[Research Committee of School/Centre]

PROF. MADYA MOHAMAD ZAILANI ABU BAKAR
Timbalan Dekan
(Akademik & Pembangunan Pelajar)
b.p. Dekan

Tarikh
Date



UserCode: SHARIDA / USMKCTLIVE / PJKIMIA

Program Code: Votebook9100

Current Program : Votebook (Header)

Current Date : 12/04/2011 12:10:22 PM

Version: 13.91, Last Updated at 01/03/2011

DB: 13.00, 09/18/2010 VB: 13.01, 03/14/2011

Switch Language : English /Malay

Wildcard : eg. Like 100%, Like 10%1, Like %1

Element 1: 304

Element 2: %

Element 4: PJKIMIA

Element 5: 6039004

Year: 2011

Detail	Excel	Budget Rule	Budget Control	Account Description	Budget Account Code	Roll over	Budget	Cash Received	Advanced	Commit	Actual	Available	Percentage
Detail	Excel	188	T	Projek Jangka Pendek	304.111.0.PJKIMIA.6039004	6,402.00	0.00	0.00	0.00	0.00	0.00	6,402.00	0.00%
		188	T	SubTotal		6,402.00	0.00	0.00	0.00	0.00	0.00	6,402.00	0.00%
Detail	Excel	189	T	Projek Jangka Pendek	304.221.0.PJKIMIA.6039004	1,650.00	0.00	0.00	0.00	0.00	0.00	1,650.00	0.00%
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Detail	Excel	189	T	Projek Jangka Pendek	304.224.0.PJKIMIA.6039004	200.00	0.00	0.00	0.00	0.00	0.00	200.00	0.00%
Detail	Excel	189	T	Projek Jangka Pendek	304.227.0.PJKIMIA.6039004	-1,052.61	0.00	0.00	0.00	2,175.99	5,588.04	-8,816.64	0.00%
Detail	Excel	189	T	Projek Jangka Pendek	304.229.0.PJKIMIA.6039004	3,771.00	0.00	0.00	0.00	0.00	525.60	3,245.40	0.00%
		189	T	SubTotal		4,634.99	0.00	0.00	0.00	2,175.99	6,113.64	-3,654.64	0.00%
Detail	Excel	190	T	Projek Jangka Pendek	304.335.0.PJKIMIA.6039004	-2,850.00	0.00	0.00	0.00	0.00	0.00	-2,850.00	0.00%
		190	T	SubTotal		-2,850.00	0.00	0.00	0.00	0.00	0.00	-2,850.00	0.00%
		9999		GrandTotal		8,186.99	0.00	0.00	0.00	2,175.99	6,113.64	-102.64	0.00%

FENTON–LIKE OXIDATION OF ACID AND REACTIVE DYES USING NATURAL–MATERIALS SUPPORTED CATALYSTS

by

NOR KHONISAH BINTI DAUD

Thesis submitted in fulfilment of the
requirements for the degree of
Master of Science

June 2010

PENGOKSIDAAN JENIS FENTON BAGI ASID DAN PENCELUP REAKTIF MENGGUNAKAN MANGKIN YANG DISOKONG OLEH BAHAN SEMULAJADI

ABSTRAK

Tujuan kajian ini dijalankan adalah untuk mengkaji sistem pengunaan mangkin berlainan fasa untuk rawatan penyahwarnaan bagi dua jenis pencelup sebagai model air sisa daripada industri tekstil iaitu Acid Red 1 (AR1) dan Reactive Black 5 (RB5). Mangkin ini dihasilkan daripada bahan yang berkos rendah dan juga bahan sisa daripada pertanian yang senang didapati di Malaysia iaitu Montmorillonite K10, granite, kaolin dan juga abu daripada sekam padi dengan mengunakan teknik peranakan. Penjerapan/penyahjerapan Nitrogen (N_2), Penyerakan Tenaga X–ray (EDX), mikroskop elektron imbasan (SEM), Spektroskop pramerah jelmaan Fourier (FTIR) dan spektroskop pembelauan serbuk X–ray (XRD) digunakan untuk pencirian mangkin. Kecekapan sistem/proses ini dipengaruhi oleh parameter seperti kesan muatan Fe(III) oksida di atas penyokong, dos mangkin, pH, kepekatan hidrogen peroksida, kepekatan awal pencelup yang digunakan dan suhu bagi tindak balas. Keadaan optimum bagi tindak balas yang diperolehi daripada proses penyahwarnaan bagi kedua–dua jenis pencelup ialah 0.070–0.14 wt.% bagi sokongan yang mengandungi Fe, 3.50–5.0 g L^{-1} bagi dos mangkin, pH 2.0–2.50 dan 8–20 mM kepekatan awal hidrogen peroksida dengan menggunakan 50 mg L^{-1} kepekatan awal pencelup pada suhu 30 ^{o}C tindak balas. Dibawah keadaan optimum, 96–99 % kecekapan penyahwarnaan dicapai bagi AR1 dan RB5 dicapai dalam masa 150 min dan 240 min bagi Fe–kaolin untuk penyahwarnaan AR1. Perubahan spektrum UV–Vis bagi sampel AR1 dan RB5 dalam larutan berair semasa perawatan

jenis Fenton dikaji. Ikatan kumpulan azo (–N=N–) lebih senang untuk dimusnahkan dibandingkan dengan kumpulan cincin aromatik bagi kedua–dua jenis pencelup dengan menggunakan proses pengoksidaan jenis Fenton. Kajian bagi kestabilan jangka panjang bagi semua jenis mangkin (Fe–MK10, Fe–RHA, Fe–granite dan Fe–kaolin) menunjukkan terdapat penyusutan aktiviti selepas empat kali kitaran penggunaan. Ini adalah disebabkan oleh kehilangan jisim mangkin dan juga pengurangan tapak aktif mangkin semasa kajian dijalankan. Ujian pelunturan mengesan Fe yang hilang daripada mangkin adalah kurang daripada 5 mg L^{-1} didapati masih mematuhi peraturan Peraturan Kualiti (sisa–sisa dan bahan buangan industri) Persekitaran 1979 yang dilaksanakan di Malaysia. Keputusan bagi kajian yang dijalankan ini menambahkan ilmu pengetahuan asas bagi perawatan air sisa yang mengandungi AR1 dan RB5 dan juga jenis–jenis pencelup azo yang lain dengan menggunakan proses pengoksidaan jenis Fenton ini.

FENTON-LIKE OXIDATION OF ACID AND REACTIVE DYES USING NATURAL–MATERIALS SUPPORTED CATALYSTS

ABSTRACT

The primary aim of this study was to prepare Fe–based catalysts for the decolorization of two types of dye as a model of real textile wastewater, Acid Red 1 (AR1) and Reactive Black 5 (RB5). The catalysts were prepared from low–cost materials and agricultural by–product abundantly available in Malaysia, namely Montmorillonite K10, granite, kaolin and rice husk ash by impregnation method. Nitrogen adsorption/desorption, Energy Disperse X–ray (EDX), Scanning Electron Microscope (SEM), Fourier Transform Infrared spectroscopy (FTIR) and X–ray powder diffraction (XRD) were used to characterize the catalysts. The efficiency of the reaction system was explored as a function of the experimental parameters such as effect of iron (III) oxide loading on the supports, catalyst dosage, pH, hydrogen peroxide concentration, initial dye concentration and reaction temperature. The optimum conditions obtained for decolorization process for both dyes were 0.070–0.14 wt.% of Fe–contained supports, 3.50–5.0 g L^{-1} of catalyst dosage, 2.0–2.50 pH and 8.0–20 mM of initial concentration of hydrogen peroxide with 50 mg L^{-1} of initial dye concentration at 30 ^{o}C reaction temperature. Under the optimal condition, 96–99 % decolorization efficiency of AR1 and RB5 were achieved within 150 min of reaction and 240 min of time reaction was needed for Fe–Kaolin to decolorize AR1. The UV–Vis spectral changes of AR1 and RB5 in aqueous solution during Fenton–like treatment were studied. It was easier to destruct the azo linkage (–N=N–) group than to destruct the aromatic rings of both dyes by Fenton–like oxidation. The study of long–term stability revealed that Fe–MK10, Fe–RHA, Fe–

granite and Fe–kaolin showed some activity decay after reuse for four consecutive cycles. This is due to the loss of catalysts (Fe–MK10, Fe–RHA, Fe–granite and Fe–kaolin) and active phase leaching during the experiments. Leaching test indicated that the leached iron from the catalyst was less than 5 mg L^{-1} which is within the Malaysian regulation of Environmental quality Act 1979. The results can provide fundamental knowledge for the treatment of wastewater containing AR1 and RB5 and other azo dyes by Fenton–like oxidation process.

DECOLORIZATION OF DYE POLLUTANTS BY FENTON-LIKE OXIDATION PROCESS USING ZEOLITE AND NATURAL CLAY BASED CATALYSTS

HAMIZURA BINTI HASSAN

UNIVERSITI SAINS MALAYSIA

2011

DECOLORIZATION OF DYE POLLUTANTS BY FENTON-LIKE OXIDATION PROCESS USING ZEOLITE AND NATURAL CLAY BASED CATALYSTS

by

HAMIZURA BINTI HASSAN

Thesis submitted in fulfillment of the
requirements for the degree
of Master of Science

MARCH 2011

PENYAHWARNAAN BAHAN PENCELUP MELALUI PROSES PENGOKSIDAAN JENIS FENTON MENGGUNAKAN MANGKIN ZEOLIT DAN BAHAN SEMULAJADI BERASASKAN TANAH LIAT

ABSTRAK

Penyahwarnaan bagi dua jenis bahan pencelup iaitu Acid Red 1 (AR1) dan Reactive Blue 4 (RB4) melalui proses pengoksidaan jenis Fenton menggunakan mangkin zeolit dan bahan semulajadi berasaskan tanah liat dalam sistem berkelompok dikaji. Pemangkin ini berjaya dihasilkan menggunakan teknik peranakan. Pencirian mangkin telah dijalankan menggunakan kaedah mikroskopi electron pengimbas (SEM), spektroskopi inframerah transformasi Fourier (FTIR), penjerapan/penyahjerapan nitrogen dan penyerakan tenaga x-ray (EDX). Kecekapan mangkin dalam proses penyahwarnaan bahan pencelup diuji melalui parameter-parameter seperti kesan ferum ion pembebanan di atas sokongan, dos bagi pemangkin, pH, kepekatan awal hidrogen peroksida dan bahan pencelup yang digunakan dan suhu bagi tindak balas. Di samping itu, penggunaan semula pemangkin dan jumlah ferum yang larut lesap dari pemangkin selepas proses penyahwarnaan turut dikaji. Melalui ujikaji penyahwarnaan secara berkelompok, keputusan menunjukkan tahap kereaktifan pemangkin bertambah sehingga mencecah tahap optimum bagi setiap peningkatan jumlah ferum ion pembebanan di atas sokongan, dos bagi pemangkin, suhu ujikaji, kepekatan awal hidrogen peroksida dan pengurangan nilai pH. Lebihan jumlah ferum ion pembebanan di atas sokongan, dos bagi pemangkin, suhu ujikaji, kepekatan awal hidrogen peroksida boleh mengakibatkan kesan pengaut kepada hidroksi radikal dan mengurangkan kadar penyahwarnaan. Keadaan terbaik yang diperolehi daripada proses penyahwarnaan bagi kedua-dua bahan pencelup ialah 0.60–1.0 wt.% bagi sokongan yang mengandungi ferum, 2.50–5.0 g/L bagi dos pemangkin, pH dari 2.5–3.0 dan 8.0–20 mM bagi kepekatan awal hidrogen peroksida dengan menggunakan 50 mg L^{-1} kepekatan awal bahan pencelup pada 30 °C suhu tindak balas. Dengan keadaan terbaik, lebih dari 98% kecekapan penyahwarnaan bagi AR1 dan RB4 berjaya dicapai dalam masa 60 min hingga 210 min masa tindak balas. Jumlah ferum yang larut lesap dari semua pemangkin mematuhi Peraturan Alam Sekeliling (2009) bagi industri efluen bagi kedua-dua penyahwarnaan bahan pencelup. Keputusan tersebut menunjukkan bahawa mangkin heterogen mempunyai tahap stability dan aktiviti yang tinggi. Ternyata kepekatan ferum ion yang rendah boleh memberi kelebihan yang besar buat Fenton heterogen proses jika dibandingkan dengan homogen Fenton proses. Keputusan menunjukkan bahawa Fenton heterogen proses merupakan proses yang berkesan untuk penyahwarnaan AR1 dan RB4 bahan pencelup.

DECOLORIZATION OF DYE POLLUTANTS BY FENTON-LIKE OXIDATION PROCESS USING ZEOLITE AND NATURAL CLAY BASED CATALYSTS

ABSTRACT

The decolorization of Acid Red 1 (AR1) and Reactive Blue 4 (RB4) dye by the Fenton-like oxidation process using zeolite and natural based catalysts in batch system were studied. Fe-zeolite Y type (Fe-ZYT), Fe-natural zeolite (Fe-NZ), Fe-ball clay (Fe-BC), and Fe-Kuala Kangsar clay (Fe-KKC) were successfully prepared via impregnation method. The prepared catalysts were characterized by Scanning Electron Microscope (SEM), Fourier Transform Infrared Spectroscopy (FTIR), X-ray powder diffraction (XRD), Nitrogen adsorption/desorption and Energy Disperse X-ray (EDX). The effectiveness of these catalysts in the decolorization of the dye as well as the influence of reaction parameters like effect of iron loading on the supports, catalyst dosage, pH, initial concentration of hydrogen peroxide and dye and reaction temperature were assessed. Besides, the reusability and the amounts of iron leached from the catalyst after the reaction completed was evaluated. Through a number of batch decolorization experiments under various conditions, it is found that the activity of the catalysts increased until they reached an optimum value by increasing iron loading on the supports, catalyst dosage, temperature, initial hydrogen peroxide concentrations and decreasing the pH. The excess of iron on the supports, catalyst dosage and initial hydrogen peroxide concentration may lead to the scavenging effect of hydroxyl radical and decreased the decolorization rate. The best conditions obtained for the decolorization process for both dyes were 0.60–1.0 wt.% Fe-contained supports, 2.50–5.0 g/L of catalyst dosage, pH from 2.5–3.0 and 8.0–20 mM of initial concentration of hydrogen peroxide with 50 mg/L of initial dye concentration at 30 °C reaction temperature. Under best conditions, more than 98% decolorization efficiency of AR1 and RB4 were achieved within 60–210 min reaction time. The amounts of iron leaching from all the catalysts prepared comply with the Environmental Quality (Industrial Effluents) Regulations, (2009) for both decolorization of AR1 and RB4. The result indicates that the heterogeneous catalyst had a long term stability and activity. Significantly lower concentration of iron ions in the bulk after the treatment could give a great advantage of the heterogeneous Fenton over the homogeneous Fenton type systems. The experimental results showed that the heterogeneous Fenton process was an effective process for the decolorization of AR1 and RB4 dyes.

SHORT TERM GRANT USM

FINAL REPORT

DEVELOPMENT OF HETEROGENEOUS CATALYSTS FOR DEGRADATION OF DYE POLLUTANTS BY ADVANCED OXIDATION PROCESSES

PROF. BASSIM H. HAMEED

School of Chemical Engineering, Engineering Campus,

Universiti Sains Malaysia

e-mail: chbassim@eng.usm.my

Fax: + 60-45941013

Development of heterogeneous catalysts for degradation of dye pollutants by advanced oxidation processes

Prof. Bassim H. Hameed

School of Chemical Engineering, Engineering Campus,
Universiti Sains Malaysia, 14300 Nibong Tebal, Penang, Malaysia
e-mail: chbassim@eng.usm.my
Fax: + 60-45941013

Abstract

The primary aim of this study was to prepare Fe-based catalysts for the decolorization of two types of dye as a model of real textile wastewater, Acid Red 1 (AR1) and Reactive Black 5 (RB5). The catalysts were prepared from low-cost materials and agricultural by-product abundantly available in Malaysia, namely Montmorillonite K10, granite, kaolin and rice husk ash by impregnation method. Nitrogen adsorption/desorption, Energy Disperse X-ray, Scanning Electron Microscope, Fourier Transform Infrared spectroscopy (FTIR) and X-ray powder diffraction were used to characterize the catalysts. The efficiency of the reaction system was explored as a function of the experimental parameters such as effect of iron (III) oxide loading on the supports, catalyst dosage, pH, hydrogen peroxide concentration, initial dye concentration and reaction temperature. The optimum conditions obtained for decolorization process for both dyes were 0.070-0.14 wt.% of Fe-contained supports, 3.50-5.0 g L^{-1} of catalyst dosage, 2.0-2.50 pH and 8.0-20 mM of initial concentration of hydrogen peroxide with 50 mg L^{-1} of initial dye concentration at 30 ^{o}C reaction temperature. Under the optimal condition, 96-99 % decolorization efficiency of AR1 and RB5 were achieved within 150 min of reaction and 240 min of time reaction was needed for Fe-Kaolin to decolorize AR1. The study of long-term stability revealed that Fe-MK10, Fe-RHA, Fe- granite and Fe-kaolin showed some activity decay after reuse for four consecutive cycles. This is due to the loss of catalysts (Fe-MK10, Fe-RHA, Fe-granite and Fe-kaolin) and active phase leaching during the experiments. Leaching test indicated that the leached iron from the catalyst was less than 5 mg L^{-1} which is within the Malaysian regulation of Environmental quality Act (Sewage and Industrial Effluents) 1979. The results can provide fundamental

knowledge for the treatment of wastewater containing AR1 and RB5 and other azo dyes by Fenton-like oxidation process.

1. Introduction

Coloured dye wastewater arises as a direct result of the production of the dye and also as a consequence of its use in the textile industry [1]. Dyes are chemicals which on binding with a material will give colour to the material. Over 7 x 10^5 tons and approximately 10,000 different types of dyes and pigments are produced worldwide annually and it is estimated that 10-15 % of the dyes are lost in the effluent during the dyeing process [2].

Reactive Black 5 (RB5) and Acid Red 1 (AR1) are the types of azo dye which are the dominant type of the dyes are widely used in the textile industries. These are designed to produce long lasting color and have very simple dyeing procedure. Coloured effluents can cause problems in several ways; dyes can have acute and/or chronic effects on exposed organisms in many rivers and waterways [3]. This kind of effluent is also resistant to biological treatment. Therefore, removal of such coloured agents from aqueous effluents is a significant environmental issue. There is currently wide range of treatment technologies for these types of wastewaters. Precipitation, ion exchange, solvent extraction, filtration and electrochemical treatment are the conventional methods for the removal of dyes from aqueous solutions [4-7]. All these methods have significant disadvantages such as incomplete ion removal, high-energy requirements and production of toxic sludge or other waste products that require further disposal.

The efficiency and simplicity of advanced oxidation processes make them a suitable choice for the removal of toxic chemicals from wastewaters in the recent years [8-11]. The use of H_2O_2 and Fenton reagents has been extensively reported [12-13]. Fenton's reagent (Fe^{2+}/H_2O_2) has been one of the most common homogeneous systems proposed for the treatment of textile wastewaters. However homogenous Fenton systems have some well-known drawbacks, e.g. a limited pH range, the production iron-contained sludge to dispose and the catalyst deactivation by iron complexing agents [14]. The use of heterogeneous solid Fenton catalysts such as iron oxide-contained supports can be an alternative. The abundance of agricultural by-products and low-cost materials in most continents of the world make it a strong candidate as supported catalysts for the removal of many pollutants from wastewaters. The Fenton-like processes have been used as a powerful source of hydroxyl radicals with H_2O_2 in the presence of metal cations, in very effective reaction conditions [15-16]. Iron salts, were adsorbed onto the surface of support, the reduction-oxidation reactions between Fe(III)/Fe(II) take place in presence of hydrogen peroxide which promote the formation of reactive components such as the hydroxyl ($^{\bullet}OH$) and the hydroperoxyl ($^{\bullet}OOH$) radicals. The radicals generated by the decomposition of hydrogen peroxide can oxidize organic compounds adsorbed over the catalyst or degrade soluble organic compounds in the vicinity of iron active ions present at both the catalyst surface and in the bulk liquid phase. Thus, the formed Fe^{2+}/Fe^{3+} complexes on the surface of support can react with H_2O_2 thus allowing iron ions to participate in the Fenton catalytic cycle [17].

The objectives are to:

(1) Prepare a series of heterogeneous catalysts for degradation of wastewater containing textile dyes.

(2) Evaluate the effectiveness of prepared catalysts for degradation of textile dyes.

(3) Characterise the prepared catalysts for their physical and chemical properties.

(4) Study the influence of reaction conditions (initial dye concentration, H_2O_2 dose, catalysts dose, pH and temperature) on the catalytic degradation activity of prepared catalysts.

2. Experimental procedures

2.1 Materials

The azo dye, Reactive Black 5 (CAS number = 17095-24-8, Synonyms = Remazol Black B, empirical formula = $C_{26}H_{21}N_5Na_4O_{19}S_6$, molecular weight = 991.82, and $\lambda_{max} = 597$ nm) and Acid Red 1 (CAS number = 3734-67-6, synonyms = Amido Naphthol Red G and Azophloxine, empirical formula = $C_{18}H_{13}N_3Na_2O_8S_2$, molecular weight = 509.42 and $\lambda_{max} = 532$ nm), was provided by Sigma-Aldrich, Malaysia and used without purification. H_2O_2 solution (30 %) was of analytical grade and purchased from Merck Chemicals, Malaysia. Distilled water was used throughout the experiments. The initial pH of the solution was adjusted using 1.0 M NaOH or 1.0 M H_2SO_4 to explore the effect of the pH.

2.2 Preparation of Catalysts

The catalysts (Fe-RHA, Fe-MK10, Fe-granite and Fe-kaolin) were prepared by the impregnation method. In this process, the specific amounts of $Fe(NO_3)_3 \cdot 9H_2O$ (Merck) (0.010-0.14 wt.% of iron ions in supports catalyst) were dissolved in a beaker containing 50 mL of distilled water. Then, supports powder (MK10, RHA, granite and kaolin) were added to this aqueous solution and were stirred constantly in the water bath until all water was evaporated. After impregnation, the samples were dried at 105 °C for 12 h, followed by calcination at 500 °C for 4 h in a muffle furnace under air atmosphere.

2.3 *Catalysts characterization*

The catalysts were characterized using various techniques to study their respective physical and chemical characteristics.

- Fourier Transform Infrared Spectroscopy (FTIR)
- Nitrogen Adsorption-Desorption Isotherms
- X-Ray Diffraction (XRD)
- Scanning Electron Microscope (SEM)
- Energy Disperse X-Ray (EDX)

2.4 *Catalytic activity*

All experiments were carried out in 250 mL-stoppered glasses (Erlenmeyer flask) placed in a thermostated water-bath with an agitation of 130 rpm for 150 min. Each experimental run was performed by taking an appropriate amount of stock dye solution followed by dilution with distilled water to 200 mL. Predetermined amounts of impregnated catalyst were then added to the flask. Also, initial solution pH values were adjusted to the desired values by using prepared 1.0 M H_2SO_4 or 1.0 M NaOH solution. The reactions commenced when predetermined amounts of H_2O_2 solution were added to the flask. Thereafter, three mL volume of samples were withdrawn periodically and analyzed using a UV-Vis spectrophotometer (Shimadzu, model UV 1601, Japan) with the maximum absorbance wavelength for RB5 and AR1 at 597 and 532 nm, respectively. At each stage, the samples withdrawn were returned into the conical flask to prevent any loss of contents. Thus, the concentration of dye in the reaction mixture at different reaction times were determined by measuring the absorption intensity at λ_{max} = 597 and 532 nm and with a calibration curve.

Prior to the measurement, a calibration curve was obtained by using the standard dye solution with known concentration. The decolorization efficiency of dye is defined as follows:

$$\text{Decolorization efficiency (\%)} = [1-(C_t/C_o)] \times 100 \quad (1)$$

where C_o (mg L^{-1}) is the initial concentration of dye and C_t (mg L^{-1}) is the concentration of dye at reaction time, t (min).

The total iron concentration in the solution was determined using Atomic Absorption Spectrophotometer (AAS) model Shimadzu AA 6650 with the maximum absorbance wavelength (λ_{max}) of iron ion obtained at 248.35 nm. Similarly, prior to the measurement of the iron concentration, a calibration curve was obtained by using the standard iron ion solution in 0.10 M HNO_3 solution with known concentration. Finally, when the decolorization of dye was completed, the samples were analyzed to determine the total iron ion leached from the catalyst.

2.5 *Catalyst Stability Test*

Stability and leaching tests of catalysts were carried out with the optimum parameters by four consecutive cycles i.e. 12 h of operation. Between each experiment, the solid catalyst was filtered using filter paper and washed with distilled water several times and dried at 60 °C for 12 h in hot air oven.

2.6 *Leaching Test*

The total iron ions in the solution was determined using Atomic Absorption Spectrophotometer (AAS) model Shimadzu AA 6650 with the maximum absorbance wavelength (λ_{max}) of iron ion was founded at 248.35 nm. Prior to the measurement, a calibration curve was obtained by using the standard iron ion solution in 0.10 M HNO_3 solution with known concentrations. After the decolorization of dye completed, the samples were analyzed to determine the total iron ions leached from the catalyst.

3. **Results**

Characterization of catalyst is important in order to determine the physical and chemical properties and characteristics which directly influence the performance of the catalysts in the decolorization process.

3.1 *Surface area and pore characteristics*

The surface area and pore characteristics including the pore volume and pore size distribution of the catalysts were analyzed using Micromeritics ASAP 2020, surface area and porosity analyzer by nitrogen (N_2) adsorption at 77 K. The results are presented in Fig. 1 and 2. According to the modern IUPAC classification, the adsorption isotherms for Fe-MK10 and Fe-kaolin samples show a typical type IV, whereas for Fe-RHA and Fe-granite show a typical type V patterns with an inflection of N_2 absorbed volume at P/P_o about 0.30 (type H 3 hysteresis loop), indicating the existence of mesoporous system.

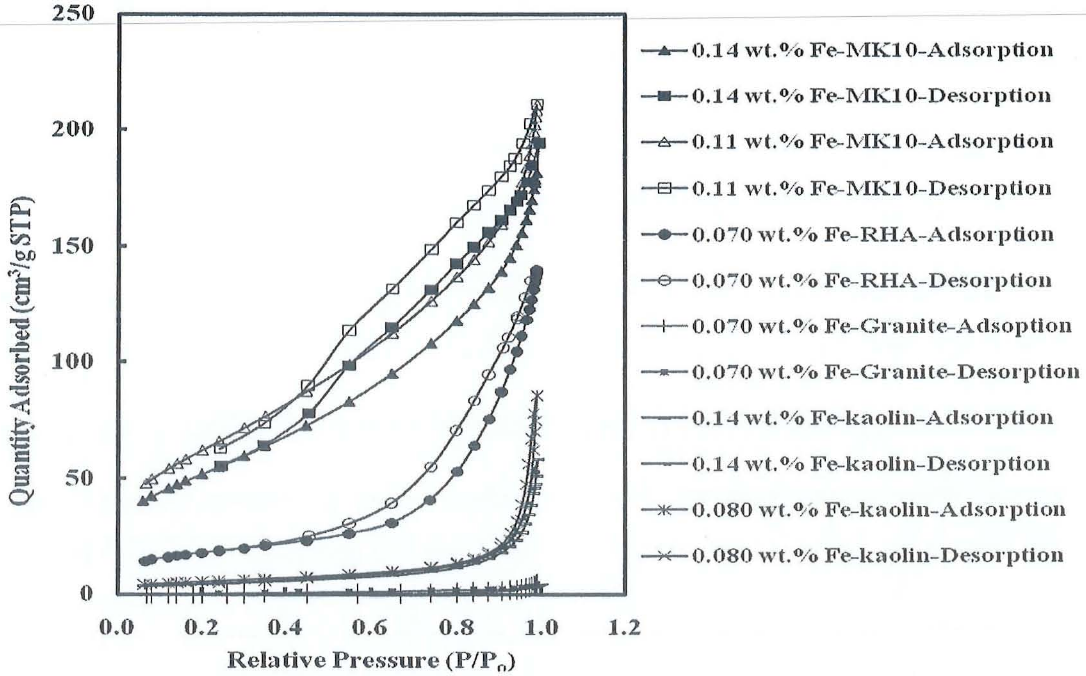


Fig. 1 N_2 adsorption/desorption isotherms of 0.11 wt.% Fe-MK10, 0.14 wt.% Fe-MK10, 0.070 wt.% Fe-RHA, 0.070 wt.% Fe-granite, 0.080 wt.% Fe-Kaolin and 0.14 wt.% Fe-kaolin catalysts

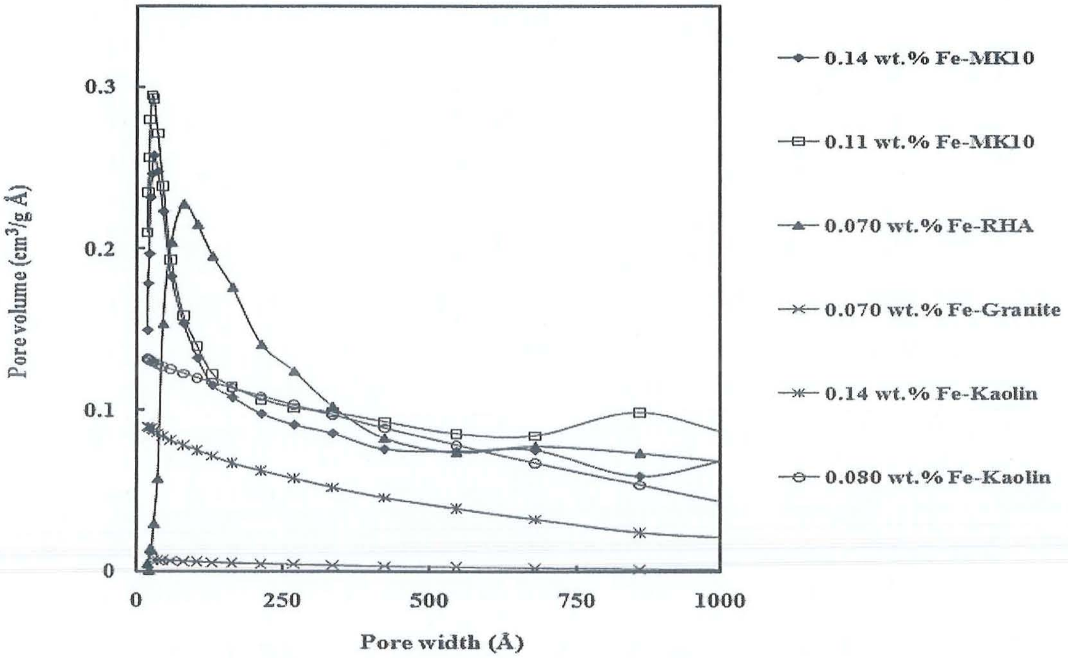
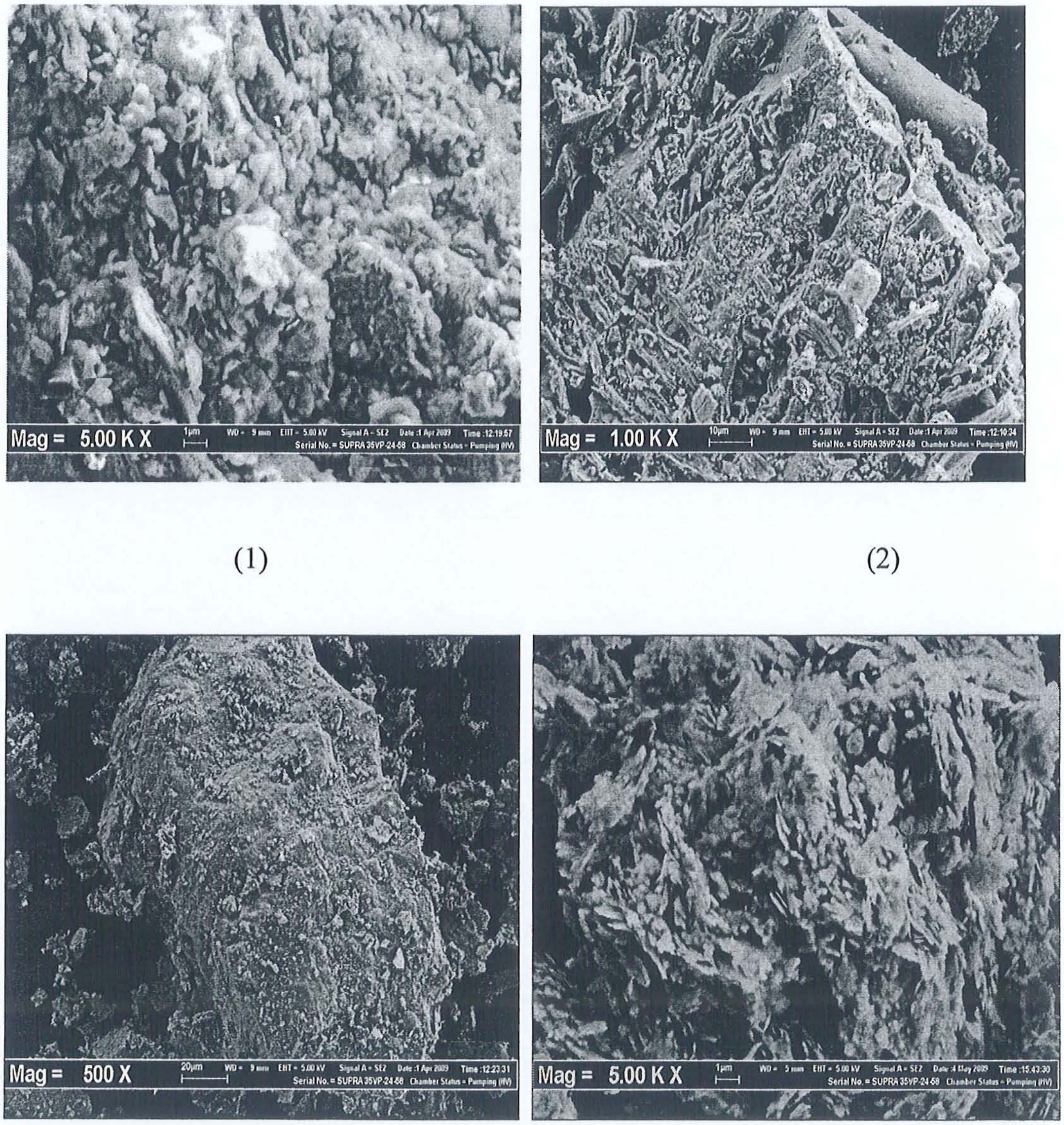


Fig. 2 Pore size distribution of 0.11 wt.% Fe-MK10, 0.14 wt.% Fe-MK10, 0.070 wt.% Fe-RHA, 0.070 wt.% Fe-granite, 0.080 wt.% Fe-kaolin and 0.14 wt.% Fe-kaolin catalysts

3.2 *Surface Morphology*

The surface morphology of the prepared catalysts was examined using scanning electron microscopy (SEM). The micrographs of prepared catalysts are presented in Plates 1-4 with different magnifications; the surface structure of the samples could be clearly seen.



(1) (2)

(3) (4)

Plates 1-4 SEM micrographs of (1) Fe-MK10 (Mag = 5000x) (2) Fe-RHA (Mag = 1000x) (3) Fe-granite (Mag = 500x) and (4) Fe-kaolin (Mag = 5000x) catalysts

3.3 Energy Dispersive X-Ray (EDX)

Elemental chemical analyses were performed to determine the composition of the original catalyst supports and the exact amount of iron in the final catalyst. The analysis was studied using energy dispersive X-ray (EDX) and the results are shown in Table 1.

Table 1 Chemical composition of prepared catalysts

Elements	Concentration (wt.%)									
	MK10	0.11 wt.% Fe-MK10	0.14 wt.% Fe-MK10	RHA	0.070 wt.% Fe-RHA	Granite	0.070 wt.% Fe-granite	Kaolin	0.080 wt.% Fe-kaolin	1.0wt.% Fe-kaolin
Fe	8.26	8.34	8.48	3.22	3.27	6.50	6.68	2.47	2.61	2.64
Si	39.82	38.73	38.49	52.97	52.78	44.59	43.65	24.89	24.81	24.06
Al	11.5	10.7	10.57	0.95	0.94	3.13	2.99	26.82	25.88	26.35
O	40.42	42.23	42.46	42.86	43.01	45.78	46.68	45.82	46.70	46.95

3.4 Fourier Transform Infrared (FTIR) analysis

Fourier transform infrared (FTIR) spectroscopy was conducted to identify the surface functional groups of the supports and impregnated catalysts. FTIR spectra (4000-400 cm^{-1}) of the MK10, 0.14 wt.% Fe-MK10 samples are presented in Fig. 3.

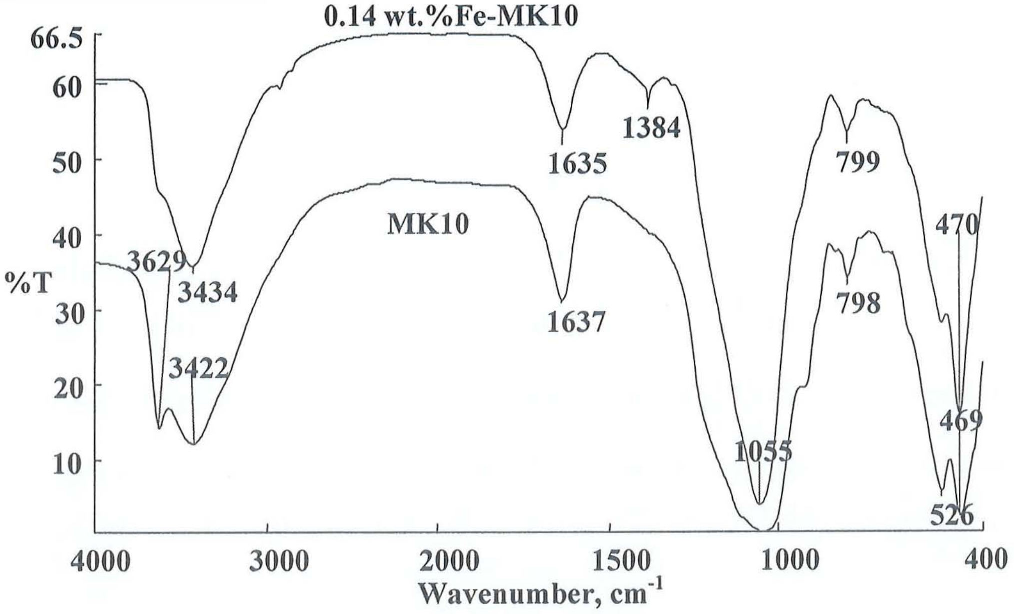


Fig. 3 FTIR spectra of MK10 and 0.14 wt.% Fe-MK10 catalyst

3.5 X-ray diffraction (XRD) analysis

X-ray diffraction analysis was used to study the iron chemical state and dispersion of Fe ion in catalysts. Fig. 4 shows the XRD diffractograms of MK10 and impregnated MK10. It can be seen that the impregnated MK10 maintains the layered structure in crystalline form, but with a remarkable loss of ordering if compared to the MK10 itself, indicating that the impregnation does not affect the individual layers but only their stacking.

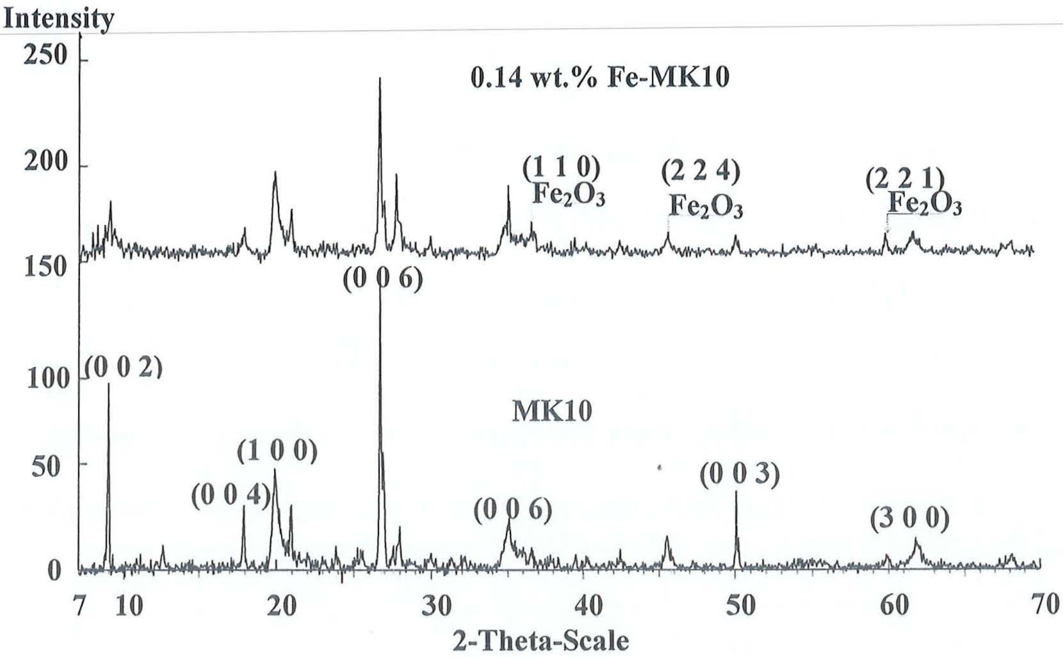


Fig. 4 XRD diffractograms of the MK10 and 0.14 wt.% Fe-MK10 catalysts

4. Decolorization of AR1 and RB5 by Fenton-like oxidation process

4.1 Effect of Iron (III) Oxide Loading on Supported Catalysts

The effect of catalyst concentration was investigated taking into account that, in general, Fenton-like oxidation process works well in the presence of small quantities of iron ions. The effect of iron (III) oxide loading on supports was investigated by varying the ferric (Fe^{3+}) ions concentration from 0.030 to 0.14 wt.% and the result is shown in Fig. 5.

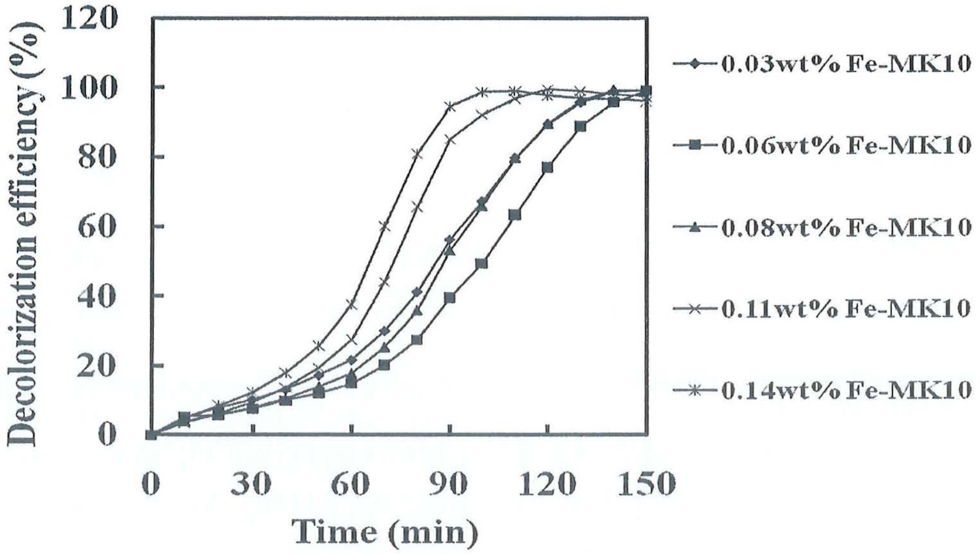


Fig. 5 Effect of ferric ions loading on the MK10 on decolorization process ($[AR1]_o$ = 50 mg L^{-1}, pH = 2.5, $[H_2O_2]_o$ = 4.0 mM, catalyst = 2.0 g L^{-1}, temperature = 30 °C and 130 rpm).

4.2 Effect of catalyst dosage

The effect of catalyst dosage on the decolorization was investigated by varying the catalyst dosage from 0.50 to 5.0 g L^{-1} and the results are presented in Fig. 6. When the amount of catalyst employed increases up to 5.0 g L^{-1} of 0.14 wt.% Fe-MK10 for decolorization of AR1, decolorization efficiency also increase. This is due to the increasing amount of active sites for H_2O_2 decomposition and less important but also of concern, for organic compounds adsorption.

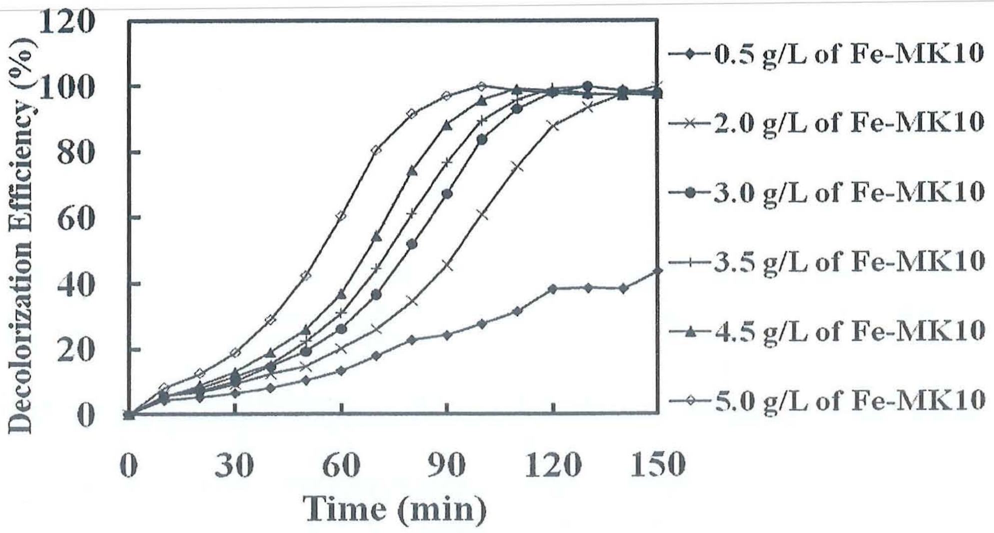


Fig. 6 Effect of catalyst dosage on the decolorization of AR1 process using 0.14 wt.% Fe-MK10 catalyst. ($[AR1]_o = 50$ mg L^{-1}, pH = 2.5, $[H_2O_2]_o = 4.0$ mM, temperature = 30 °C and 130 rpm).

4.3 Effect of pH

The influence of initial pH of the dye solution on the Fe-MK10/H_2O_2 process efficiency was studied with initial pH values of 1.5, 2.0, 2.5, 3.0, 3.5, 4.0 and 5.0 and without any modifications or control of pH during the process. Fig. 7 shows the decolorization of AR1 as a function of the initial pH of the solution at various reaction times.

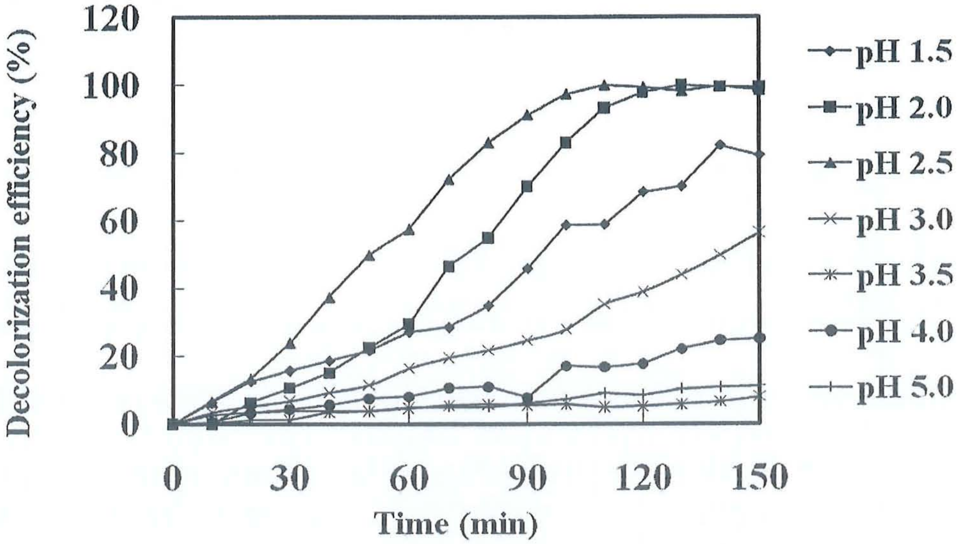


Fig. 7 Effect of pH on the decolorization of AR1 using 0.14 wt.% Fe-MK10. ($[AR1]_o$ = 50 mg L^{-1}, $[H_2O_2]_o$ = 4.0 mM, temperature = 30 °C and 130 rpm).

4.4 Effect of initial concentration of hydrogen peroxide

The selection of an optimal hydrogen peroxide concentration for the decolorization of AR1 and RB5 by heterogeneous Fenton oxidation process is important from practical point of view due to the cost of hydrogen peroxide. Fig. 8 shows the effect of initial hydrogen peroxide concentration on the decolorization of AR1 during the treatment. The effect of the hydrogen peroxide was analyzed by varying it initial concentration between 4 mM and 32 mM.

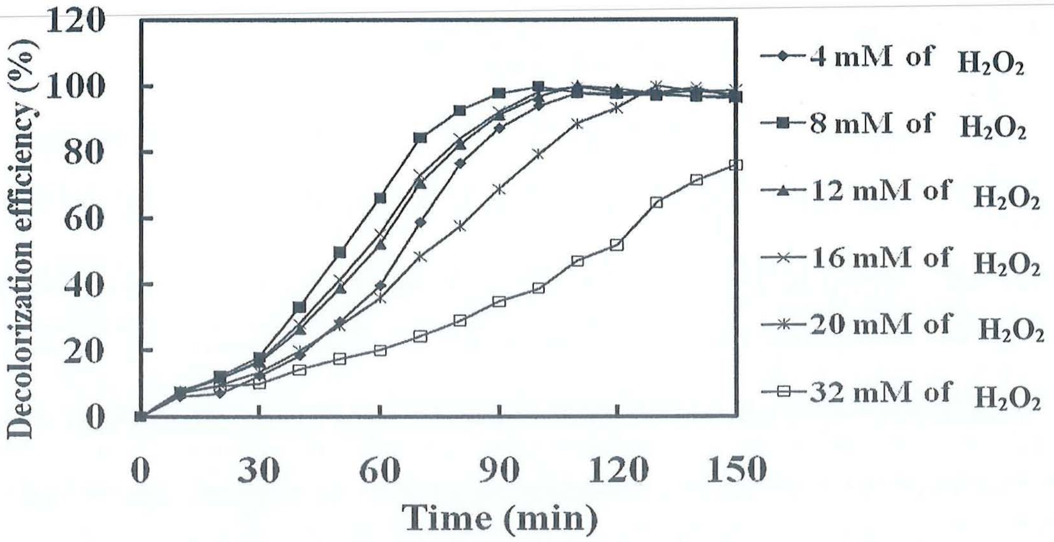


Fig. 8 Effect of initial concentration of hydrogen peroxide on the decolorization of AR1 using 0.14 wt.% Fe-MK10. ($[AR1]_o$ = 50 mg L^{-1}, temperature = 30 °C and 130 rpm).

4.5 Effect of initial concentration of dye

The effect of initial concentration on the decolorization of AR1 and RB5 was investigated with known range of initial concentration (25-100 mg L^{-1}). Fig. 9 shows the changes of AR1 concentration with the reaction time. It was observed that higher the concentration of dye, shorter is the reaction period needed to decolorize AR1 completely until some limitation, the process will be decreased. The fact that this occurred might be due to the lifetime of hydroxyl radicals is very short (only a few nanoseconds), they can only react where they are formed. Therefore, as increasing the quantity of dyes molecules per volume unit logically enhances the probability of collision between organic matter and oxidizing species, leading to an increase in the decolorization efficiency.

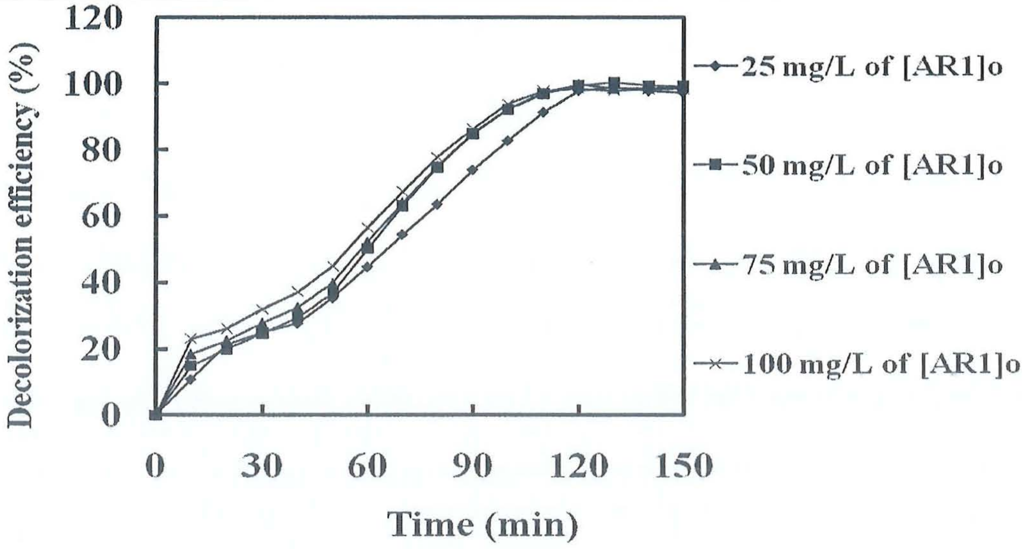


Fig. 9 Effect of initial concentration of AR1 on the decolorization process using 0.14 wt.% Fe-MK10. (Temperature = 30 °C and 130 rpm).

4.6 Effect of temperature

In order to determine the effect of reaction temperature on the decolorization of AR1 and RB5, a series of experiments were conducted by varying the temperature from 30 ^{o}C to 50 ^{o}C. The results are illustrated in Fig. 10. It can be seen that the temperature exerts strong effect on the decolorization rate of AR1 and the decolorization was accelerated by a rise in temperature, which was expected due to the exponential dependency of the kinetic constants with the reaction temperature as shown in Arrhenius Equation. This is because higher temperature increased the reaction rate between hydrogen peroxide and any form of ferrous/ferric iron (chelated or not), thus increasing the rate of generation of oxidizing species such as $^{\bullet}$OH radical or high-valence iron species.

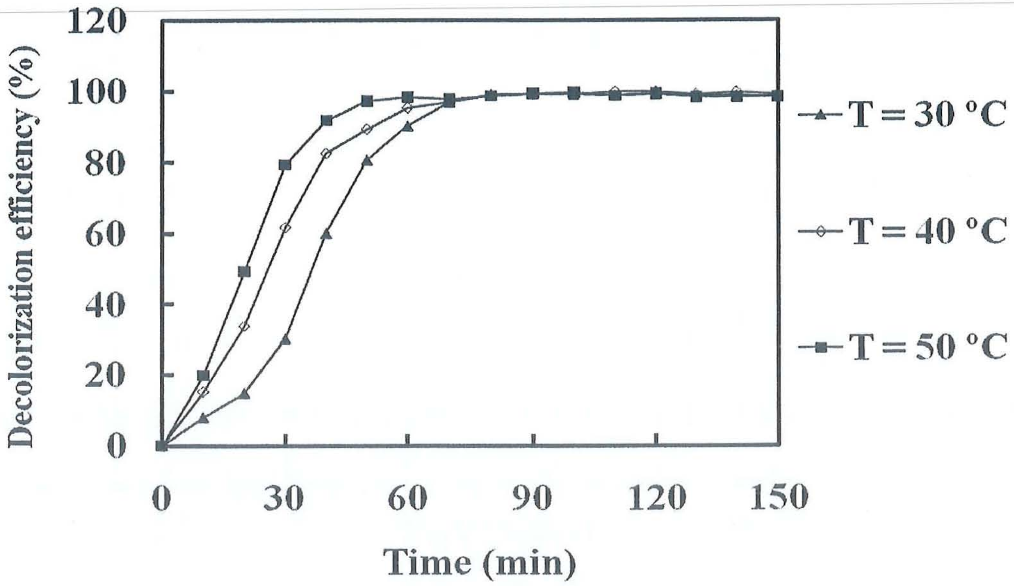


Fig. 10 Effect of reaction temperature on the decolorization of AR1 using 0.14 wt.% Fe-MK10. (Speed of shaker = 130 rpm).

4.7 *Catalyst Stability Test*

For a practical implementation of a heterogeneous catalytic system, it is crucial to evaluate the stability of the catalysts. For that purpose, a sample that shows a low iron leaching, but presenting simultaneously good catalytic performance, should be selected. Fig. 11 shows the performance reached in term of AR1 decolorization in four consecutive cycles.

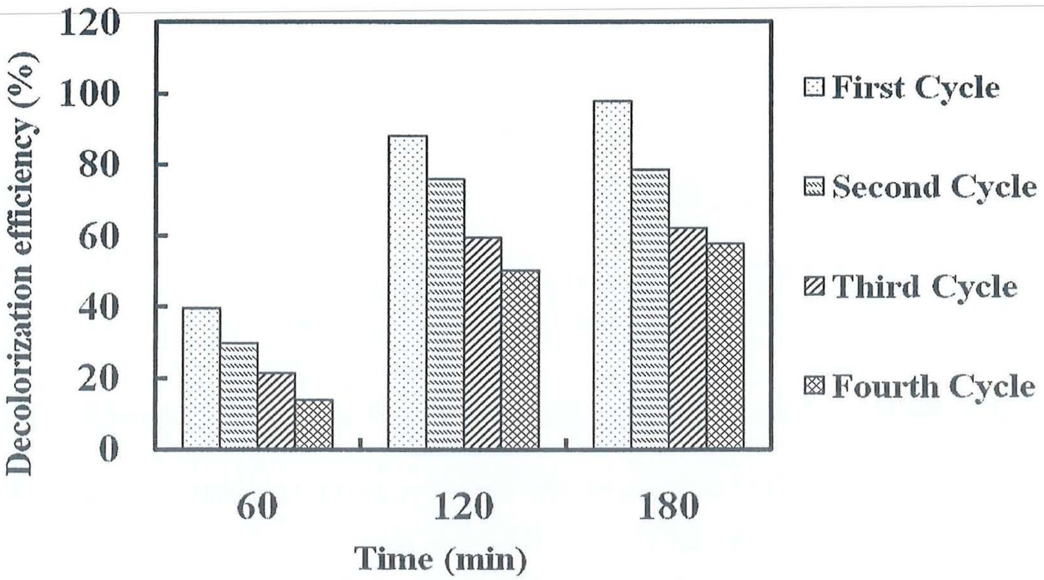


Fig. 11 Stability test on the AR1 decolorization process using 0.14 wt.% Fe-MK10.

4.8 Leaching test

Leaching tests were carried out to check the potential of leaching of iron ions from the catalysts after decolorization process of AR1 and RB5 completed and the results were shown in Table 2. In all of the experiments, concentration of the iron ions were below than 5 mg L^{-1} and this conforms to the standard of Environmental Quality (Sewage and Industrial Effluents) Regulations, 1979.

Table 2 Leaching test in decolorization of AR1 and RB5 dye solutions

Dye	Catalyst	Cycle	Concentration of iron ion (mg L^{-1})
AR1	0.14 wt.% Fe-MK10	1	2.09
		2	2.35
		3	0.77
		4	1.34
	0.070 wt.% Fe-RHA	1	4.77
		2	1.54
		3	0.56
		4	0.94
	0.070 wt.% Fe-granite	1	3.67
		2	0.36
		3	1.06
		4	0.23
	0.080 wt.% Fe-kaolin	1	3.22
		2	2.49
		3	1.34
		4	0.45
RB5	0.11 wt.% Fe-MK10	1	2.20
		2	2.03
		3	1.27
		4	1.88
	0.070 wt.% Fe-RHA	1	3.85
		2	0.49
		3	0.20
		4	0.02
	0.070 wt.% Fe-granite	1	4.08
		2	2.04
		3	1.60
		4	0.84
	0.14 wt.% Fe-kaolin	1	3.05
		2	2.01
		3	1.37
		4	0.56

5. Conclusions

Based on the overall experimental results obtained and discussed in chapter four, the summaries are made as listed below:

- Four different materials (montmorillonite K10, rice husk ash, granite and kaolin) have been employed as supports for iron particles with the aim of using them in the Fenton-like oxidation of Acid Red 1 (AR1) and Reactive Black 5 (RB5) dye solutions. The catalysts have been prepared through impregnation method using ferric nitrate nonahydrate ($Fe_2(NO_3)_3 \cdot 9H_2O$) show better catalytic behaviour in this process.
- The characterization results showed that all the catalysts prepared in this study were mesoporous in nature with followed the H3 type hysteresis and type IV and V isotherm according to modern IUPAC classifications. The SEM analyses show that not much change on the morphology structure can be visualize between supports and impregnated catalysts. From the EDX analyses, the chemical composition of prepared catalysts indicates the presence of iron, silica, oxide and alumina as major constituents with different percentage in the catalysts. Generally, the different percentage of contents in prepared catalysts gives their structures credibility as good catalysts. FTIR results revealed that the shift of band and disappear and/or decrease in the intensities of bands can be indirect evidence of the incorporation of ferric ion into supports. The XRD results showed the MK10, Fe-MK10, granite, Fe-granite and kaolin in crystalline form whereas for RHA, Fe-RHA, Fe-kaolin in amorphous form. Small peaks of anhydrous (Fe_2O_3) oxides were formed after calcinations of the impregnated catalysts by the removal of the organic moieties at 500 °C. This component is indicative of the presence of iron oxide in the impregnated catalyst.

- The efficiency of the reaction system was explored as a function of the experimental parameters such as effect of iron (III) oxide loading on the supports, catalyst dosage, pH, hydrogen peroxide concentration, initial dye concentration and reaction temperature. The optimum conditions obtained for 99 % decolorization efficiency of the process for both dyes were 0.070-0.14 wt.% of Fe-contained supports, 3.50-5.0 g L^{-1} of catalyst dosage, 2.0-2.50 pH and 8.0-20 mM of initial concentration of hydrogen peroxide with 50 mg L^{-1} of initial dye concentration at 30 °C reaction temperature.

- The experiments of long-term stability showed that Fe-MK10, Fe-RHA, Fe-granite and Fe-kaolin showed some activity decay after reuse for four consecutive cycles. This is due to the loss of catalyst and active phase leaching during the experiments.

- All the prepared catalysts exhibit not only good catalytic activity but also reasonable small iron leaching (below the Environmental Quality (Sewage and Industrial Effluents) Regulation 1979 values), indicating that the active phases are strongly fixed to the support.

List of publications:

The results of this project were published as follow:

1. Daud, N.K. and Hameed, B.H. (2010). Decolorization of Acid Red 1 by heterogeneous Fenton-like process using rice husk ash-based catalyst. Journal of Hazardous Material, 176, 938–944. **(Impact Factor 2009: 4.144)**
2. Daud, N.K. and Hameed, B.H. (2010). Short Communication, Fenton-like oxidation of reactive black 5 solutions using iron exchanged Montmorillonite K10 as a catalyst. Journal of Hazardous Material, 176, 1118–1121. **(Impact Factor 2009: 4.144)**
3. Daud, N.K., Hameed, B.H. and Ahmad, M.A. (2010). Decolorization of Acid Red 1 dye solution by Fenton-like process using Fe-Montmorillonite K10 catalyst. Chem. Eng. Journal, 165, 111-116. **(Impact Factor 2009: 2.816).**
4. N.K. Daud, B.H. Hameed (2011), Acid Red 1 dye decolorization by heterogeneous Fenton-like reaction using Fe/kaolin catalyst, Desalination, 269, 291-293. **(Impact Factor 2009: 2.034)**
5. Ai Ni Soon, B.H. Hameed, Heterogeneous catalytic treatment of synthetic dyes in aqueous media using Fenton and photo-assisted Fenton process, Desalination 269 (2011) 1–16. **(Impact Factor 2009: 2.034)**
6. H. Hassan, B.H. Hameed, Oxidative decolorization of Acid Red 1 solutions by Fe–zeolite Y type catalyst, Desalination, Accepted manuscript, March 2011. **(Impact Factor 2009: 2.034)**
7. H. Hassan, B.H. Hameed, Fe-ball clay as effective heterogeneous Fenton type catalyst for the decolorization of Reactive Blue 4, Chemical Engineering Journal, Under major revision, (MS No: CEJ-D-10-02593) April 2011.

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Decolorization of Acid Red 1 by Fenton-like process using rice husk ash-based catalyst

N.K. Daud, B.H. Hameed*

School of Chemical Engineering, Engineering Campus, Universiti Sains Malaysia, 14300 Nibong Tebal, Penang, Malaysia

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ABSTRACT

The decolorization of Acid Red 1 (AR1) in aqueous solution was investigated by Fenton-like process. The effect of different reaction parameters such as different iron ions loading on rice husk ash (RHA), dosage of catalyst, initial pH, the initial hydrogen peroxide concentration ($[H_2O_2]_o$), the initial concentration of AR1 ($[AR1]_o$) and the reaction temperature on the decolorization of AR1 was studied. The optimal reacting conditions were found to be 0.070 wt.% of iron (III) oxide loading on RHA, dosage of catalyst = $5.0\,g\,L^{-1}$, initial pH = 2.0, $[H_2O_2]_o = 8\,mM$, $[AR1]_o = 50\,mg\,L^{-1}$ at temperature 30 °C. Under optimal condition, 96% decolorization efficiency of AR1 was achieved within 120 min of reaction.

1. Introduction

Colored effluents from textile industries represent one of the major problems concerning textile wastewaters [1], where the total dye consumption of the textile industry worldwide is in excess of 10^7 kg/year, and an estimation of 90% of this ends up on fabrics. Consequently, about 10% or more of dyes are discharged into waste streams without treatment by the textile industry worldwide [2]. Dyes, as they are intensely colored, represent special problem in wastewater. Most of the dyes are difficult to decolorize due to their complex structure and synthetic origin. The discharge of dye wastewater in the environment is aesthetically undesirable and has serious environmental impact [3]. Unfortunately with the complicated color-causing compounds, the decolorization of these wastes is a difficult and challenging task [4]. The removal of color from dyeing industries effluents is one of the major problems faced by the textile dyeing industry whereas from an environmental point of view, the removal of synthetic dyes has a great concern [5].

Nowadays, various chemical and physical processes, such as elimination by adsorption onto activated carbon, coagulation by a chemical agent, ozone oxidation, hypochlorite oxidation, electrochemical method, etc. are applied for the treatment of dye waste effluents [6–8]. Nevertheless, these methods are usually non-destructive, inefficient, costly and resulted in the production of secondary waste products. Therefore, purification of dye wastewater is becoming a matter of great concern and it is necessary to develop novel and cost-effective technologies to treat dye wastewater [9].

Advanced oxidation technologies (AOTs) are innovative methods for water treatment and are extremely useful in the case of substances resistant to conventional technologies. AOTs are oxidation processes which generate hydroxyl radicals ($^\bullet OH$) that are very effective in degrading organic pollutants because of their strong oxidant power ($^\bullet OH + H^+ + e^- \rightarrow H_2O$; $E^0 = 2.80\,V$) and non-selective species [10,11]. O_3/H_2O_2, O_3/UV, H_2O_2/UV, $TiO_2/air/UV$, Fe (II)/H_2O_2 (Fenton's reagent), Fe (III)/H_2O_2 (Fenton-like reaction), an oxidant (H_2O_2, O_3) and ultrasonic irradiation are the main types of AOTs that have been suggested in recent years [12–16]. Various combinations of them are employed for the complete mineralization of pollutants. Among these AOTs, Fenton's reagent is particularly attractive because of the low costs, the lack of toxicity of the reagents (i.e., Fe (II) and H_2O_2), the absence of mass transfer limitation due to its homogeneous catalytic nature and the simplicity of the technology [17]. However, it should be pointed out that the homogeneous Fenton process has a significant disadvantage. Homogeneously catalyzed reactions need up to 50–80 ppm of Fe ions in solution, which is well above the Malaysian Regulation of Environmental Quality Act 1974 that allows only below than 5 ppm of Fe ions in treated water to dump directly into the environment [18]. In addition, the removal/treatment of the sludge-containing Fe ions at the end of the wastewater treatment is expensive and needs large amount of chemicals and manpower.

To overcome the disadvantages of the homogeneous Fenton process, and also considering the possibility of recovering catalyst,

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* Corresponding author. Tel.: +60 45996422; fax: +60 45941013.
E-mail address: chbassim@eng.usm.my (B.H. Hameed).

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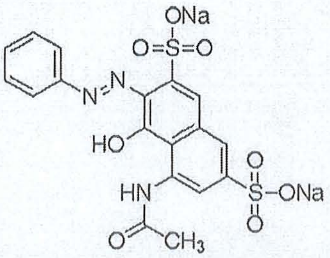
Table 1
Chemical structure and characteristics of AR1.

C.I. number	18050
Synonyms	Amido Naphthol Red G, Azophloxine
Empirical formula	$C_{18}H_{13}N_3Na_2O_8S_2$
Molecular weight	509.42
λ_{max} (nm)	532
Molecular structure	

some attempts have been made to develop heterogeneous catalysts, prepared by loading iron (III) oxide onto a porous support [19–20]. The use of heterogeneous solid Fenton catalysts such as iron (III) immobilized on rice husk ash (RHA) can be an alternative. The abundance of agricultural by-products (such as RHA) in most continents of the world and also its low costs make it a strong and viable material as catalyst support for the removal of many pollutants from wastewaters. The Fenton-like processes have been used to produce highly reactive hydroxyl radicals with H_2O_2 in the presence of metal cations under suitable reaction medium and conditions [21–22]. Iron salts are adsorbed onto the surface of RHA and in a suitable aqueous medium; the reduction–oxidation reactions between Fe (III)/Fe (II) take place in the presence of hydrogen peroxide which promotes the formation of reactive components such as the hydroxyl (•OH) and the hydroperoxyl (•OOH) radicals. The radicals generated by the decomposition of hydrogen peroxide can oxidize organic compounds adsorbed over the catalyst or degrade soluble organic compounds in the vicinity of iron active ions present at both the catalyst surface and in the bulk liquid phase. Thus, the Fe (III)/Fe (II) complex formed on the surface of RHA can react with H_2O_2 thus allowing iron ions to participate in the Fenton catalytic cycle [23].

In this work, decolorization of AR1 dye solution in batch process was carried out using iron (III) immobilized on RHA as active heterogeneous catalyst. The effectiveness of this catalyst in decolorization of the dye, as well as the influence of reaction parameters on the catalytic activity was discussed.

2. Materials and methods

2.1. Chemicals and reagents

Acid Red 1 (AR1) was obtained from Sigma–Aldrich as commercially available dye and used without further purification. The main characteristics of AR1 are presented in Table 1. Hydrogen peroxide (30%, w/w) was purchased from Sigma–Aldrich (M) Sdn Bhd, Malaysia. RHA was obtained from BERNAS Company (Malaysia) Bhd. All chemicals were of analytical grade and were used without any further purification. Distilled water was used throughout this study.

2.2. Preparation of Fe-RHA catalyst

The iron (III) oxide on RHA catalyst (here referred to as Fe-RHA catalyst) was prepared by the incipient impregnation method [24], in which distilled water is used to solubilize the Fe $(NO_3)_3 \cdot 9H_2O$ (Merck). Then, RHA was added to this aqueous solution and was stirred constantly in the water bath until all water was evaporated. After impregnation, the sample was dried at 105 C for 12 h, followed by calcination at 500 °C for 4 h in a muffle furnace.

2.3. Catalytic activity of Fe-RHA

All experiments were carried out in 250 mL-stoppered glasses (Erlenmeyer flask) placed in a thermostated water bath with an agitation of 130 rpm for 120 min. Each experimental run was performed by taking an appropriate amount of stock dye solution followed by dilution with distilled water to 200 mL. Predetermined amounts of Fe-RHA catalyst were then added to the flask. Also, initial solution pHs were adjusted to the desired values using prepared 1.0 M H_2SO_4 or 1.0 M NaOH solution. The reactions commenced when measured concentration of hydrogen peroxide solution was added to the flask. Thereafter, 3 mL of samples solution was withdrawn periodically and analyzed.

The effect of the iron (III) oxide loading on the RHA in the decolorization of AR1 was also investigated. Briefly, different amounts of the metal ion which varied between 0.010 and 0.070 wt.% were used with 200 mL of 50 mg L^{-1} AR1 solution. The other parameters of the solution were fixed at pH 2.5, 4.0 mM of hydrogen peroxide, 2.0 g L^{-1} catalyst dosage at temperature of 30 °C and rpm of 130. Similarly, the concentration of the catalyst dosage in the range of 1.0–5.0 g L^{-1} was also studied.

Furthermore, the activity of this catalyst to decolorize AR1 was tested by varying other parameters such as pH in the range 1.50–5.0, initial concentration of H_2O_2 between 4.0 and 32 mM, AR1 concentration and temperature of the solution. In all the experimental runs, as described above, other parameters were kept constant and samples were being withdrawn at regular intervals of time for the analysis of the product solution.

2.4. Analytical procedure

2.4.1. Characterization of Fe-RHA catalyst

Scanning electron microscope (SEM) was used to study the surface morphology of the RHA and Fe-RHA. The analysis was carried out using a scanning electron microscope (Model SEM-JEOL-JSM6301-F) with an Oxford INCA/ENERGY-350 microanalysis system.

Energy Dispersive Spectrometry (EDX) was performed to determine the chemical composition in the RHA and Fe-RHA using the same instrument with SEM (Model SEM-JEOL-JSM6301-F) with an Oxford INCA/ENERGY-350.

Specific Brunauer–Emmett–Teller (BET) surface area and pore size distribution for 0.070 wt.% Fe-RHA was determined with a Micromeritics ASAP 2020, surface area and porosity analyzer by N_2 adsorption at 77 K.

Fourier transform infrared (FTIR) spectroscopy was conducted to study the surface chemistry of the RHA and Fe-RHA by identifying the functional groups presented on the samples using Model Perkin Elmer FTIR-2000, US. The spectra were measured from 4000 to 400 cm^{-1}. The analysis was done automatically by software attached to the system (Spectrum version 5.0.2).

2.4.2. Reaction solution analysis

The UV–vis spectra of dye were recorded from 200 to 800 nm using a UV–vis spectrophotometer (Shimadzu, model UV 1601, Japan) with a spectrometric quartz cell (1 cm path length). The maximum absorbance wavelength (λ_{max}) of AR1 was found to be 532 nm. Therefore, the concentration of dye in the reaction mixture at different reaction times was determined by measuring the absorption intensity at λ_{max} = 532 nm and from a calibration curve. Prior to the measurement, a calibration curve was obtained using the standard AR1 solution with known concentrations. Because the reaction continued after sampling, the measurement of absorbance

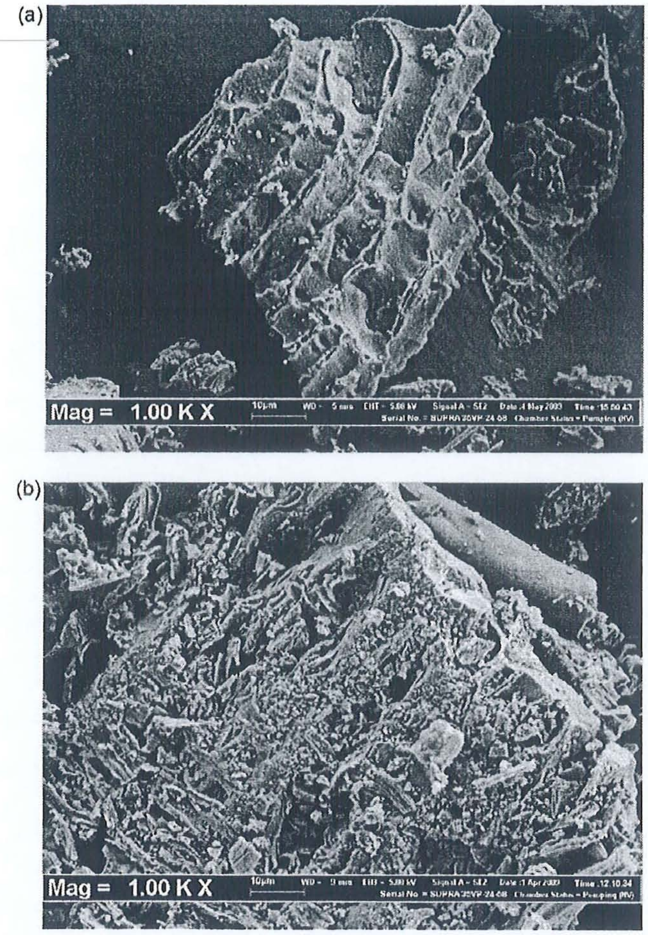


Fig. 1. SEM images of (a) RHA and (b) 0.070 wt.% Fe-RHA.

of reaction solution was done within 1 min. The decolorization efficiency of AR1 is defined as follows:

$$\text{decolorization efficiency}\,(\%) = \left[1 - \left(\frac{C_t}{C_0}\right)\right] \times 100 \qquad (1)$$

where C_0 (mg L^{-1}) is the initial concentration of AR1 and C_t (mg L^{-1}) is the concentration of AR1 at reaction time, t (min).

The total iron ion concentration in the solution was determined using Atomic Absorption Spectrophotometer (AAS) model (Shimadzu AA 6650) with the maximum absorbance wavelength (λ_{max}) of iron ion obtained at 248.35 nm. Similarly, prior to the measurement of the iron ion concentration, a calibration curve was obtained using the standard iron ion solution in 0.10 M HNO_3 solution with known concentration. Finally, when the decolorization of AR1 was completed, the samples were analyzed to determine the total iron ion leached from the catalyst.

3. Results and discussion

3.1. Characterization of catalyst

Fig. 1(a) and (b) shows the SEM images of RHA and impregnated Fe-RHA. Surface morphology of the RHA was retained and not much change although after incorporation with iron (III) oxide.

The chemical compositions of the 0.070 wt.% Fe-RHA and RHA were measured by EDX and are shown in Table 2. The results revealed that the iron concentration of the Fe-RHA catalyst was 3.22 wt.%, while it was only 3.17 wt.% in RHA. Iron was introduced into the RHA after impregnation. Slight variations are noticed between the expected and determined iron contents of the samples, which is due to the high hydration degree of solid at the stages of the preparation procedure, thus making difficult to obtain the targeted iron contents [25].

Table 2
Chemical composition of 0.070 wt.% Fe-RHA and RHA determined by EDX.

Chemical compound	RHA	0.070 wt.% Fe-RHA
O	41.59	40.20
Fe	3.17	3.22
Si	55.24	56.58

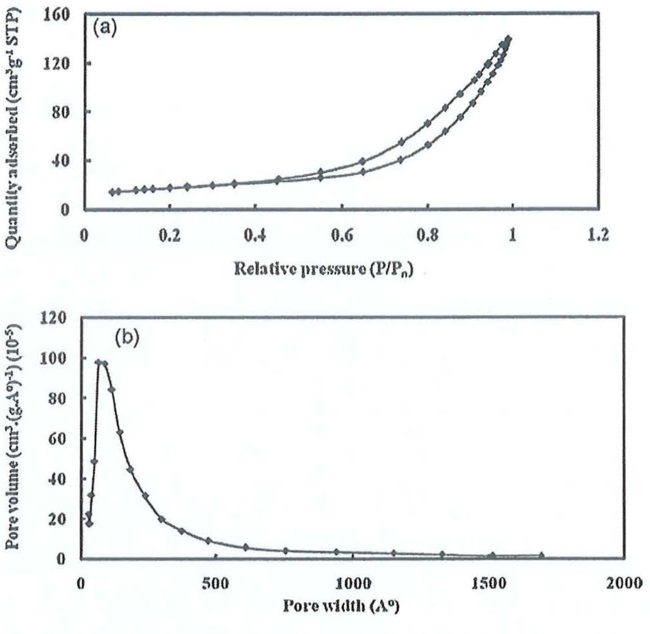


Fig. 2. (a) N_2 adsorption/desorption isotherms of 0.070 wt.% Fe-RHA at 77 K. (b) Pore size distribution of 0.070 wt.% Fe-RHA.

Nitrogen adsorption analysis showed that the textural properties of RHA were retained after the surface modification of metal ions and exhibiting typical type IV according to BET classification and hysteresis loops type H1 according to IUPAC classification as shown in Fig. 2(a) and (b) [26]. This analysis also showed that this catalyst had BET surface area, pore size and pore volume of 61.33 m^2 g^{-1}, 135.52 Å and 0.21 cm^3 g^{-1}, respectively.

FTIR spectra of the RHA and impregnated RHA are shown in Fig. 3. In the high wave number region, the spectrum is dominated by the stretching vibrations of the hydroxyl groups bonded to metallic cations and water molecules (2861–3467 cm^{-1}). Bend-

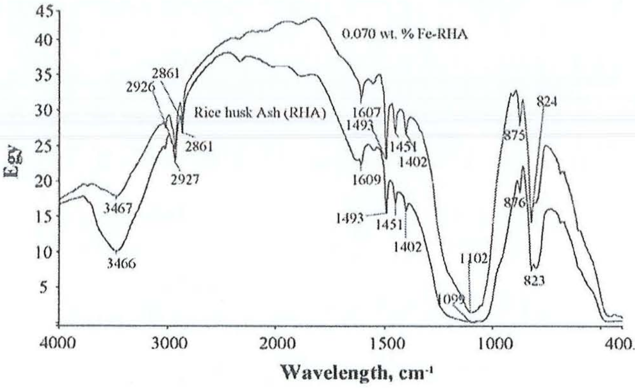


Fig. 3. FTIR spectra of RHA and 0.070 wt.% Fe-RHA.

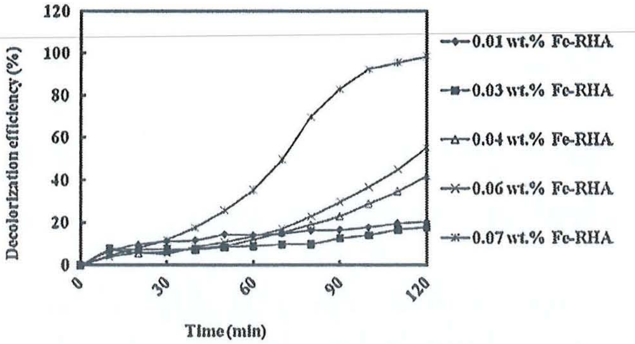


Fig. 4. Effect of iron loading on RHA on the decolorization of AR1. Reaction conditions: initial concentration of AR1, $[AR1]_o = 50\ mg\ L^{-1}$, initial concentration of hydrogen peroxide, $[H_2O_2]_o = 4\ mM$, pH = 2.5, dosage of catalyst = $2.0\ g\ L^{-1}$, T = 30 °C and agitation speed = 130 rpm.

ing of water molecules also produces an important effect close to $1630\ cm^{-1}$ [27], while the bond characteristic of the samples dominates the region of low wave numbers, the band at 1493, 1451, 1402, 1102–1009, 876–823 cm^{-1}, assigned to phenyl bond, $-CH_2-$ scissor vibration, $CO-NH_2$ that are primary amides, $C-NH_2$, primary aliphatic amines and Si–H deformation, respectively.

3.2. Effect of iron loading on RHA

The effect of iron loading on RHA was investigated by varying the iron ion concentration from 0.010 to 0.070 wt.% and was shown in Fig. 4. By increasing iron loading on the RHA, the decolorization rate increased efficiently and 96% decolorization was achieved for 0.070 wt.% within 120 min. Hence, 0.070 wt.% of iron (III) oxide loading was found to be optimum for maximum efficiency. An increase of the amount of ferric ions involved in the process resulted in an increase in the number of $^{\bullet}OH$ radical significantly.

3.3. Effect of catalyst dosage

The influence of the catalyst dosage on decolorization efficiency against time is illustrated in Fig. 5. The results indicated that the decolorization of AR1 was significantly influenced by the dosage of catalyst and the optimum dosage was observed at $5.0\ g\ L^{-1}$ of catalyst with the decolorization efficiency was 96%. The fact that noticed, higher decolorization efficiency was achieved at the highest catalyst dosage mainly attributed to the higher production of $^{\bullet}OH$ radical with more ferric ions in Fenton-like reaction.

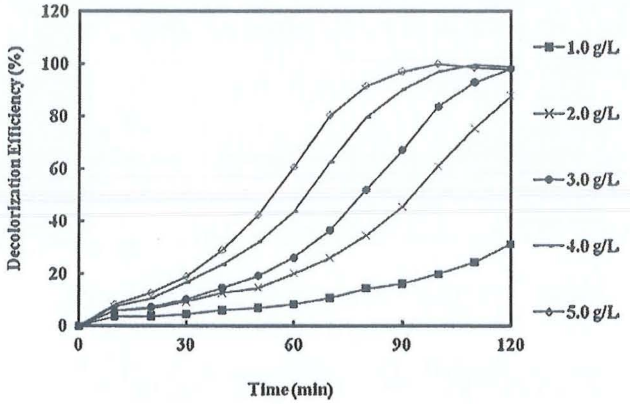


Fig. 5. Effect of dosage of catalyst on the decolorization of AR1. Reaction condition: initial concentration of AR1, $[AR1]_o = 50\ mg\ L^{-1}$, initial concentration of hydrogen peroxide, $[H_2O_2]_o = 4 mM$, pH = 2.5, 0.070 wt.% Fe-RHA, temperature = 30 °C and agitation speed = 130 rpm.

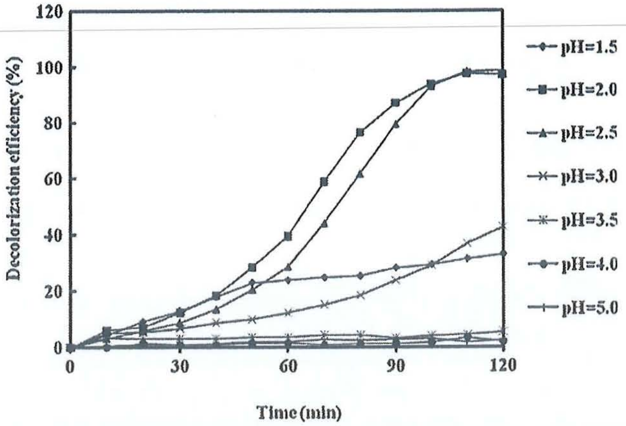


Fig. 6. Effect of pH on the decolorization of AR1. Reaction conditions: initial concentration of AR1, $[AR1]_o = 50\ mg\ L^{-1}$, initial concentration of hydrogen peroxide, $[H_2O_2]_o = 4\ mM$, dosage of catalyst = $5.0\ g\ L^{-1}$ with 0.070 wt.% of Fe-RHA, temperature = 30 °C and agitation speed = 130 rpm.

3.4. Effect of pH

The effect of initial pH value of solutions on the decolorization of AR1 was studied in the pH range of 1.5–5.0 and the result was shown in Fig. 6. The results indicated that the decolorization of AR1 was significantly influenced by the pH of the solution. The optimal pH value for the decolorization of AR1 achieved at pH 2.0 with 96% of decolorization of AR1 within 120 min reaction. An important observation here revealed that at low pH (pH < 2.0), the reaction could be slowed down because H_2O_2 can stay stable probably by solvating a proton to form an oxonium ion. An oxonium ion ($H_3O_2^+$) makes H_2O_2 electrophilic to enhance the stability and presumably to reduce substantially the reactivity with ferrous ion [28].

$$H_2O_2 + H^+ \rightarrow H_3O_2^+ \quad (2)$$

$$^{\bullet}OH + H^+ + e^- \rightarrow H_2O \quad (3)$$

At the same time, the formed complex species $[Fe\ (H_2O)_6]^{2+}$ and $[Fe\ (H_2O)_6]^{3+}$ also react more slowly with H_2O_2. In addition, the scavenging effect of the $^{\bullet}OH$ radical by H^+ is severe (Eq. (3)) [29–30]. On the other hand, in case of pH > 3.0, the oxidation efficiency rapidly decreased, not only by the decomposition of H_2O_2 but also by the deactivation of a catalyst with the formation of ferric hydroxide complexes leading to a reduction of $^{\bullet}OH$ radical.

3.5. Effect of initial concentration of H_2O_2

H_2O_2 plays the role of an oxidizing agent in this process. The selection of an optimal H_2O_2 concentration for the decolorization of AR1 is important from practical point of view due to the cost of H_2O_2 [9]. Fig. 7 shows the effect of initial H_2O_2 concentration on the decolorization of AR1 against time. The results obtained show: 8.0 mM was the optimum value for the H_2O_2 concentration when the initial concentration of the AR1 was $50\ mg\ L^{-1}$ and the initial pH 2.0. The reaction went more slowly when the concentration was lower (4.0 mM) or higher (32 mM). At low concentration, H_2O_2 cannot generate enough $^{\bullet}OH$ and the oxidation rate is logically slow. The increase of the oxidant concentration from 4.0 to 8.0 mM led to an increase in the reaction rate, as expected, because more radicals will be formed. Nevertheless, for a very high H_2O_2 concentration (32 mM), the performance decreased. At higher H_2O_2 concentrations, the scavenging of $HO^{\bullet}$ radicals will occur, which can be expressed by the following reaction:

$$H_2O_2 + HO^{\bullet} \rightarrow H_2O + HO_2^{\bullet} \quad (4)$$

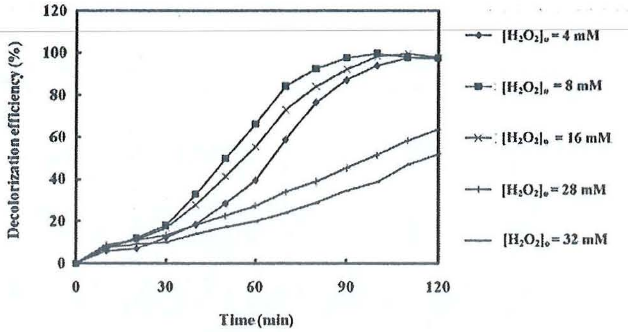


Fig. 7. Effect of initial concentration of hydrogen peroxide on the decolorization of AR1. Reaction conditions: initial concentration of AR1, $[AR1]_o = 50\,mg\,L^{-1}$, dosage of catalyst = $5.0\,g\,L^{-1}$ with 0.070 wt.% Fe-RHA, temperature = 30 °C, agitation speed = 130 rpm and pH = 2.0.

Although other radicals ($HO_2^\bullet$) are produced, their oxidation potential is much smaller than that of the $HO^\bullet$ species [31].

3.6. *Effect of initial concentration of AR1*

Fig. 8 shows the changes of AR1 concentration with the reaction time. The efficiency of Fenton-like process as a function of initial concentration of the dye was evaluated. As the lifetime of hydroxyl radicals is very short (only a few nanoseconds), they can only react where they are formed. Increasing the quantity of AR1 molecules per volume unit logically enhances the probability of collision between organic matter and oxidizing species, leading to an increase in the degradation efficiency [25].

3.7. *Effect of temperature*

Temperature is critical to the reaction rate, the product yield and distribution [32]. The results are illustrated in Fig. 9. It can be seen that the temperature exerts a strong effect on the decolorization efficiency of AR1 and the decolorization was accelerated by a rise in temperature (30, 40 and 50 °C). This is because higher temperature increased the reaction rate between H_2O_2 and the catalyst, thus increasing the rate of generation of oxidizing species such as $^\bullet OH$ radical or high-valence iron species.

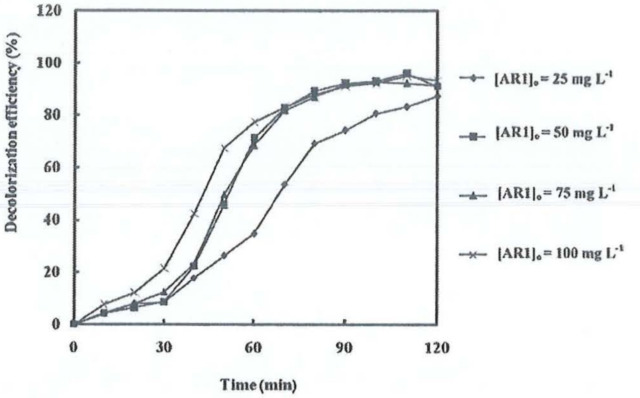


Fig. 8. Effect of initial concentration AR1 concentration on the decolorization of AR1. Reaction conditions: initial concentration of hydrogen peroxide, $[H_2O_2]_o = 8\,mM$, dosage of catalyst = $5.0\,g\,L^{-1}$ with 0.070 wt.% Fe-RHA, temperature = 30 °C, agitation speed = 130 rpm and pH = 2.0.

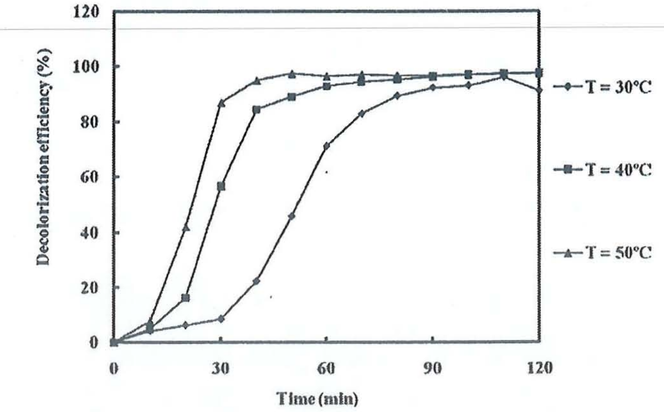


Fig. 9. Effect of temperature on the decolorization of AR1. Reaction conditions: initial concentration of AR1, $[AR1]_o = 50\,mg\,L^{-1}$, initial concentration of hydrogen peroxide, $[H_2O_2]_o = 8\,mM$, dosage of catalyst = $5.0\,g\,L^{-1}$ with 0.070 wt.% Fe-RHA, agitation speed = 130 rpm and pH = 2.0.

3.8. *Spectral changes of AR1 during decolorization process*

Fig. 10 shows the UV–vis spectrum obtained for the AR1 solution during the decolorization process taken along time in a typical experiment. Regarding the dye spectrum, it is characterized by two bands in the ultraviolet region located at 322 and 354 nm and by one band in the visible region, with a maximum located at 532 nm. The absorbance peaks in the ultraviolet region are due to the benzene and naphthalene rings of AR1, respectively [32], while the band in the visible region is due to the chromophore-containing azo linkage [33]. If one compares the original spectrum ($t = 0$ min) with that achieved within 120 min of decolorization, it is evident that the treated dye sample was almost colorless and did not show significant absorbance in the visible region, indicating that color removal was practically complete. The disappearance of the absorbance peak at 532 nm reflects, unequivocally, the breakdown in the chromophoric group. However, the spectrum in the ultraviolet region shows that the dye was not completely mineralized, even though the absorption intensity was reduced within the ultraviolet range. The slower decrease of the intensities of the

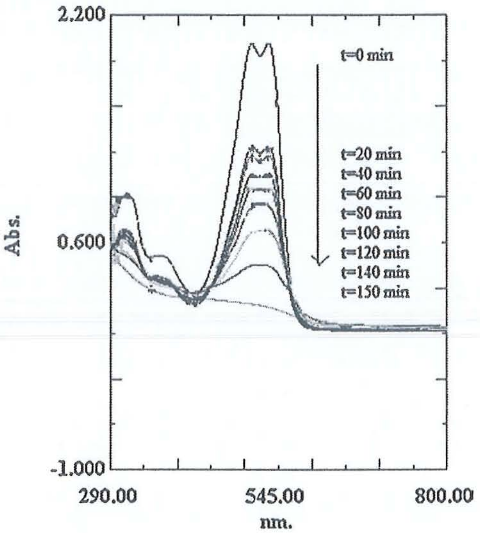


Fig. 10. Absorbance spectra. Reaction conditions: initial concentration of AR1, $[AR1]_o = 50\,mg\,L^{-1}$, initial concentration of hydrogen peroxide, $[H_2O_2]_o = 8\,mM$, dosage of catalyst = $5.0\,g\,L^{-1}$ with 0.070 wt.% Fe-RHA, agitation speed = 130 rpm, temperature = 30 °C and pH = 2.0.

bands at 322 and 354 nm, with respect to that of the azo bond, can be attributed to the formation of intermediates, resulting from the decolorization of the azo dye, which still contain benzoic- and naphthalene-type rings [34].

3.9. Catalyst stability test

The reuse and leaching tests were performed in order to evaluate the catalytic activity of Fe-RHA during successive experiments and thus to observe the possibility of catalyst reuse. The catalyst was used in four consecutive cycles, i.e. 8 h of operation using fresh dye solutions at optimum conditions (50 mg L^{-1} of AR1 concentration, pH 2.0, 30 °C, 8.0 mM H_2O_2 and 5.0 g L^{-1} of 0.070 wt.% Fe-RHA catalyst) and was analyzed duplicate. The uncertainty of the experimental results was determined and represents about 2% of uncertainty. Between each experiment, the catalyst was removed by filtration and then washed with distilled water for several times and dried at 60 °C for 12 h. It is obvious that the initial activity decreased gradually during successive cycles. The activity reduction observed may be due to the loss of catalyst and active phase leaching. Nevertheless, catalyst deactivation may occur due to a diversity of factors, as pointed by Guo and Al-Dahhan [35], including reduction of the catalyst specific area, poisoning of the catalytic agents by compounds formed during oxidation and surface deposition. Leached iron into the solution was measured in 120 min usual cycle time and found less than 5.0 mg L^{-1} (3.77, 1.54, 0.56 and 0.94 mg L^{-1} of ferric ions for the four successive cycles) which is obeyed the Malaysian Regulation of Environmental Quality Act 1974.

3.10. Comparative study between heterogeneous and homogeneous Fenton process

To make a clear description of the effect of heterogeneous Fe-RHA catalyst on the decolorization of AR1, an experiment in homogeneous Fenton process was carried out using the same concentration of ferric ions that were leached out from heterogeneous catalyst during the four cycles (i.e. 3.77, 1.54, 0.56 and 0.94 mg L^{-1} of ferrous ions) under the same operating condition (pH = 2.0, H_2O_2 = 8.0 mM, $[AR1]_o$ = 50 mg L^{-1}, time = 120 min and temperature = 30 °C). It was found that the decolorization efficiencies were 62.45, 43.98, 15.34 and 17.84%. This suggests that the homogeneous process due to leaching also could have contributed in decolorization of the dye.

4. Conclusion

The iron (III) immobilized on RHA has been tested and used as catalyst in decolorization of AR1 in Fenton-like process. The study showed that the heterogeneous Fenton-like process of Fe-RHA can decolorize AR1 effectively. The initial dye concentration, the increase in catalyst loading, and hydrogen peroxide concentration favor the decolorization efficiency. The optimal operational parameters obtained for this study were found to be 0.070% by weight of iron (III) oxide loading on RHA, 5.0 g L^{-1} of 0.070 wt.% Fe-RHA, solution pH 2.0, 8.0 mM H_2O_2 dosage at 30 °C. Decolorization processes led to 96% decolorization of AR1 within 120 min. Above all, the process is economical because of the availability of the raw materials (RHA) employed.

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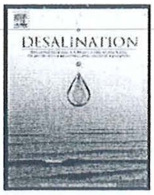

Acid Red 1 dye decolorization by heterogeneous Fenton-like reaction using Fe/kaolin catalyst

N.K. Daud, B.H. Hameed *

School of Chemical Engineering, Engineering Campus, Universiti Sains Malaysia, 14300 Nibong Tebal, Penang, Malaysia

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ABSTRACT

In this work, the decolorization of Acid Red 1 (AR1) by Fe (III) oxide-kaolin catalyst was studied. The effects of iron (III) oxide loading on kaolin, catalyst dosage, pH and initial concentration of hydrogen peroxide (H_2O_2) on decolorization of AR1 were studied. The best catalytic results showed that at a reaction temperature of 30 °C, pH 3.0, 8.0 mM of H_2O_2 and 4.0 g/L of 0.080 wt.% Fe-kaolin, 98.46% decolorization was achieved within 240 min treatment. It was also observed that catalytic behaviour could be reproduced in consecutive experiments with low iron leaching.

1. Introduction

Heterogeneous Fenton process uses oxidation agent (hydrogen peroxide) and employs iron immobilized on a large variety of solid supports [1]. Hydroxyl radicals are not only among the most powerful oxidation agents, but also have higher oxidation potential than other chemicals commonly used in wastewater treatment [2]. However, this high oxidizing power correlates with a relative lack of selectivity due to the rapid evolution of hydroxyl radicals that tend to attack the molecules in close vicinity [3].

Selection of catalyst support is important during the preparation of heterogeneous Fenton-like catalyst. At present, the catalyst supports include organic (such as C-Nafion and resin) and inorganic materials (such as HY zeolite, C fabrics and pillared clays) [4]. A good heterogeneous catalyst should meet two requirements; it must have high catalytic activity and low Fe dissolution [5]. From the literature, it was found that different heterogeneous Fenton-like catalysts showed different performances. For example, Tekbas et al., [6] reported that the use of heterogeneous Fenton type catalyst to remove organic pollutants with the assistance of UV radiation in which 90% decolorization of RO 16 azo dye was achieved. Chen et al., [7] also successfully investigated the heterogeneous photo-Fenton process in decolorization of reactive brilliant orange X-GN over iron-pillared montmorillonite and about 98.6% decolorization was achieved.

The objective of this work was to decolorize a non-biodegradable azo dye Acid Red 1 (AR1) by heterogeneous Fenton-like process using Fe (III) oxide/kaolin catalyst. The effects of the iron (III) oxide loading on kaolin, catalyst dosage, pH and H_2O_2 concentration on the efficiency of the treatment were studied.

2. Experimental

2.1. Preparation of catalyst

Kaolin powder was supplied by R&M marketing, Essex, UK Company with CAS number 1332-58-7. The catalyst (Fe (III) oxide/kaolin) was prepared by the impregnation method [8]. Specific amount of Fe $(NO_3)_3 \cdot 9H_2O$ (Merck) (0.030–0.14 wt.% of iron ions in the catalyst) was dissolved in a beaker containing 50 mL of distilled water. Then, kaolin was added to this aqueous solution, stirred constantly and heated until all water was evaporated. After impregnation, the sample was dried at 105 °C for 12 h, followed by calcination at 500 °C for 4 h in a muffle furnace.

2.2. Decolorization of AR1

All experiments were carried out in batch mode using conical flasks filled with 200 mL of the AR1 solution at concentration of 50 mg/L. At a fixed pH, a given mass of the catalyst and a given volume of a 30% hydrogen peroxide (H_2O_2) were added to the AR1 solution. The mixture was maintained under constant agitation. Thereafter, samples were withdrawn periodically and analyzed using a UV–Vis spectrophotometer (Shimadzu, model UV 1601, Japan) with the

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* Corresponding author. Fax: +60 45941013.
E-mail address: chbassim@eng.usm.my (B.H. Hameed).

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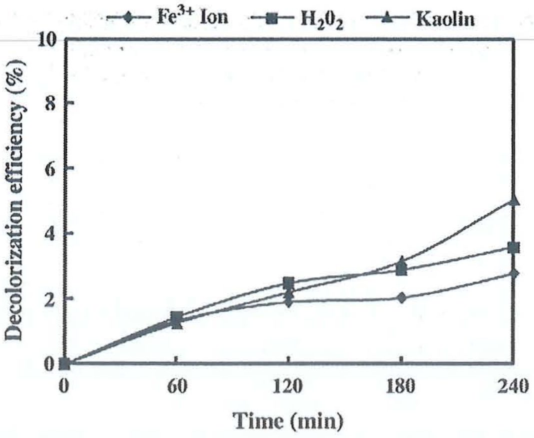

Fig. 1. Un-catalyzed AR1 removal by ferric ion (0.050 mM), hydrogen peroxide (4 mM) and adsorption on kaolin (2.0 g/L). Reaction conditions: initial concentration of AR1, $[\mathrm{AR1}]_o = 50$ mg/L, pH = 2.5, temperature 30 °C and agitation speed = 130 rpm.

maximum absorbance for AR1 at 532 nm. At each stage, the sample withdrawn was returned into the conical flask to prevent any loss of contents.

The total iron concentration in the solution was determined using Atomic Absorption Spectrophotometer (AAS) model Shimadzu AA 6650 with the maximum absorbance wavelength (λ_{max}) of iron ion obtained at 248.35 nm.

3. Results and discussion

3.1. Decolorization of the AR1 with Ferric ion, hydrogen peroxide or kaolin alone

Fig. 1 shows that only a small decrease of the AR1 concentration occurred within 240 min in the absence of the catalyst. Indeed for adsorption process using kaolin, only 5.05% of the dye was adsorbed in time-span 240 min whereas only 2.79% and 3.59% decolorization occurred for ferric ion and hydrogen peroxide alone, respectively. This result is certainly in agreement with the literature. Ramirez et al. [9] has also reported slow decolorization process of azo-dye Orange II using un-catalysed hydrogen peroxide.

3.2. Decolorization of AR1 under different parameters of process

Decolorization of AR1 solution by Fenton-like oxidation using Fe-kaolin catalysts was studied in batch process with different parameters: iron (III) oxide loading on kaolin, catalyst dosage, pH and hydrogen peroxide concentration. All the best results of these parameters in the decolorization process are reported in Table 1.

The effect of iron (III) oxide loading on kaolin was investigated by varying the ferric (Fe^{3+}) ions concentration on the support (0.030, 0.060, 0.080, 0.11 and 0.14 wt.%). The decolorization efficiency influenced by the concentration of ferric ions loading on supports and 98.51% decolorization was observed for the best result (0.080 wt.%) within 240 min reaction.

The effect of Fe-kaolin dosage on the decolorization was investigated by varying the Fe-kaolin dosage (1.0, 2.0, 3.0, 4.0 and 5.0 g/L). It can be seen for the best decolorization efficiency, a suitable catalyst dosage for the decolorization of AR1 by heterogeneous Fenton-like process is 4.0 g/L at the concentration of the dye and H_2O_2 employed.

Since solution pH plays an important role in the catalytic oxidation by hydrogen peroxide, experiments were carried out at different initial pH values (1.5, 2.0, 2.5, 3.0, 3.5, 4.0 and 5.0) without any adjustment of pH during the experiments for an initial AR1 concentration of 50 mg/L. It was observed (Table 1) that the decolorization of AR1 was significantly influenced by the pH value of the solution and the highest decolorization efficiency was achieved at pH 3.0 with 98.37% decolorization efficiency. At low pH (pH <3.0), the reaction could be slowed down because H_2O_2 can stay stable probably by solvating a proton to form an oxonium ion ($H_3O_2^+$). An oxonium ion ($H_3O_2^+$) makes H_2O_2 electrophilic to enhance the stability and presumably reduce substantially the reactivity with ferrous ion. The formed complex species $[Fe\ (H_2O)\ _6]^{2+}$ and $[Fe\ (H_2O)\ _6]^{3+}$ react more slowly with H_2O_2 In and the scavenging effect of the OH radical by H^+ was severe [10]. On the other hand, in case of pH >3.0, the oxidation

Table 1
Effects of four parameters on the decolorization of AR1 at different reaction conditions.

Fe(III) oxide loading on kaolin (wt.%)	Catalyst dosage (g/L)	pH	$[H_2O_2]$ (mM)	Decolorization efficiency (%) at reaction time, t (min)			
				60	120	180	240
0.030	2.0	2.5	4.0	3.84	10.72	21.40	37.69
0.060	2.0	2.5	4.0	4.19	16.41	38.60	78.87
0.080	2.0	2.5	4.0	4.93	24.46	40.86	98.51
0.11	2.0	2.5	4.0	2.94	12.01	36.61	80.03
0.14	2.0	2.5	4.0	4.03	9.59	30.21	75.45
0.080	1.0	2.5	4.0	6.53	17.16	52.83	56.15
0.080	2.0	2.5	4.0	7.55	29.11	82.85	84.95
0.080	3.0	2.5	4.0	11.53	78.21	94.16	96.06
0.080	4.0	2.5	4.0	20.81	90.22	95.02	98.81
0.080	5.0	2.5	4.0	11.33	67.42	95.03	96.04
0.080	4.0	1.5	4.0	6.89	15.93	24.83	22.32
0.080	4.0	2.0	4.0	5.24	6.79	12.46	17.45
0.080	4.0	2.5	4.0	5.37	8.94	21.16	46.44
0.080	4.0	3.0	4.0	11.91	34.48	73.09	98.37
0.080	4.0	3.5	4.0	0.22	1.73	7.51	15.76
0.080	4.0	4.0	4.0	0.23	0.45	1.94	4.08
0.080	4.0	5.0	4.0	1.43	0.95	0.95	0.47
0.080	4.0	3.0	4.0	13.76	42.61	84.25	93.89
0.080	4.0	3.0	8.0	11.27	57.49	89.75	98.46
0.080	4.0	3.0	12.0	9.93	49.45	88.38	92.69
0.080	4.0	3.0	16.0	7.98	37.80	84.77	93.64
0.080	4.0	3.0	20.0	9.08	38.62	84.04	91.68
0.080	4.0	3.0	32.0	8.80	27.87	71.44	90.07

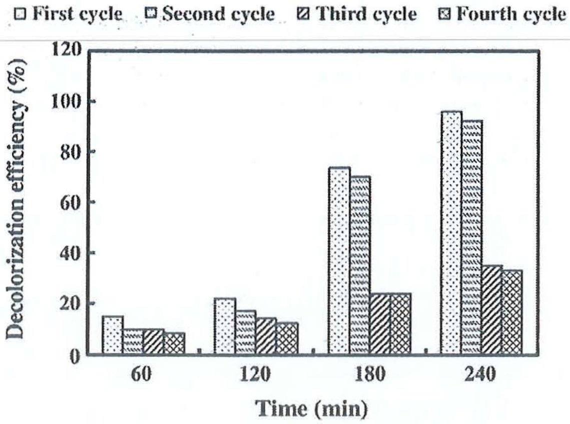

Fig. 2. Reusability test of the Fe-kaolin. Reaction conditions: initial concentration of AR1, $[AR1]_o = 50$ mg/L, initial concentration of hydrogen peroxide, $[H_2O_2]_o = 8.0$ mM, dosage of catalyst = 4.0 g/L with 0.080 wt.% of iron ions in catalyst, agitation speed = 130 rpm, temperature = 30 °C and pH = 3.0.

efficiency rapidly decreased, not only by decomposition of H_2O_2 but also by deactivation of a ferrous catalyst with the formation of ferric hydroxide complexes leading to a reduction of ˙OH radical [11].

The influence of different concentrations of H_2O_2 on the decolorizing of AR1 in the heterogeneous Fenton-like process was investigated from 4.0, 8.0, 12, 16, 20 and 32 mM. The enhancement of decolorization rate by addition of H_2O_2 was due to increase in ˙OH radicals. However, it should be pointed out that when the concentration of H_2O_2 was over 8.0 mM, the removal of AR1 decreased slightly. This can be explained by the scavenging of OH radicals at a higher concentration of H_2O_2, leading to decrease in the number of OH radicals in solution. Hence, a dosage of 8.0 mM H_2O_2 can be used as the optimum dosage for the decolorization of AR1.

The results of the effects of four parameters on the decolorization of AR1 at different reaction conditions are listed in Table 1. Under the best reaction conditions, 98.46% decolorization efficiency was obtained within 240 min at 4.0 g/L of 0.080 wt.% Fe-kaolin with 8.0 mM of hydrogen peroxide in pH 3.0 of AR1 solution.

3.3. The stability of Fe-kaolin catalyst

The stability of the Fe-kaolin catalyst was tested by contacting fresh AR1 solutions with 4.0 g/L of 0.080 wt.% of Fe-kaolin catalyst from previous cycles for the decolorization of AR1 under identical reaction conditions. This experiment was run in four consecutive cycles. As can be observed in Fig. 2, 98.46% decolorization efficiency of AR1 was achieved within 240 min of reaction in the first cycle. In the second, third and fourth cycles, 92.78, 35.66 and 33.81% decolorization of AR1 were achieved respectively. From the results, the reaction performances are significantly affected. This might be due to the loss of catalyst rather than active phase leaching. Other authors reported similar results, but they attributed the loss of activity to poisoning of the active catalytic sites due to adsorbed organic species [12]. Catalyst deactivation may occur due to a diversity of factors including reduction of the catalyst specific area, poisoning of the catalytic agents by compounds formed during oxidation and surface deposition [13]. Leaching tests were carried out to check the potential of leaching of iron ions from the catalysts after decolorization process of AR1 completed. It was found that concentration of iron ion in the solution after reuse of the catalyst (0.080 wt.% Fe-kaolin) for four consecutive cycles were 3.22, 2.49, 1.34 and 0.45 mg/L, respectively.

4. Conclusions

The results revealed that under the best reaction conditions of a reaction temperature 30 °C, pH 3.0, 8.0 mM H_2O_2, 4.0 g/L of 0.080 wt.% Fe-kaolin catalyst, 98.46% of AR1 decolorization was achieved within 240 min treatment. The experiments of stability showed that Fe-kaolin showed some activity decay after reuse for four consecutive cycles. This may be due to the loss of catalyst and active phase leaching during the experiments. Fe-kaolin catalyst exhibited good catalytic activity decolorization of AR1.

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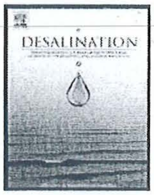

Oxidative decolorization of Acid Red 1 solutions by Fe–zeolite Y type catalyst

H. Hassan, B.H. Hameed *

School of Chemical Engineering, Engineering Campus, Universiti Sains Malaysia, 14300 Nibong Tebal, Penang, Malaysia

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A study of the decolorization of azo dye, Acid Red 1 (AR1), in an aqueous solution using Fe–zeolite Y type (Fe–ZYT) catalyst has been carried out. The effects of different reaction parameters such as initial iron ions loading on zeolite Y type (ZYT), catalyst dosage, solution pH and initial concentration of H_2O_2, dye solution and reaction temperature on the decolorization of AR1 were studied. The best reacting conditions were 0.80 wt.% of iron ions loading on ZYT, catalyst dosage = 2.50 g/L, initial pH = 2.5, $[H_2O_2]_o = 16$ mM, and $[AR1]_o = 50$ mg/L at temperature 30 °C. Under these conditions, 99% decolorization efficiency of AR1 was achieved within 60 min of reaction time. The results indicated that Fe–ZYT was a promising catalyst for the heterogeneous Fenton system.

1. Introduction

Colorants are widely used in textiles, printing, dyeing, and food industries. Significant losses of these dyes can occur during the dyeing and finishing operations and are released into wastewater treatment system. Dyes in wastewater can create esthetic problems, limit the possible use of water and obstructs light penetration and oxygen transfer into water bodies, hence affecting the aquatic life [1]. In addition, these effluents are a threat to ecosystems due to its toxicity and resistance to destruction by biological treatment methods.

Azo dyes, which are characterized by nitrogen to nitrogen double bond (—N N—), are the largest and most important class of synthetic organic dyes that are widely used in industries today because of its cost effectiveness in synthesis, firmness and variations in color compared to natural dyes [2]. Yearly, 800,000 tonnes of dyes are produced in the world and about 50% of them are azo dyes [3]. Azo dyes are not biodegradable by aerobic treatment processes [4]. In addition, under anaerobic condition, they are reduced to potentially carcinogenic aromatic amines which cause long term health concerns [5,6].

The Fenton-like processes are used as a powerful source of hydroxyl radical from H_2O_2 in the presence of transitional metal cations, such as iron $Fe^{2+}/Fe^{3+}/H_2O_2$, to decompose many organic compounds including dyes. However, the usage of homogeneous Fenton has a number of disadvantages such as the formation of different Fe(III) complexes as solution pH changes, requirement of narrow range of pH value for reaction and the need for the removal of remaining iron ions after the treatment [7].

Heterogeneous Fenton process demonstrates its capability for degradation of dyes and organic pollutants to the required low limit of concentration with a wider pH range. In heterogeneous catalyst, the iron cation is "immobilized" within the structure and in the pore/interlayer space of catalyst. As a result, the catalyst can maintain its ability to generate hydroxyl radicals from H_2O_2, and iron hydroxide precipitation is prevented [8]. In heterogeneous Fenton most of the reactions take place either at the surface of the supports or in the pores of the support, and only a very small portion occurred in the bulk. The reactions at the inner pores could be limited by double diffusion (H_2O_2 in and OH radicals out of the support pores). The hydroxyl radicals possess inherent properties that enable it to attack organic pollutants in water to obtain a complete mineralization into CO_2, water and mineral acids [9]. Selection of catalyst supports is important during the preparation of heterogeneous catalyst. A good heterogeneous catalyst should meet two requirements: it must have high catalytic activity and low iron dissolution. The use of heterogeneous solid Fenton catalyst such as Fe contained zeolite and clays can be an alternative method [10].

Zeolites are hydrated aluminosilicates with a cage-like structure. Their internal and external surface areas may extend to several hundred m^2/g, while their cation exchange capacities are up to several milliequivalents per kilogram. Zeolites have an open porous structure capable of accommodating a wide variety of exchangeable cations, including iron [11,12]. Zeolites are ideal catalysts because the dimension of their pores is similar to that of the reacting molecules [13–15]. Thus, zeolites can function as both selective adsorbents and '*in-situ*' oxidation catalysts [16]. The size and shape of the nanopores in synthetic zeolites can vary according to the experimental conditions as do their macroscopic properties [12,13,16]. Being strongly bound to exchange sites within the pore structure, the transition metals (e.g., iron, copper) are not prone to leach out or precipitate during the process [13].

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* Corresponding author. Fax: +60 45941013.
E-mail address: chbassim@eng.usm.my (B.H. Hameed).

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In this work, the decolorization of the non-biodegradable azo dye, Acid Red 1 (AR1) by using iron immobilized on zeolite Y type (ZYT) as active heterogeneous catalyst was studied. The effects of different initial iron ions loading on ZYT, initial concentration of the dye and H_2O_2, catalyst dosage, initial pH and temperature of the dye solution on the decolorization efficiency of the process were discussed.

2. Materials and methods

2.1. Chemicals and reagents

Azo dye, AR1 and hydrogen peroxide (30%, w/w) were purchased from Sigma-Aldrich (M) Sdn Bhd, Malaysia. The structural diagram of AR1 is shown in Fig. 1. The Fe $SO_4 \cdot 7H_2O$ was obtained from Merck, Germany. Zeolite Y type was purchased from Zeolyst International. All chemicals were of analytical grade and were used without any further purification. The pH of the solution was adjusted by 1.0 M H_2SO_4 or 1.0 M NaOH.

2.2. Preparation of Fe–zeolite Y type

The Fe–zeolite Y type (here refer to as Fe–ZYT) was prepared by impregnation method [17]. In this process, $FeSO_4 \cdot 7H_2O$ (Merck) was dissolved in a beaker containing distilled water. Then, ZYT was added to this aqueous solution and was stirred by a glass rod uniformly in the water bath at 100 °C until all water was evaporated. After completing the impregnation, the solids were dried at 85 °C for 12 h and then calcined at 500 °C for 4 h in a muffle furnace.

2.3. Catalyst characterization

The morphology of the ZYT and Fe–ZYT was observed, by using Scanning Electron Microscopy (SEM) (SEM-JEOL-JSM6301-F). The composition of the original ZYT and the exact amount of iron in the synthesized catalyst and after reaction with AR1 were carried out using Energy Dispersive X-ray (EDX) (Oxford INCA 400, Germany). The apparatus is linked to the SEM.

Fourier Transform Infrared (FTIR) spectra were recorded in the 4000–400 cm^{-1} region with a Perkin-Elmer 1730 FTIR spectrometer, using a He–Ne laser source in KBr pellet (1 mg sample with 300 mg KBr) and 15 scan per minute to improve the signal-to-noise ratio.

Brunauer Emmett–Teller (BET) specific surface areas were determined by adsorption of nitrogen at 77 K, by using a Micromeritics, ASAP 2020 surface area and porosity analyzer.

The crystalline structure of the ZYT and Fe–ZYT was analyzed by Siemen d-5000 diffractometer, using CuKα radiation and a graphite secondary beam monochromator at 40 kV and 30 mA with filtered CuKα radiation ($\lambda = 1.5418$ Å) with a measuring time of 2 s per point.

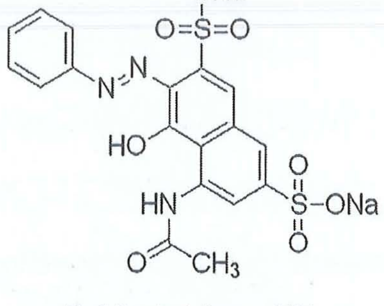

Fig. 1. Structural diagram of AR1.

2.4. Catalytic activity

All experiments were carried out in a 250 mL-stoppered glasses (Erlenmeyer flask) filled with 200 mL diluted solutions (25–100 mg/L). The pH was adjusted by addition of 1.0 M H_2SO_4 or 1.0 M NaOH to the solution followed by an addition of catalyst. The reactions were initiated by adding predetermined amounts of H_2O_2 solution to the flask. The flasks were then placed in a thermostated water bath shaker and agitation was provided at 130 rpm for 60 min. The concentrations of dyes were analyzed by using a double beam UV/Vis spectrophotometer (Shimadzu, model UV 1601, Japan) at a wavelength of 532 nm. For each stage, the samples withdrawn were returned into the conical flask to prevent any loss of contents.

The effect of iron ions loading on the ZYT for the AR1 removal was studied over the iron ions loading range from 0.20 to 1.0 wt.%. Briefly, 2.50 g/L of Fe–ZYT at different iron ions loading (0.20–1.0 wt.%) was agitated in a thermostated water-bath shaker at 30 °C, 130 rpm and 60 min. The solution pH and H_2O_2 concentration were maintained at 2.5 and 4 mM, respectively.

In addition, the activity of this catalyst to decolorize AR1 was tested by varying other parameter such as pH solution in the range of 2.0–5.0, initial concentration of H_2O_2 between 4.0 and 32 mM, AR1 concentration from 25 to 100 mg/L and temperature in the range of 30–50 °C. In all the experimental runs, other parameters were kept constant and samples were being withdrawn at regular intervals of time for the analysis of the product solution.

2.5. Analytical methods

The UV–vis spectra of AR1 was recorded from 200 to 800 nm using a UV/Vis spectrophotometer (Shimadzu, model UV 1601, Japan) with a spectrometric quartz cell (1 cm path length). The maximum absorbance wavelength (λ_{max}) of AR1 was found at 532 nm. In order to decrease the experimental error, the samplings and measurement of absorbance of reaction solution were done within 1 min since the reaction could continue after sampling. The decolorization efficiency (%) of AR1 was defined as follows:

$$\text{Decolorization efficiency}(\%) = \left(\frac{C_o - C_t}{C_0}\right) \times 100 \tag{1}$$

where C_o (mg/L) is the initial concentration of AR1 and C_t (mg/L) is the concentration of AR1 at reaction time, t (min).

2.6. Leaching tests

After the oxidation with hydrogen peroxide, the catalysts were removed by filtration and the total iron concentration in the liquid phase was determined by using Atomic Absorption Spectrophotometer (AAS) model Shimadzu AA 6650 with the maximum absorbance wavelength (λ_{max}) of iron ion at 248.35 nm. Prior to the measurement, a calibration curve was obtained by using the standard iron ion solution in 0.10 M HNO_3 solution with known concentrations.

3. Results and discussion

3.1. Catalyst characterization

Elemental chemical analyses were performed to determine the composition of original ZYT support and the exact amount of iron in the final Fe–ZYT catalyst after it had undergone impregnation process and the result is listed in Table 1. The result showed that the main elements detected by EDX included iron, silica, oxide and alumina with different percentage of concentrations. The iron concentration of the 0.80 wt.% Fe–ZYT catalyst is 3.50 wt.%, while it is only 2.68 wt.% in the original ZYT. Slight variations were noticed between the expected

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Table 1
Chemical compositions of zeolite Y type (ZYT), 0.80 wt.% Fe–zeolite Y type (Fe–ZYT) and 0.80 wt.% Fe–zeolite Y type (Fe–ZYT) after undergoing oxidation with AR1 determined by EDX.

Element	Concentration (wt.%)		
	ZYT	0.80 wt.% Fe–ZYT	0.80 wt.% Fe–ZYT after oxidation with AR1
O	41.38	45.97	48.42
Fe	2.68	3.50	2.87
Al	16.92	13.35	14.23
Si	39.02	37.18	34.48

and determined iron content of the samples, which is due to the high hydration degree of solid at the stages of the preparation procedure, thus making it difficult to obtain the targeted iron contents [18]. Similar result was also reported by Ramirez et al. [19] in their study of Fenton-like oxidation of Orange II solutions using saponite clay as heterogeneous catalyst.

The stability of the support was also evaluated in terms of percentage of iron remains on the catalyst support after Fenton oxidation process. Table 1 showed that small amount of iron concentration was lost from the support after it had undergone oxidation with AR1 solution. This indicating that the active phases are strongly fixed to the support (possibly iron strongly bonded to oxide compound which is dispersed in the solid, inside or outside the porosity). This characteristic makes it possible for the heterogeneous catalyst to have long term stability, without generating iron hydroxide sludge [19].

Fig. 2 shows the microscopy image of original ZYT and 0.80 wt.% Fe–ZYT. The ZYT appeared as conglomerate of irregular polyhedra. No differences are observed in surface morphologies between the original and Fe-containing zeolite. The surface is smooth without any obvious deposit of iron particles. This implies that iron particles were dispersed homogeneously into the micropores of zeolite, which is thought to be responsible for the stability and activity of the catalyst [20].

In order to investigate the surface characteristics of ZYT and Fe–ZYT, FTIR analyses were carried out in the range 4000–400 cm^{-1} (Fig. 3). There are two groups of frequency of vibrations in all zeolites: internal vibrations of T–O (considered insensitive to structure) and vibration of external linkages between tetrahedral, due to topology and the mode of structure arrangement [21]. The results as presented in Fig. 3 show that the FTIR spectrum of ZYT and Fe–ZYT is in good agreement with typical zeolite structures [22]. The FTIR band connected with the internal Si–O (Si) and Si–O(Al) vibrations in tetrahedral or alumino- and silico-oxygen bridges lies in the range of 1200–400 cm^{-1}. The bands due to the presence of zeolite water lie in the range of 1600–3700 cm^{-1}. There are several types of zeolitic water. Water on the silicate minerals exists in two forms; as intact molecules and as OH groups formed on dissociation of water interacting with metal (Si^{4+}, Al^{3+}, and Be^{3+}) and O^{2-} ions. The OH group is less acidic if the number of aluminum atoms increases because Al possesses less electronegativity. There are bands due to pseudo-lattice vibrations of structural units (500–700 cm^{-1}) and the bands connected with lattice vibrations (below 400 cm^{-1}) [23]. A sharp decrease in the intensity of the absorption bands of pseudo-lattice vibrations of structural units at 578.98 cm^{-1} for Fe–zeolite Y type compared to zeolite Y type. The absorption band at 3188.99 cm^{-1} and 1401 cm^{-1} represents OH groups of water and C–O–H bend of water, respectively. All these bands disappeared completely when the impregnated zeolite Y type was calcined at 500 °C. Physically adsorbed water is mainly eliminated at temperature greater than 100 °C. Hydroxyl is removed through the associative desorption mechanism at ~100–300 °C or higher. Hydroxyl groups leave the surface mainly at 200–500 °C, moreover the isolated OH groups are eliminated at higher temperatures. At temperatures greater than 400 °C almost all OH-groups on the silicate surfaces are isolated [23]. It can be concluded that impregnation and calcination process can cause structural modification of the natural zeolite Y type.

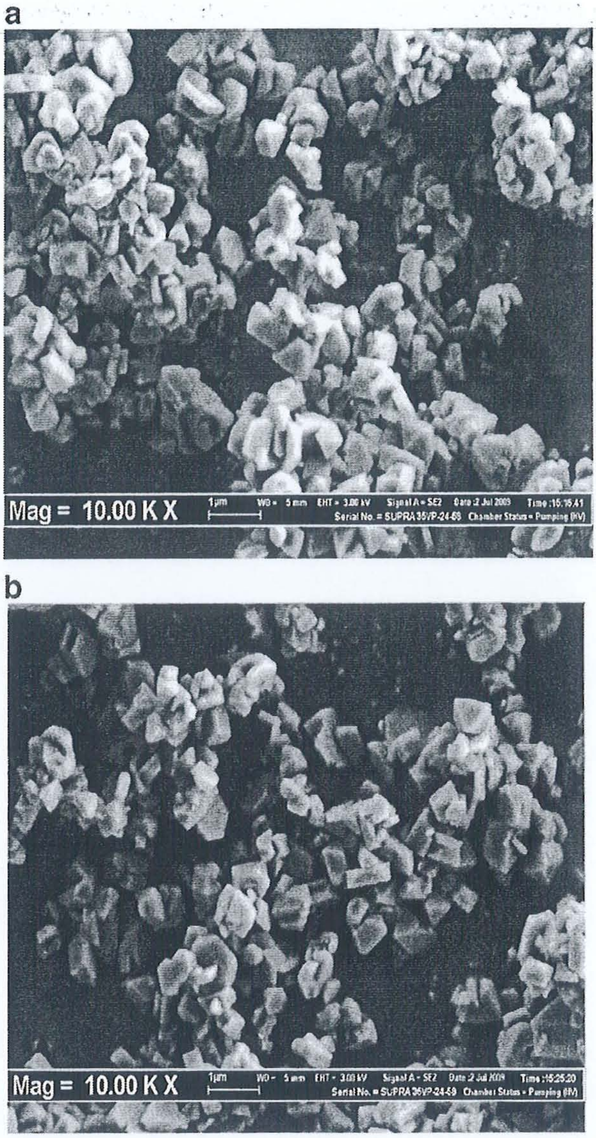

Fig. 2. SEM images of (a) zeolite Y type (b) 6.47 wt.% of Fe-zeolite Y type (Magnification : 10 kX).

X-ray diffraction analysis was used to study the iron chemical state and dispersion of iron ions in catalysts. Fig. 4 shows the XRD spectra for ZYT and impregnated ZYT. The diffractogram showed that both samples are in crystalline phase and reveals a typical zeolite Y type structure. The main minerals found in the catalyst are Faujasite (Ca-exchanged hydrated) and Aluminum Silicate Hydroxide. X-ray diffraction results obtained for Fe–ZYT showed that impregnation of ZYT with iron ions did not change the d-spacing on the lattice structure of Fe–ZYT to any significant degree, as similar peaks with those for the natural zeolite were obtained. This strongly suggests that the impregnation with iron reagent was effective only on the surface of the zeolite and not on the crystal of the zeolite catalyst [24]. However, even though both ZYT and Fe–ZYT showed almost the same peaks, the Fe–ZYT catalyst showed peak intensities different at 2θ = 23.72° from the ZYT sample, which could be an indication of structural arrangement of Fe–ZYT due to the impregnation process. Two sharp and small peaks of iron oxide were formed after calcinations of the impregnated ZYT which were detected at 2θ value of 32.48° and 56.32°. These results imply that, ferrous species

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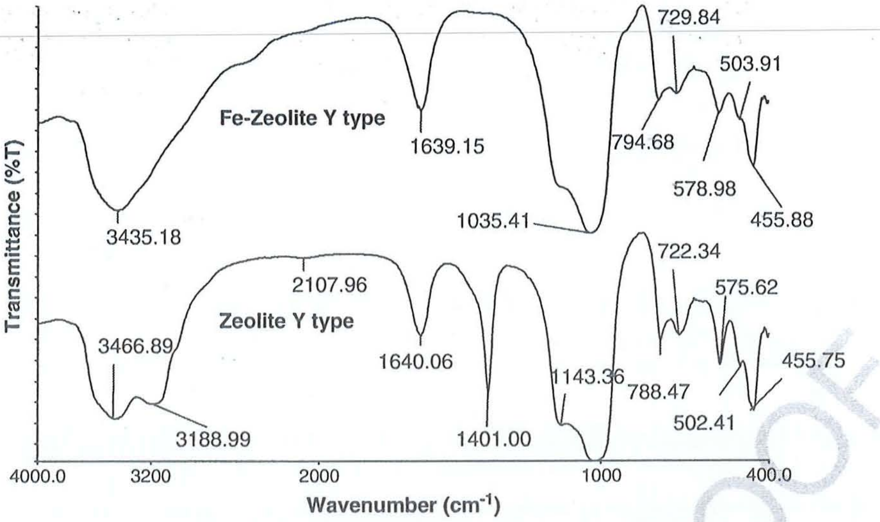

Fig. 3. FTIR spectra of the zeolite Y type and Fe-zeolite Y type.

were oxidized to form a layer of Fe_2O_3 on the surface of the zeolites along with the increasing of calcinations temperature.

The Brunauer Emmett–Teller (BET) surface area, pore volume and pore size of 0.80 wt.% Fe–ZYT are 627.888 $m^2\,g^{-1}$, 0.343 $cm^3\,g^{-1}$ and 21.840 Å, respectively.

3.2. Catalytic performance of Fe–Zeolite Y type

In order to elucidate the influence of different mechanism participating in the decolorization of AR1 by heterogeneous Fenton process, comparative experiments were undertaken in the presence of (i) AR1 + H_2O_2 only, (ii) AR1 + raw ZYT only (adsorption on ZYT) (iii) AR1 + Fe–ZYT only (adsorption on Fe–ZYT) (iv) AR1 + ZYT + H_2O_2 (decolorization of AR1 with the presence of iron ions in the raw ZYT) (v) AR1 + Fe^{2+} + H_2O_2 (homogeneous Fenton) and (vi) AR1 + Fe–ZYT H_2O_2 (heterogeneous Fenton). The relative decolorization efficiency of AR1 under these different conditions is presented in Table 2. From the results shown in Table 2 it can be observed that in the (i) condition, the decolorization efficiency of AR1 is the lowest and almost negligible. This behavior might be attributed to the low oxidation potential of hydrogen peroxide as compared to hydroxyl or perhydroxyl radicals [25]. In the presence of raw ZYT and Fe–ZYT only, less than 13% decolorization of AR1 can be achieved to the adsorption of AR1 by solid sample. Therefore, it could be concluded that adsorption of the dye molecules onto ZYT and Fe–ZYT solid particles does not play a significant role in the decolorization process. In the presence of raw ZYT and H_2O_2, slightly higher AR1 decolorization was achieved.

For the homogeneous Fenton process, the ferrous ion concentration was selected as 1.4475 mg/L which was detected in the aqueous solution after the third cycle of oxidation under optimum parameters. Homogeneous Fenton oxidation may occur via the reaction of hydrogen peroxide and ferrous ion that leached from the catalyst in the bulk solution. Table 2 clearly shows that heterogeneous system is faster than homogeneous system. The difference in the rate of reaction may be seen as due to the synergistic effect resulting from the adsorption property of zeolite [26]. The adsorbed pollutant molecules in the immediate vicinity of immobilized iron ions are easily attacked by the generated ˙OH radicals which would result in faster decolorization of AR1. Therefore it can be concluded that the main role in overall decolorization efficiency of AR1 can be attributed to the reaction taking place at the solid surface of Fe–ZYT due to the activity of the heterogeneous catalyst rather than the leached iron ions. Similar results was observed by Centi et al. [27] who compared the catalytic efficiency of the homogeneous Fenton process with heterogeneous Fenton-like reaction by using Fe-ZSM-5 catalyst.

3.3. Effect of iron ions loading on zeolite Y type

The effect of iron ions loading on zeolite Y type was investigated by varying the iron ions concentration from 0.20 to 1.0 wt.%. The results indicated that the decolorization of AR1 is remarkably dependent on the ferrous ion concentration at fixed initial concentration of hydrogen peroxide and AR1 and the results are illustrated in Fig. 5. It can be observed that the decolorization of AR1 was limited at 0.20 wt.% of iron

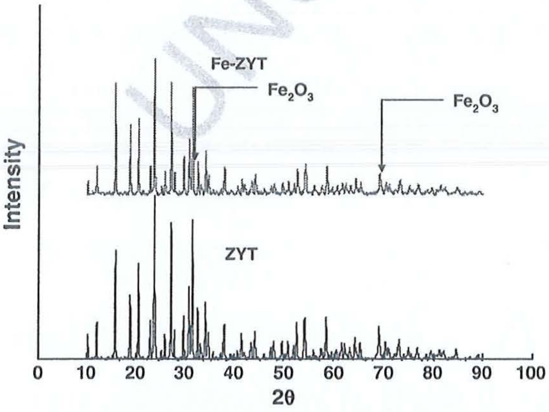

Fig. 4. XRD diffractograms of the ZYT and Fe-ZYT catalysts.

Table 2
Effect of various experimental parameters on decolorization of AR1.

Mechanisms in the decolorization of AR1	Decolorization efficiency (%) within 60 min reaction time
AR1 + H_2O_2 only	2.49
AR1 + raw ZYT only (adsorption on ZYT)	12.81
AR1 + Fe–ZYT only (adsorption on Fe–ZYT)	12.93
AR1 + ZYT + H_2O_2 only	13.81
AR1 + Fe^{2+} + H_2O_2 (homogeneous Fenton)	89.57
AR1 + Fe–ZYT + H_2O_2 (heterogeneous Fenton)	98.85

Reaction conditions: initial concentration of AR1, $[AR1]_o = 50$ mg/L, initial concentration of hydrogen peroxide, $[H_2O_2]_o = 16$ mM, pH = 2.5, catalyst concentration = 2.50 g/L, temperature = 30 °C and agitation speed = 130 rpm.

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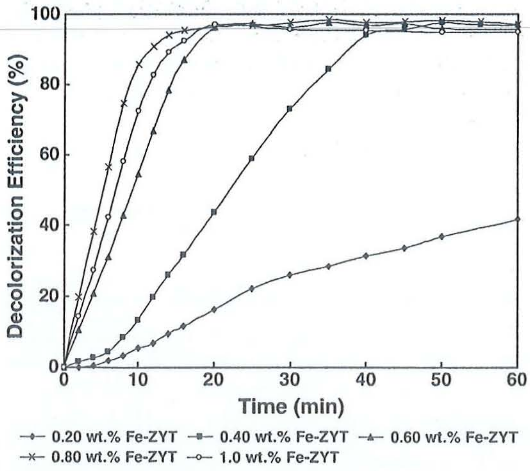

Fig. 5. Effect of iron ions loading on zeolite Y type on the decolorization of AR1. Reaction conditions: initial concentration of AR1, $[AR1]_o = 50$ mg/L, initial concentration of hydrogen peroxide, $[H_2O_2]_o = 4$ mM, pH = 2.5, catalyst dosage = 2.50 g/L, temperature = 30 °C and agitation speed = 130 rpm.

ions loading and only 26.1% of AR1 was decolorize within 30 min of reaction time. In the presence of 0.80 wt.% of iron ions loading, a great improvement of decolorization of AR1 could be observed and the decolorization efficiency achieved was 99% within 30 min of reaction. Hence, the best loading of iron ions was selected as 0.80 wt.% for the decolorization of 50 mg/L of AR1. With further increase in the iron ions loading up to 1.0 wt.%, the decolorization efficiency was decreased to 95.6% within 30 min of reaction time. This trend was likely due to the inhibition effect shown by the iron ions.

3.4. Effect of catalyst dosage

The influence of catalyst dosage on decolorization efficiency of AR1 versus time is illustrated in Fig. 6. It can be seen that increasing the catalyst dosage has a positive impact on the decolorization efficiency of AR1. The decolorization efficiency increased from 94.8% to 98.7% within 30 min of reaction time when the catalyst dosage increased from 0.50 to 2.50 g/L. This behavior can be explained by the fact that higher dosage will give higher overall amounts of iron ions in the zeolite framework as well as higher concentration of iron ions in the bulk, which in turn increase the number of hydroxyl radical significantly. Also, higher dosage of Fe–ZYT increased the power of the system for AR1 adsorption [28]. The best catalyst dosage for the decolorization of AR1 was experimentally detected at 2.50 g/L.

3.5. Effect of solution pH

The pH of the solutions controls the production rate of hydroxyl radical and the concentration of iron ions. Hence, pH is an important operational variable or parameter in actual wastewater treatment and Fenton process, respectively [29]. The influence of solution pH on the decolorization of AR1 was conducted at different pH values of 2.0, 2.5, 3.0, 4.0 and 5.0. The result is illustrated in Fig. 7. The best solution pH was obtained at pH 2.5. At pH 4 and 5, the decolorization of AR1 was 19.7% and 18.7%, respectively within 30 min of reaction time. This could be explained by the formation of ferrous/ferric hydroxide complexes which lead to the deactivation of ferrous catalyst [30].

In the acidic medium, the zeolite framework will not undergo any disintegration of structure since it has a high value of Si/Al ratio which is 5.1 [31]. It is well known that the acid tolerance of zeolite catalyst depend on their Si/Al ratio; the higher the Si/Al ratio, the higher the acid resistance [32]. The acidic medium is needed since the optimal solution pH of Fenton oxidation process mostly falls in the pH range of 2.5–3.5 [33].

3.6. Effect of the initial H_2O_2 concentration

Hydrogen peroxide was decomposed at the surface of Fe–ZYT to generate $^{\cdot}OH$ radical. The effect of H_2O_2 dosage on the decolorization of AR1 was examined by varying the initial concentration of H_2O_2 from 4 to 20 mM and the result is as shown in Fig. 8. The results indicated that the decolorization efficiency of AR1 was increased from 93.4%, to 99.8% when the initial H_2O_2 concentration was increased from 4 to 16 mM. This is due to the oxidative power of Fenton process, which was improved with increasing $^{\cdot}OH$ radical in solution by the decomposition of H_2O_2. However, when H_2O_2 concentration was increased from 16 to 20 mM, at the same operation conditions, the decolorization efficiency of AR1 decreased. This may be explained by the

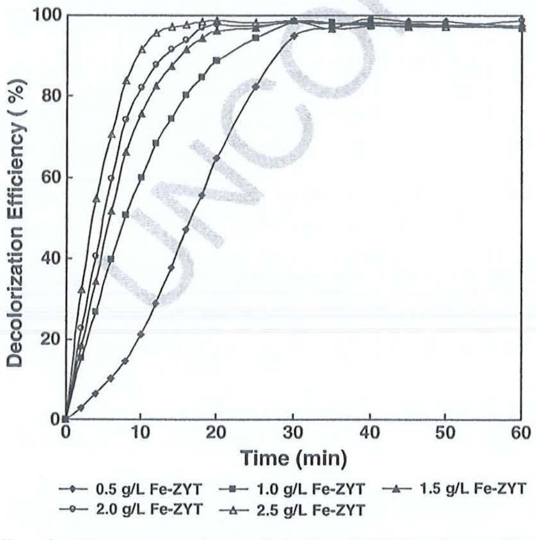

Fig. 6. Effect of catalyst dosage on the decolorization of AR1. Reaction condition: initial concentration of AR1, $[AR1]_o = 50$ mg/L, initial concentration of hydrogen peroxide, $[H_2O_2]_o = 4$ mM. pH = 2.5, 0.80 wt.% of iron ions in catalyst, temperature = 30 °C and agitation speed = 130.

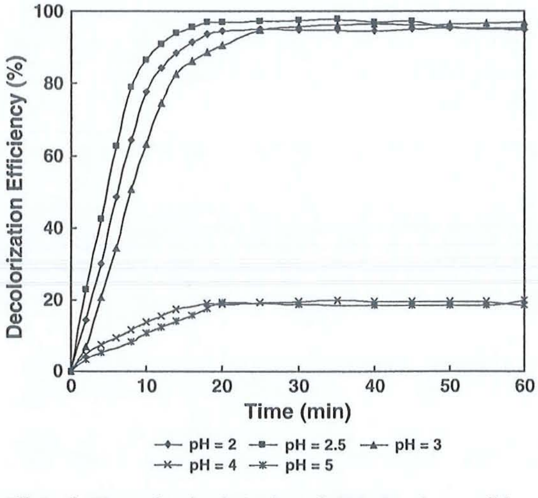

Fig. 7. Effect of pH on the decolorization of AR1. Reaction conditions: initial concentration of AR1, $[AR1]_o = 50$ mg/L, initial concentration of hydrogen peroxide, $[H_2O_2]_o = 4$ mM, catalyst dosage = 2.50 g/L with 0.80 wt.% of iron ions in catalyst, temperature = 30 °C and agitation speed = 130 rpm.

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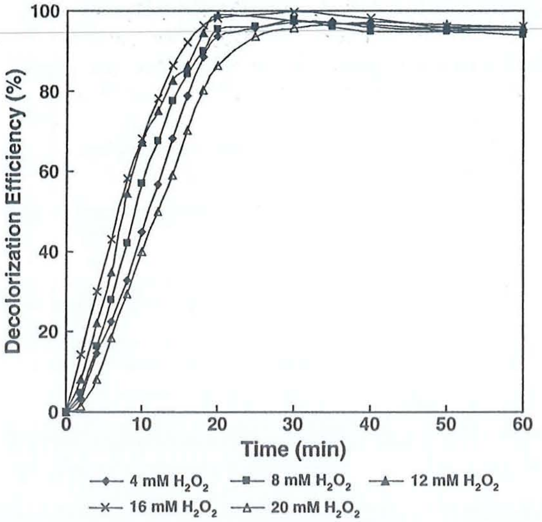

Fig. 8. Effect of initial concentration of hydrogen peroxide on the decolorization of AR1. Reaction conditions: initial concentration of AR1,$[AR1]_o = 50$ mg/L, catalyst dosage = 2.50 g/L with 0.80 wt.% of iron ions in catalyst, temperature = 30 °C, agitation speed = 130 rpm and pH = 2.5.

fact that at high concentration of H_2O_2, there is a scavenging effect of excessive H_2O_2 to $HO_2^{\bullet}$ (Eq. (2)) [34].

$$H_2O_2 + HO^{\cdot} \rightarrow H_2O + HO_2^{\bullet} \tag{2}$$

Such reaction reduces the probability of attack of organic molecules by hydroxyl radicals, and causes the decolorization rate to drop. Although other radicals ($HO_2^{\bullet}$) are produced, their oxidation potentials is much smaller than that of the $^{\bullet}OH$ species. It can be concluded that an initial H_2O_2 concentration higher than 16 mM corresponds to an unprofitable consumption of H_2O_2. Watts et al. [35] reported that different mechanism may be occurring on the surface at high hydrogen peroxide concentration and the sorption rate could be a controlling factor of the whole catalytic oxidation reaction.

3.7. Effect of the initial AR1 concentration

To study the influence of initial dye concentration on the rate of decolorization, the experiments were performed using 4 different initial AR1 concentration (25, 50, 75 and 100 mg/L) by maintaining the other parameters constant. The results are illustrated in Fig. 9. The results indicated that decolorization efficiency increased when the initial dye concentration increased. Concentration plays a very important role in reactions according to the collision theory of chemical reactions. The collisions theory states that for a chemical reaction to occur, the reacting particles must collide in correct orientation with each other so that the breaking and formation of chemical bonds can occur and they also should possess energy that is equal to or more than the minimum energy called activation energy. It was two reactants being in a closed container. All the molecules contained within are colliding constantly. By increasing the concentration of one or more reactants, the frequency of collisions between reactants molecules is increased and the frequency of effective collisions that causes a reaction to occur will also be high. The lifetime of hydroxyl radicals is very short (only a few nanoseconds) and they can only react where they are formed. Therefore, as increasing the quantity of dyes molecules per volume unit logically enhances the probability of collision between organic matter and oxidizing species, leading to an increase in the decolorization efficiency [18].

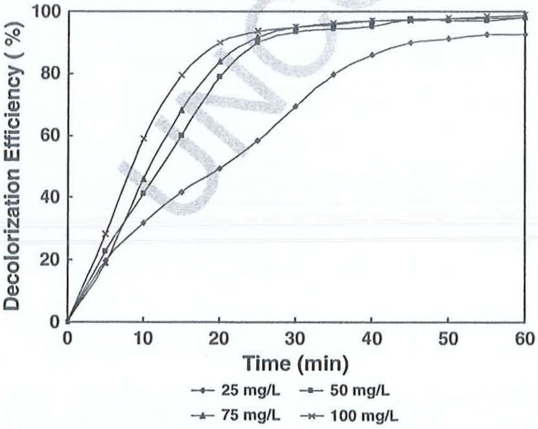

Fig. 9. Effect of initial concentration AR1 concentration on the decolorization of AR1. Reaction conditions: initial concentration of hydrogen peroxide, $[H_2O_2]_o = 16$ mM, catalyst dosage = 2.50 g/L with 0.80 wt.% of iron ions in catalyst, temperature = 30 °C, agitation speed = 130 rpm and pH = 2.5.

3.8. Effect of temperature

In order to determine the effect of reaction temperature on the decolorization efficiency of AR1, a series of experiments were conducted by varying temperature from 30 °C to 50 °C. The results are illustrated in Fig. 10. The results indicated that the decolorization of AR1 was significantly influenced by the reaction temperature and the decolorization was accelerated by a rise in temperature. This is because higher temperature increased the reaction rate between hydrogen peroxide and the catalyst, thus increasing the rate of generation of oxidizing species such as $^{\bullet}OH$ radical or high-valence iron species [29]. In addition, a higher temperature can provide more energy for the reactant molecules to overcome reaction activation energy [36].

3.9. Spectral changes of AR1 during decolorization process

To study the decolorization of AR1, UV–Visible absorption spectra of 50 mg/L AR1 solution were considered before and after the treatment with Fenton reagents (iron ions loading = 0.80 wt.%, [Fe-zeolite Y type]

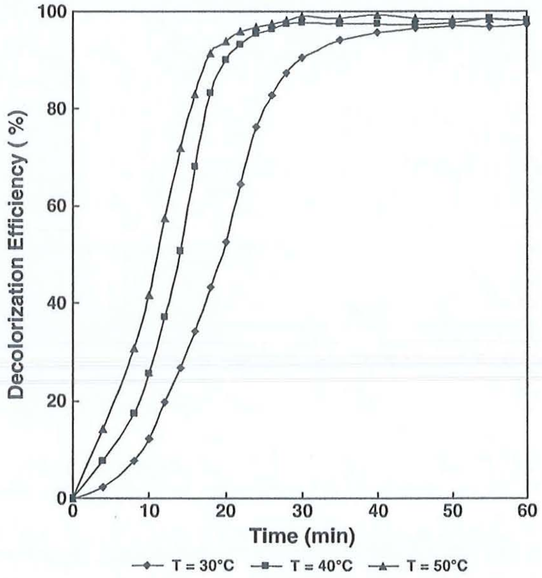

Fig. 10. Effect of temperature on the decolorization of AR1. Reaction conditions: initial concentration of AR1, $[AR1]_o = 50$ mg/L, initial concentration of hydrogen peroxide, $[H_2O_2]_o = 16$ mM, catalyst dosage = 2.50 g/L with 0.80 wt.% of iron ions in catalyst, agitation speed = 130 rpm and pH = 2.5.

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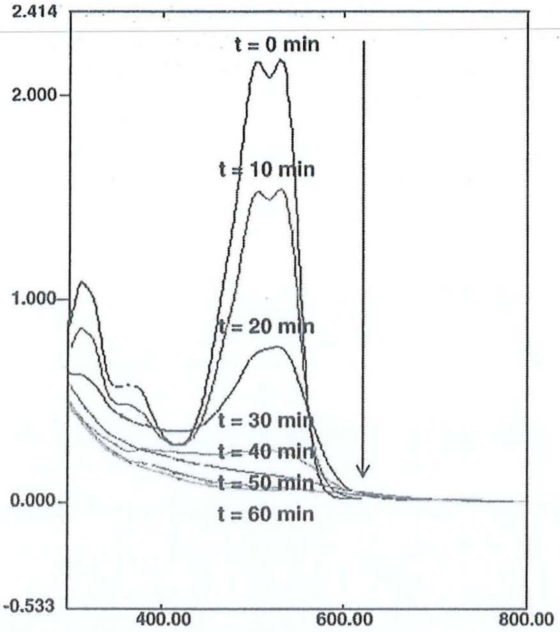

Fig. 11. Absorbance spectra. Reaction conditions: initial concentration of AR1, $[AR1]_o = 50$ mg/L, initial concentration of hydrogen peroxide, $[H_2O_2]_o = 16$ mM, catalyst dosage = 2.50 g/L with 0.80 wt.% of iron ions in catalyst, agitation speed = 130 rpm, temperature = 30 °C and pH = 2.5.

2.50 g/L, $[H_2O_2]_0 = 16$ mM, pH = 2.50, and T = 30 °C), as it can observed in Fig. 11. Before treatment, UV–Visible spectra of AR1 was characterized by one main band in the visible region, with its maximum absorption at 532 nm, and by two bands in the ultraviolet region located at 322 nm and 354 nm. The peaks at 322 nm and 354 nm were ascribed to the benzene and naphthalene rings bonded to the —N N— of AR1, respectively [37], while the band in the visible region was attributed to the chromophore-containing azo linkage of the dye molecules in the solution [38]. It was clearly observed that the adsorption peak at 532 nm diminished very fast and finally disappeared completely under 60 min of reaction time, indicating a rapid decolorization of AR1. The decrease was also meaningful with respect to —N N— bond of the azo dyes, as the most active site for attack [39]. The ultraviolet band at 322 nm and 354 nm was also observed to vanish but at a lower rate than that of visible band which indicated that the destruction of naphthalene rings is difficult. This behavior is due to the fact that the $OH^{\bullet}$ radicals first attack azo groups and opens the —N N— bonds, destructing the benzene and naphthalene rings and consequently causing decolorization [40]. The transition of the UV–vis adsorption spectra of AR1 confirmed that heterogeneous Fenton process was an effective treatment for dye containing wastewater to some extent.

3.10. Catalyst stability and leaching test

Stability is an important property for effective catalysts. The stability test was performed in order to evaluate the catalytic activity of Fe–ZYT during successive experiments and thus to observe the possibility of catalyst reuse. The catalysts were used in three consecutive experiments by using fresh dye solutions at optimum conditions (50 mg/L dye concentration, pH 2.5, 30 °C, 16 mM H_2O_2 and 2.50 g/L catalyst). Between each experiment, the catalyst was removed by filtration and then washed by distilled water for several times and dried at 110 °C for 12 h. About 99% decolorization efficiency of AR1 was observed within 60 min of reaction in the first run. In the second and third runs, the decolorization efficiency of AR1 was decreased to 94.96% and 94.54%, respectively. The results showed that the Fe–ZYT catalyst showed a good catalytic activity with a small drop in catalytic activity. This is particularly interesting from the practical point of view due to the possibility of using this catalyst for a longer operation time. In all the three successive experiments, it should be noted that the leaching of iron ions, although it took place, the leached amounts were not enough to significantly affect the catalytic activity in three consecutive runs. It was found that the concentration of iron ion in the solution after reuse of the catalyst for three consecutive cycles were 0.6041, 1.2304 and 1.4475 mg L^{-1}.

4. Conclusions

Fe–zeolite Y type has been proved to be an effective heterogeneous catalyst for decolorization of azo dye, (AR1), in an aqueous solution. It has been found that the solution pH, the initial H_2O_2 concentration, the initial iron ions loading on ZYT, the initial dye concentration and the temperature are the main factors that have strong influences on the decolorization of AR1 by Fenton oxidation process. The best operation parameters for the Fenton oxidation of AR1 were 0.80 wt.% of iron ions loading, 2.50 g/L of catalyst dosage, and 16 mM of H_2O_2 for 50 mg/L initial dye concentration at an initial pH 2.50 with 30 °C temperature. Under these conditions, 99% decolorization efficiency of AR1 in aqueous solution was achieved within 60 min of reaction time. From the result discussed above, Fe–ZYT catalysts demonstrated not only a good catalytic activity but also a reasonably small iron leaching. This characteristic makes it possible for all the catalysts to have long term stability, without generating iron hydroxide sludge.

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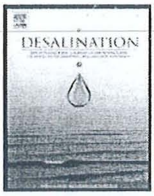

Heterogeneous catalytic treatment of synthetic dyes in aqueous media using Fenton and photo-assisted Fenton process

Ai Ni Soon, B.H. Hameed *

School of Chemical Engineering, Engineering Campus, Universiti Sains Malaysia, 14300 Nibong Tebal, Penang, Malaysia

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ABSTRACT

Heterogeneous catalysis by Fenton oxidation process has gained tremendous recognition in recent times. This importance was the driving force in this review which mainly focuses on the heterogeneous catalytic Fenton processes for synthetic dye abatement in wastewater for the past five years, though some earlier researches which were fruitful in the field will also discussed. The outstanding experimental results obtained by using heterogeneous catalytic Fenton system for dye removal are also compiled and described. This includes the development of the stable heterogeneous catalyst towards minimal leaching, long-term stability and high catalytic activities. It also outlines the catalytic deactivation encountered by researchers and the remedies to prevent the deactivation associated with Fenton process or photo-assisted Fenton process. Current limitation and future prospect using heterogeneous catalytic Fenton process for the dye removal are discussed.

Contents

1. Introduction

Presently, great concerns are expressed in the mass media on the critical issues of water pollution. These include improper treatment of industrial waste, improper sewage planning, oil spillages to the oceans through the routine shipping, acid rains from nitrogen oxides due to exhaustion from the combustion process of fossil fuels, dumping of toxic waste into the sea causing death of marine life, alga bloom resulting from extensive use of fertilizers in agricultural activities, mining and refining of uranium and thorium from marine nuclear waste, etc. All these different sources of water pollution contain hazardous mixtures which come from organic and inorganic

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* Corresponding author. Fax: +60 45941013.
E-mail address: chbassim@eng.usm.my (B.H. Hameed).

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pollutants in addition to heavy metals which have adverse effects on the environment, aquatic life and human health. Earlier investigations revealed that an account of more than 25% of the total world population [1] suffer from health [2] and hygienic problems related to water pollution.

Some major organic pollutants are derived from synthetic dyes [3–5]. Synthetic dyes are extensively produced in the 21st century owing to their unique properties such as high wet fastness profile, brilliant shades, and relative low cost and simple synthesis methods. These characteristics have successfully made dying industries such as textile, leather, painting and printing to choose as priority good colourants in their products. Synthetic dyes are categorized by their application fields, namely acid, reactive, disperse, vat, metal complex, mordant, direct, basic and sulfur dyes [6]. Synthetic dyes are normally resistant to mild degradation [7,8], as their molecular structure contains complex aromatic amide groups with alkyl, halogen, nitro, hydroxyl, sulfonic acid, substituent(s), and inorganic sodium salts. The dye effluents are generated after a series of wet processing activities that contains high concentration of non-biodegradable compounds, toxic substances, detergents and soaps, oil and grease, sulfide, sodas, and alkaline rich wastes. Over 12–15% of the overall synthetic dyes production is lost as dye effluent during these wet processing activities [4,9]. Based on the worldwide demand, it is estimated that over 100,000 commercial dyes are in existence [10] and more than 7×10^5 tonnes are produced annually [11]. According to current EU regulations, synthetic dyes based on benzidine, 3,3′-dimethoxybenzidine and 3,3′-dimethylbenzidine have been classified as carcinogens of category 2, that is, as "substances which should be regarded as if they are carcinogenic to man" [12]. Potential health effects are recognized for some dyes although the acute toxicity of synthetic dyes is low [13]. Because of an increasing social and political pressure on environment, governments are set to implement more stringent act and regulation to manage these hazards. Besides this, the demand for an efficient and environmental friendly colour removal technology is also getting more attention the world over.

Advanced oxidation processes (AOPs), considered as non-waste generating technologies, represent a robust alternative wastewater treatment for dye effluent when common wastewater treatment technologies such as sedimentation, adsorption, flocculation, filtration, reverse osmosis are insufficiently effective [14,15]. AOPs have been postulated as pretreatment step prior to biological treatment apart from disinfection and deactivation of pathogenic microorganism that are difficult to degrade biologically [16–19]. AOPs have the ability of exploiting the high reactivity of •OH radicals in driving oxidation processes [20]. The •OH radicals can be generated *in situ* through either one or the combination of chemical oxidation by using ozone, hydrogen peroxide with or without the radiation assisted sources such as ultrasounds, ultraviolet, solar visible and thermal. In more advance process, the •OH radicals can be generated by gamma radiation, microwaves, pulsed electron beam and the ferrate reagent [21–26]. By tailoring the conditions of the reaction, •OH radicals which possess powerful oxidizing potential up to +2.8 V can attack a wide variety of toxic contaminants [27]. AOPs have the proven ability for destroying dissolved organic contaminants such as halogenated hydrocarbons (trichloroethane, trichloroethylene), aromatic compounds (benzene, toluene, ethylbenzene, xylene-BTXE), volatile organic compounds (VOCs), pentachlorophenol (PCP), nitrophenols, detergents and pesticides, as well as inorganics contaminants such as cyanides, sulfides and nitrites [28].

Despite major drawbacks encountered by homogenous Fenton process in the last decade, Fenton process still receives much attention with more emphasis on heterogeneous processes [29]. This review paper intends to describe the fundamental aspect of Fenton process and discuss the benefits and application of heterogeneous Fenton processes for synthetic dye abatement. At present, reviews on the other alternative heterogeneous catalysis for the AOPs to treat wastewater were reported by Pirkanniemi et al. [30] on general heterogeneous water phase catalysis as an environmental application; Liotta et al. [20] on phenol degradation using zeolite, hydrotalcite-like compounds, clay and resins by the means of AOPs system; Ramirez et al. [31] on the application of clays and iron-oxide minerals as supports or active catalysts in Fenton-like reactions. The efficiency through various preparation methods to modify and/or enhance the catalytic performance in heterogeneous Fenton process for synthetic dyes removal has not been broadly reviewed. Hence, our aim is to properly compile the recent development on the heterogeneous catalytic processes using iron bearing solid catalysts for the dye removal in aqueous solution with some fruitful observation.

2. Homogenous vs. heterogeneous Fenton system performance for synthetic dyes treatment

Fenton process is a part of AOPs that can degrade recalcitrant compounds under mild conditions and the control of the catalyst concentration is simple [32]. The process can be conducted both homogeneously and heterogeneously under various combinations as shown in Fig. 1. The active sites in the Fenton process are derived from iron ions which serve as catalyst to break down the hydrogen peroxide molecules into numerous hydroxyl radicals. The term "Fenton's reagent" refers to the mixture of hydrogen peroxide and iron ions. The rate of reaction in the Fenton process can be further enhanced by the application of ultraviolet irradiation sources also known as photo-assisted Fenton system [33,34].

In the homogeneous phase, the chemical changes that take place are solely dependent on the nature of the interactions of the reacting substances between Fenton's reagents with compounds to be degraded [35]. However, in heterogeneous phase, the physical steps in addition to chemical changes take place on the surface of the catalyst at the active sites where mass transfer limited adsorption of reactant molecules occurs. At the end of the reaction, the product molecules are desorbed and leave the active sites available for a new set of reactant molecules to attach to the surface and react [36]. Undeniably, these complex steps make the surface characteristics [30] and the pore structure of the solid catalyst become important since these will strongly affect their kinetic rate, efficiency and stability towards solid catalyzed Fenton reaction. The synthesis of solid catalysts takes place in a series of successive steps including deposition from the solution of the transition metal salt onto the support, drying and calcination, and eventually the process of reduction or sulfidation [37].

Homogenous Fenton process can be activated by their active sites either with Fe^{2+}or Fe^{3+}. Whereas, active sites in heterogeneous Fenton processes can be the surface of iron ions existing in multiple forms of $[Fe(OH)_2]^+$, $[Fe(H_2O)]^{2+}$, $[Fe(H_2O)_6]^{3+}$, $[Fe_2(OH)_2]^{4+}$, Fe-polycation, Fe_2O_3 and α-FeOOH [38]. Among these iron ions, the presence of active site of α-FeOOH (Goethite) as claimed by He et al. [39] has a high influence on the catalytic activities in photo-oxidation of azo dyes.

The key features of the homogenous Fenton system are their reagent conditions, i.e. $[Fe^{2+}]$, $[Fe^{3+}]$, $[H_2O_2]$ and the reaction characteristics (pH and the concentration of organic and inorganic constituents) [35]. The Fenton reaction mechanisms, kinetics and stoichiometry in relation to homogenous Fenton process has been well defined by Bolong et al. [40], Gogate et al. [41], Neyens et al. [35], Pignatello et al. [42] and Emami et al. [43]. The homogenous Fenton system has been wisely applied in real industrial wastewaters such as chemical industry for pesticides removal in southern Poland [44], El-Nasr pharmaceutical industry for antibiotic removal in South-East of Cairo [45], tannery industrial treatment plant in Brazil [46], River Damodar contains the various stubborn industrial wastewater in India [19], and with the application of Fenton process, results in significant reduction of toxicity, improvement of biodegradability, colour, COD, BOD, TSS, oil grease and odour removal. These processes, of course, are rather cumbersome they are involved addition post-treatment to neutralize the pH before released. Furthermore, due to several limitations that accompany the homogenous Fenton process, the

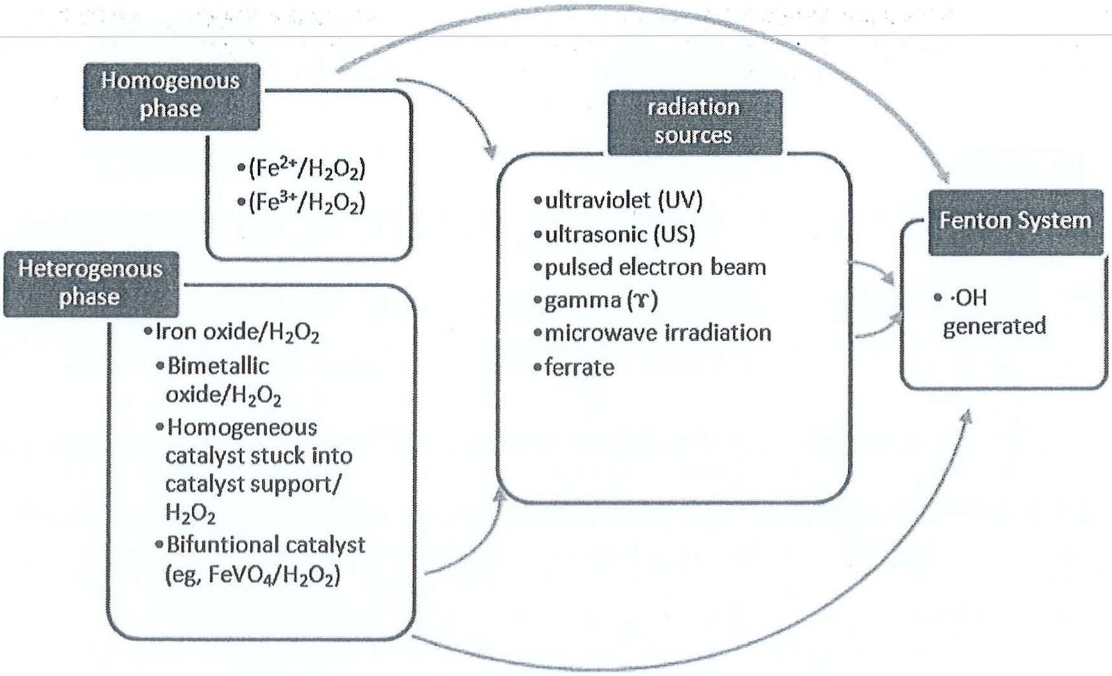


Fig. 1. Overall Fenton system classification.

operating cost for wastewater treatment plant has become expensive due to high H_2O_2 consumption and this poses a major barrier to the application of this treatment in less wealthy countries of the world. Some of these limitation include the formation of the sludge because of the post-treatment process, limited reaction pH range 2.5–3.5 which is also very acidic, H_2O_2 scavenger, high iron loss to environment, difficulty of the iron ions recovery and the wastewater cannot be discharged with the iron ions if above European Union limits (<2 ppm) [47,48].

These have made the development of a heterogeneous catalyst for the degradation of wastewater pollutants in Fenton system imperative. Heterogeneous catalysts are much easier to separate from liquid products; they are noncorrosive and environmentally benign. They can diminish the final concentration of iron ions in the bulk after treatment, thus with the assistance of UV irradiation, the formed Fe^{3+} complexes can be destroyed, allowing Fe^{3+} ions to participate in the Fenton catalytic cycle [49]. The rate constant of photo-assisted Fenton reaction will decrease when the UV light wavelength increased from 254 nm (UVC region) to 365 nm (UVA region). UVA with wavelength of 365 nm, which is the region of solar light accounts for 98.7% of the ultraviolet radiation that reaches the Earth's surface. The current trend in this field recently is shifting attention and the interest to the visible light radiation to replace UVC radiation with the hope to reduce the energy cost. Theoretically, solar radiation is expected to have better performance especially in Mediterranean countries where the solar source is abundant and highly available. However, the cost consideration for the reactor modeling, fluctuation of the solar energy sources and time requirement for the reaction, still appear as a challenge that needed to be addressed. In the past years, ferric ion complexes were used as a kind of photocatalyst in the homogenous phase degradation of synthetic dyes and the ligand of the ferric iron complexes such as (OH^-, H_2O, HO_2^-, Cl^-, R–COO^-, R–OH, R–NH_2, etc) have been reported active under visible light wavelength [50]. Despite UVA as a transition door towards visible radiation sources, other lamps source such as halogen lamps, metal halide lamps are also employed in the heterogeneous Fenton experimental system.

When considering heterogeneous solid phase, their density, pore volume, pore size distribution, porosity and surface area become crucial factors that need to be taken into consideration prior to access the reaction. Based on IUPAC, pore sizes are classified into three regimes: microporous (<2 nm), mesoporous (between 2 and 50 nm), macroporous (>50 nm). For heterogeneous Fenton reaction, many researchers revealed that mesoporous structure is preferable for synthetic dyes degradation [51–53]. Briefly, the solid surface can be designed or modified to give higher activity, selectivity and longer catalyst lifetime. It has been suggested that the mechanism could be described as either of the adsorption of the H_2O_2 molecule onto ≡Fe(III) sites to form "Fenton reagent" which in turn degrade the dye or the adsorption of the organic molecules on the ≡Fe(III) sites before the degradation happen in the heterogeneous phase of Fenton process [54,55]. Most of the time, total organic carbon (TOC) instead of the gas chromatography or liquid chromatography is used as a analytical tool to estimate the remains of its secondary organic compounds. Details of the mechanism involved and the reaction pathway still remains sketchy in the heterogeneous catalytic Fenton process for the synthetic dyes removal [56,57]. The stoichiometry and chemical pathway for the synthetic dyes removal in aqueous solution is not yet clear and intermediate identification was reported in a general manner in the literature. Further research is required to unravel this phenomenon.

Rigorous proof of heterogeneity can be obtained only by filtering the catalyst at the reaction temperature before completion of the reaction and testing the filtrate for activity [58]. To distinguish the homogenous catalyst from the heterogeneous catalyst, there are three observables through their reaction kinetic, 1) kinetic reproducibility; 2) the observation of sigmoidal kinetics for the catalytic reaction; and 3) comparison of the kinetics of the catalytic reaction with the kinetic of pre-catalyst decomposition [59].

In Table 1, homogeneous and heterogeneous catalyzed Fenton reactions under different phenomena are compared. Although heterogeneously catalyzed Fenton system is still in the laboratory testing stage, nevertheless, the future prospect in its application seems very bright which is owed to its ease of separation and an odyssey towards the concepts of green environmental catalyst. Succinctly, for versatility and low cost operations in heterogeneous catalyzed Fenton system, we have presented the recent progress on different kind of iron catalyst immobilized on an inorganic support (i.e. zeolite, clay, activated carbon, alumina, fly ash, etc) for synthetic dyes removal.

Table 1
Comparison of homogeneous and heterogeneous catalyzed Fenton reactions under different phenomena.

Phenomena	Homogeneous Fenton	Heterogeneous Fenton
Phase	- Same phase as the reagents.	- Involved solid-liquid phase.
Mechanism	- Chemical reaction is involved solely in the degradation process.	- Dual processes of physical absorption and desorption in addition to chemical reaction take place.
Catalytic activities	- Fast [41].	- Reaction rate is enhanced by the application of ultraviolet irradiation source [33,34]. - Nanosize solid catalyst, as observed, can accelerate the reaction rate [61,62,70].
Actives sites	- Fe^{2+}, Fe^{3+}, $Fe\text{-}OOH^{2+}$, iron complexes ion [35].	- Dispersed on surface in the form of iron oxides, iron complexes ion, iron ions [38].
pH	- Tight acidic pH range for the reaction and need pH adjustment before and after [47].	- Broad pH range [72,92].
Sludge treatment	- High amount of treated effluent is precipitated as ferric hydroxide sludge when the reaction solution was neutralized in the post-treatment [40].	- Minimal ferric hydroxide is formed due to leaching of the active components into the bulk solution [31].
Catalyst loss	- High catalyst loss after reaction takes place. Additional recovery separation steps are required for the catalyst after treatment in order to comply with the national environmental regulation [47].	- Iron loss is limited because the active phase is anchored on the surface of porous solid materials [91].
Catalyst recovery	- Possible but time consuming and cost ineffective [48].	- Ease of recovery and recycling is guaranteed [68].
Deactivation	- Irreversible reaction with products [42].	- The leaching of active sites from the support occurred at low pH and subsequently catalytic activity is lost [49].
	- Refractory towards certain chemical pollutants slow down the reaction [41].	- Degradation is slowed down due to catalyst poisoning [55].

3. Clay based catalyst for synthetic dye removal

All clay minerals are made of two distinct building blocks: tetrahedrons and octahedrons. The tetrahedron on the left has oxygen atoms at the corners, and there is silicon in the centre. Octahedron has six oxygen or hydroxyl atoms in the corners, and an aluminum or magnesium ion at the centre. Different combinations of tetrahedral and octahedral sheets form different clay minerals. Clay is abundant in nature and combined with the functionality of iron can be easily customize for specific application. Typically natural clay needs to be purified before it is use as support material because of the presence of impurities that limits their use in catalytic application and sometimes can be detrimental to the reaction [60]. The use of clay as support for the dye removal was first studied most extensively by Feng's group. Under photo-assisted Fenton system, Laponite clay based iron successfully complete the decolourization of their model dye pollutant, Reactive Red HE-3B, in 30 min and almost 76% mineralized in 120 min [61]. Reactive Red HE-3B consists of two main characteristic absorption bands, one is in UV region (291 nm), and another is in visible region (512 nm), respectively. Based on the UV–visible spectra in Fig. 2, it is observed that the visible band at 512 nm disappeared faster than UV band at 291 nm after 30 min and this can be said that the HE-3B exhibits a stronger absorption at 291 nm than at 512 nm. The sequence starts with the •OH radicals attacking the azo groups and disintegrating the N N bonds, destructing the long conjugated π systems linked by two azo group, and consequently causing discolouration. Hereby, the authors proposed that the adjacent ring structure is one of the main intermediates and discoloration of dyes undergoes a much faster kinetics than mineralization [61].

By using the same catalyst, Orange II also can be completely decolourized in less than 45 min while mineralized up to 70% in 90 min under their optimum conditions [62]. Table 2 compiled the recent experimental results using the clay based catalyst for synthetic dye removal.

3.1. Preparation methods and surface morphology towards dye degradation

Laponite, montmorillonite, saponite, and bentonite clays are well known by their own unit phyllosilicates structured to make them have the suitable choice as catalyst support with simple synthesis methods by cation exchange with homogenous catalyst, for example aluminum (Al^{3+}) replaced by iron (Fe^{3+}). Most of the clay based catalysts in Fenton process were preferably prepared by pillaring method [62]. It is believed that pillaring process alters the basal space of the clay, which lead to the high amounts of active sites such as iron ion catalyst dispersed on the surface of pillared clay. The catalytic activity of the pillared clay was attributed to the accessible iron species, whose amount is regulated not only by the introduced iron species but also by the basal space that subsequently depends on the aluminum species present in the matrix [63]. The iron-pillared interlayered clays (Fe-PICs) using iron oxocations after calcination were found to give rise to the pillared layers that give higher specific surface area. Sodium carbonate is commonly used as a pillaring agent in pillaring process. By using the method mentioned above, synthetic laponite clay based iron successfully increased the surface area from 370 to 472 m^2/g. [61,62]. After calcination, the catalyst characterized

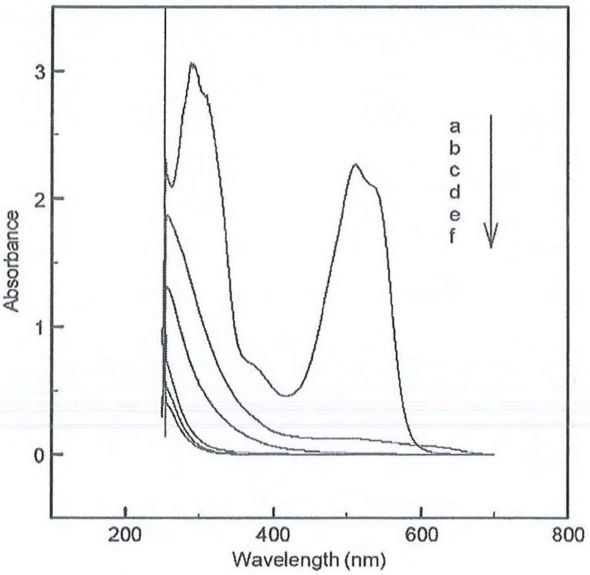


Fig. 2. UV–visible spectra of the 100 mg/L HE-3B solution before and after treatment with 500 mg/L H_2O_2, 1.0 g/L Fe-Lap-RD, and 2×8 W UVC at pH = 3.0 and 25 °C for 120 min. (a) 0 min, (b) 15 min, (c) 30 min, (d) 60 min, (e) 90 min, and (f) 120 min [61]. Reprinted from Water Research, 37, J.Feng, X.Hu, P.L.Yue, H.Y.Zhu, G.Q.Lu, Discoloration and mineralization of Reactive Red HE-3B by heterogeneous photo-Fenton reaction. Copyright (2003), with permission from Elsevier.

Table 2
Effects of clay based catalysts applied in Fenton system for dye removal.

Dye	Catalyst/support	Decolourization conversion	Mineralization conversion	Conditions	Ref.
Reactive Red HE-3B	Pillared synthetic laponite clay based Fe nanocomposite	100% in 30 min	76% in 120 min	pH 3.0; 1.0 g/L catalyst; 100 mg/L dye; 500 mg/L H_2O_2; 2 × 8 W UVC; 25 °C	[61]
Orange II	Same as above	100% in 45 min	70% in 90 min	pH 3.0; 1.0 g/L catalyst; 0.2 mM dye; 9.6 mM H_2O_2; 8 W UVC; 25 °C	[62]
Orange II	Pillared bentonite clay based Fe nanocatalysts	100% in 30 min	100% in 120 min	pH 3.0; 1.0 g catalyst; 0.2 mM dye; 10 mM H_2O_2; 8 W UVC; 30 °C	[78]
Indigo Carmine	Same as above	NA	60% in 120 min	pH 7.0; 1.0 g catalyst; 0.2 mM dye; 10 mM H_2O_2; 8 W UVC; 30 °C	[69]
Orange II	Pillared bentonite clay based Fe nanocomposite	100% in 60 min	65% in 120 min	pH 6.6; 1.0 g/L catalyst; 0.2 mM dye; 10 mM H_2O_2; 8 W UVC; 30 °C	[64]
Acid Black 1	Pillared laponite clay based Fe nanocomposite	na	100% in 120 min	pH 3.0; 1.0 g/L catalyst; 0.1 mM dye; 6.4 mM H_2O_2; 8 W UVC	[65]
Orange II	Pillared bentonite clay based Fe nanocomposite (Fe-B) film	100%	50-60%	pH 3.0; 1.0 g/L catalyst; 0.2 mM dye; 10 mM H_2O_2; 8 W UVC	[68]
Acid Black 1	Pillared acid activated bentonite clay based Fe	100% in 60 min for pH 3.0 94% in 120 min for pH 9.0	85% in 120 min for pH 3.0 17% in 120 min for pH 9.0	1.0 g/L catalyst; 0.2 mM dye; 10 mM H_2O_2; 8 W UVC	[66]
Orange II	Nanocomposites Fe supported on bentonite clay	100% in 60 min	100% in 120 min	pH 3.0; 0.2 mM dye; 10 mM H_2O_2; 1.0 g/L catalyst; 8 W UVC	[70]
Orange II	Nanocomposites Fe supported on laponite clay	100% in 60 min	90% in 120 min	Same as above	[70]
Reactive Brilliant Red X-3B	Fe pillared bentonite (Fe-B)	> 98% after 100 min	na	pH 3.0; 10^{-4} mol/L dye; 0.5 g/L catalyst; 10^{-2} mol/L H_2O_2; UV^+	[73]
Reactive Brilliant Red X-3B	Al–Fe pillared bentonite (Al/Fe-B)	> 98% after 100 min	na	Same as above	[73]
Acid Light Yellow G	Hydroxyl-Fe-pillared bentonite by cation exchange	> 98% in 120 min	65% in120 min	pH (3–9); 1.0 g/L catalyst; 50 mg/L dye; 10 mmol/L; 6 W UVA	[76]
Rhodamine B	Layered iron (II) bipyridine complex–clay hybrid by intercalation ($Fe(bpy)_3^{2+}$-laponite clay)	na	41% in 450 min	pH 7.0, 4.4×10^{-5} M $Fe(bpy)_3^{2+}$; 5.0 mg FeBL, 2.0 mM H_2O_2, 2×10^{-5} M dye, Visible light irradiation ($\lambda > 420$ nm)	[80]
Orange II	Hydroxyl-Fe-pillared bentonite by cation exchange	100% in 40 min	95% in120 min	pH (3.0–9.0); 1.0 g/L catalyst; 0.2 mM dye; 10 mmol/L; 6 W UVC	[75]
Acid Black 1	Bimetallic Cu/Fe clay by CVD method	100% in 30 min for pH 3.0 97% in 30 min for pH 9.0	93%, in 120 min for pH 3.0 94% in 120 min for pH 9.0	0.5 g/L catalyst; 0.1 mM dye; 6.4 mM H_2O_2; 8 W UVC; 30 °C	[72]
Orange II	Al-PILC impregnated with Fe (natural saponite)	99% in 4 h for 70 °C 96% in 4 h for 30 °C	91% in 4 h for 70 °C 82% in 4 h for 30 °C	pH 3.0; 90 mg/L catalyst; 0.1 mM dye; 6 mM H_2O_2;	[55]
Methylene Blue	Iron-pillared montmorillonite <250 μm	93% in 180 min	na	pH 3.0; 1.0 g/L catalyst; 0.2 mM dye; 10 mM H_2O_2; UV^+	[60]
Methylene Blue	Iron-pillared montmorillonite for (250–450) μm	85% in 180 min	na	Same as above	[60]
Brilliant Orange X-GN	Iron-pillared montmorillonitic via pillaring	98.6% in 140 min UV^+ ~80% in 140 min visible irradiation	52.9% in 140 min UV^+ 40.7% in 140 min visible irradiation	pH 3.0; 0.6 g/L catalyst; 100 mg/L dye; 4.9 mmol/L H_2O_2; 30 °C	[79]
Orange II	Hydroxyl-Fe-pillared bentonite (H-Fe-P-B)	100% in 120 min	>60% in 120 min	pH 3.0; 1.0 g/L catalyst; 56 mg/L dye; 10 mM H_2O_2; 30 °C; 6 W UVA	[77]
Orange II	laponite clay based Fe nanocomposite (Fe-Lap-RD)	100% in 120 min	98% in 300 min	pH 3.0; 1.0 g catalyst; 2 mM dye; 100 mM H_2O_2; 2 × 8 W UVC	[71]
Orange II	Bentonite clay based Fe nanocomposite (Fe-B)	100% in 210 min	93% in 300 min	Same as above	[71]

*na – not applicable; UV^+ – UV type are not specify in detail.

by them mainly consists of maghemite (Fe_2O_3) and iron silicate hydroxide ($Fe_2SiO_{10}(OH)_2$). Catalytic activity of laponite clay based iron had been examined under different operating conditions. At their optimal conditions compiled in Table 2, complete decolourization of 100 mg/L HE-3B can be achieved in 30 min and the total organic carbon removal ratio can attain 76% in 120 min; also complete decolourization of 0.2 mM Orange II can be achieved in 45 min and 76% of the total organic carbon removed in 120 min. In their experiment the catalytic activity in heterogonous catalysts is much better than homogenous catalyst. This is indicating that the heterogeneous Fenton has taken part besides homogenous Fenton alone during dye degradation. Besides, it was reported that degradation performance of conventional pillaring clay based catalysts are found to yield better than Fe^{3+}-doped TiO_2 by sol–gel method [64]. The pillaring technique was then further improved by their group by studied their characterization through different thermal aging methods and calcination temperatures to tailor the reaction conditions in Fenton process, it was found that Acid black 1 have been completely mineralize within 120 min with minimal iron leaching [65]. A schematic representation of this delaminated–pillared structure is shown in Fig. 3 [53].

Clay can be pretreated with acid to activate the clay structure and composition to their desired properties for specific reaction. For heterogeneous catalytic Fenton reaction, clay was activated by three different mineral acids, that is, hydrochloric acid, nitric acid and sulphuric acid respectively. Among the three acid activated clays, Yip et al. [66] claimed that using sulphuric acid to purify the support can minimize the leaching problem as the presence of the sulfonate group can be more efficiently modified by the surface of the support and replace unnecessary metal ions on the active sites with H^+. The morphologies of the natural clay (Sample A) and acid activated clay (Sample B) as observed by scanning electron microscope (SEM) are

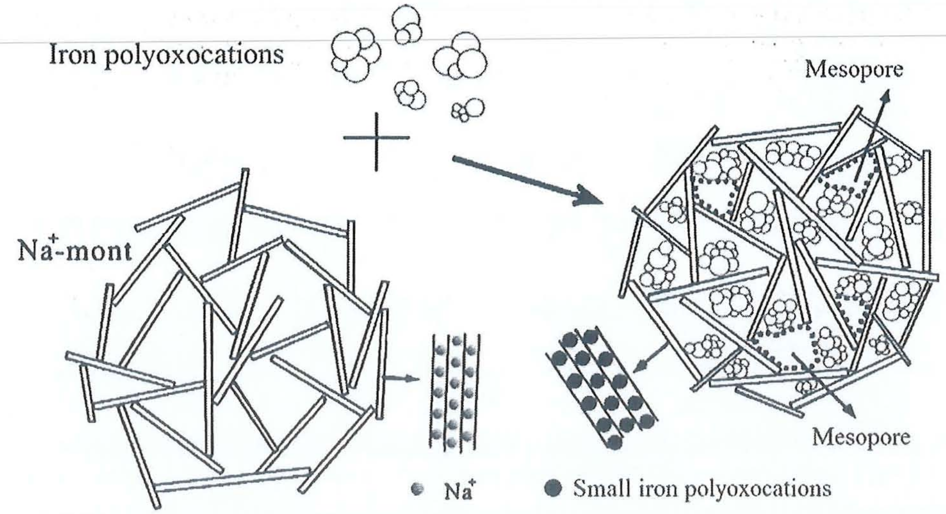


Fig. 3. Schematic representation of the iron-delaminated pillared clays [53].
Reprinted from Microporous and Mesoporous Materials, 88, Yuan Peng, He Hongping, Bergaya Faïza, Wu Daqing, Zhou Qin, Zhu Jianxi, Synthesis and characterization of delaminated iron-pillared clay with meso-microporous structure. Copyright (2006), with permission from Elsevier.

shown in Fig. 4 [67]. It is observed that the smectite lamellae will be more porous in sample B, because of the "holes" left by the removed ions, and more spaced because of the weaker inter-laminar bonds, due to replacement of iron ions with water molecules. No doubt the acid activated clay based catalyst can significantly improve the catalytic activity by immobilizing more iron on the support. For example, when Acid Black 1 was tested with acid activated clay based iron catalyst in the photo-assisted Fenton reaction, it was found that the leaching problem reduced by almost 72% compared to clay based iron catalyst without acid activated [66].

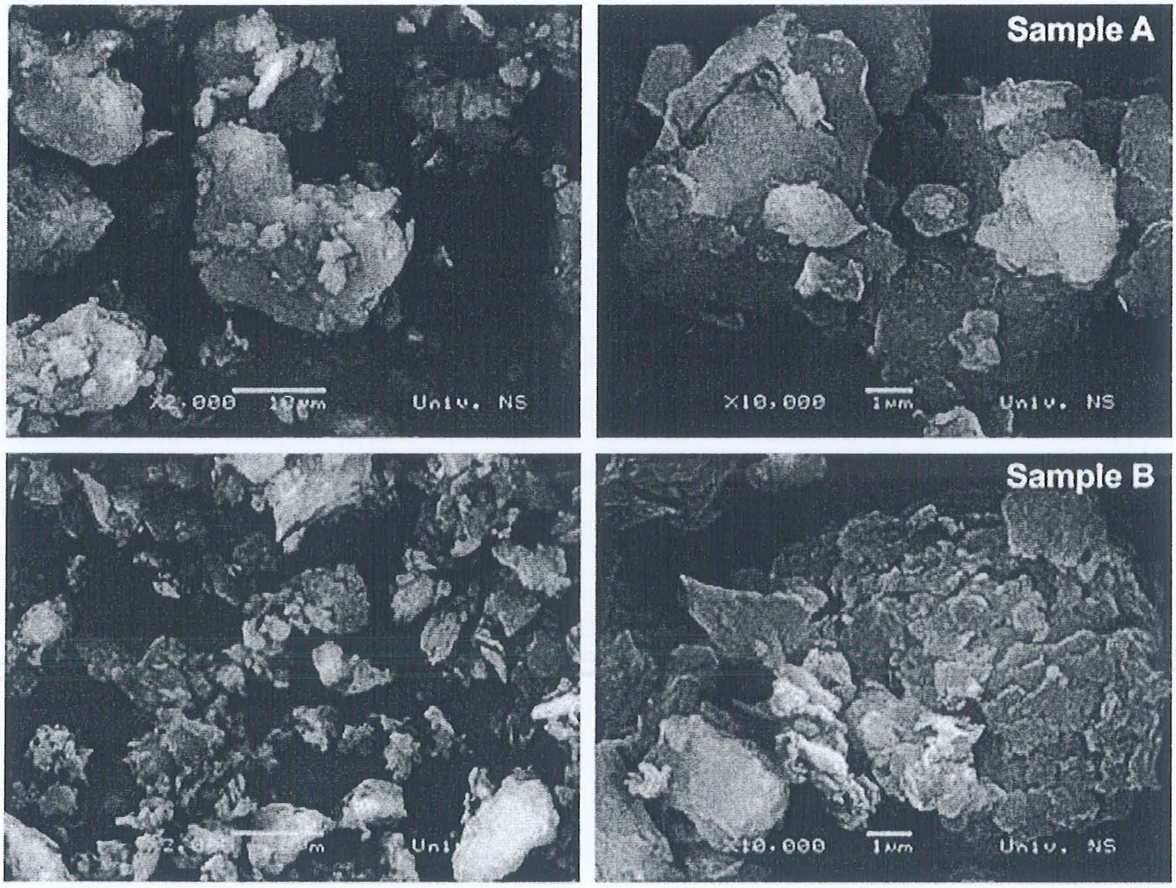


Fig. 4. SEM images of natural clay (Sample A) and acid activated (Sample B) smectite clay [67].
Reprinted from Chemical Engineering Journal, 137, Tatjana Novaković, Ljiljana Rožić, Srđan Petrović, Aleksandra Rosić, Synthesis and characterization of acid activated Serbian smectite clays obtained by statistically designed experiments, Copyright (2008), with permission from Elsevier.

Bentonite clay based irons is also explored by the Feng and coworkers using earlier preparation methods to degrade Orange II. Under the same conditions, the overall results for bentonite-based iron is much better compared to laponite-based iron with complete mineralization within 120 min [68]. Bentonite clay based iron was also studied by them using similar method to degrade the Indigo Carmine to study the catalytic performance under initial solution at neutral pH, the result revealed that bentonite clay based iron also possesses catalytic performance up to 60% mineralization in 120 min. However, the solution pH dropped from neutral pH to pH 3.0 at 60 min and then increased to pH 3.2 at 120 min [69]. The authors explained that during mineralization of Indigo Carmine at initial solution's pH, many acidic intermediates are formed such as formic acid, oxalic acid, glycolic acid containing two carbons; and maleic acid, tartaric acid anthranic acid containing C_n ($n \geq 4$), etc. Apparently, the formation of organic acidic intermediates definitely resulted in a rapid decrease in solution pH. After 60 min reaction, the slight increase in solution pH could be caused by the gradual mineralization of the acidic intermediates into other smaller molecules such as carbon dioxide and water.

Both laponite clay iron and bentonite-based iron nanocatalysts successfully demonstrated high catalytic activity and having the long-term stability up to four runs at the initial solution at pH 3.0 [70]. To access the possibility for their catalyst in real industrial application, the bentonite clay based iron was coated on the inner wall surface of the photo reactor as a fixed bed catalyst and its degradation efficiency was compared with a suspended Fe-bentonite. The result revealed that bentonite clay based iron coated film lowered the catalytic activities than suspended Fe-bentonite. However, in terms of leaching of iron into the solution, bentonite clay based iron coated film showed lower leaching than suspended Fe-bentonite [68]. Till recent, their group is still working closely on the clay based iron in various conditions such as dye pollution as high as 2 mM, and activity tests carried out in comparison with better catalysts [71]. All the results demonstrated that the clay based catalyst may have higher possibilities of being introduced for industrial applications in the near future.

Belver et al. [37] studied the catalyst preparation methods using natural saponite clay by, 1) intercalation of the clay with polymerised Fe solutions, 2) intercalation of the clay with polymerised mixed Al–Fe solutions, and 3) impregnation of Al-pillared clay with Fe precursors. The third method which is by impregnation with four type of Fe precursors, namely Fe(II) acetate, Fe(II) oxalate, Fe(II) acetylacetonate and Fe(III) acetylacetonate is more efficient by providing better ordered layered structure, higher basal spacings and easier reducibility than pillaring method reported earlier. By their impregnation method, the clay based catalyst has a layered structure with a basal spacing of 18.2 Å and a BET specific surface area 240 m^2/g.

Ramirez et al. [55] suggested that the nature of the catalyst's precursor, hydrogen peroxide concentration, temperature and pH of the reaction medium have a significant effect towards the degradation rate and intermediary oxidized compounds. A total of twelve numbers of supported Fe-saponite catalysts with different weight% in the support have been prepared, it was found that 17.0 wt.% of Fe in 1.0 g/L catalyst completely decolourized Orange II and over 96% mineralization under their optimum conditions: pH 3.0, 6 mM H_2O_2 and 0.1 mM Orange II at ambient temperature of 30 °C [55]. All the catalysts exhibit not only good catalytic activity but also a reasonable iron leaching. This indicated that the active phases are strongly fixed to the support (possibly iron is strongly bonded to the aluminum pillars or engaged in small oxide clusters dispersed in the solid, inside or outside the pore). This characteristic makes possible the saponite clay based iron to have long-term stability between (77.1–81.6)% mineralization, without generating iron hydroxide sludge throughout the four consecutive experimental runs.

Yip et al. [72] had further studied the introduction of bimetallic Cu/Fe pillared into the clay interlayer by using chemical vapour deposition (CVD) method. The bimetallic catalyst intercalated to the clay was shown to have their catalytic properties distinctly different from those of the parent metals by providing higher catalytic activity and insensitive towards pH. The clay based bimetallic catalyst was able to decolourize Acid Black 1 completely in a short time 30 min and achieved mineralization as high as 85–94% in 120 min between pH range 3.0 and 7.0 [72]. At pH lower than pH 3.0, copper easily leach out from the support compared to iron, sooner the heterogeneous reaction turns to homogenous reaction.

Both Fe pillared bentonite (Fe-B) and Al–Fe pillared bentonite (Al/Fe-B) have been prepared by Li et al. [73] using similar pillaring method reported earlier to access their oxidation activities on azo dye Reactive Brilliant Red X-3B using heterogeneous photo-assisted Fenton process. Both catalysts were able to decolourize the Reactive Brilliant Red X-3B in 100 min. Overall, Al/Fe-Bentonite owned higher BET surface area 194.2 m^2/g than Fe-B 114.6 m^2/g to give rises to more degradation activities on surface, higher surface acidity to prevent leaching and higher adsorption capacity to absorb the dye molecules to the surface. Al/Fe-Bentonite possesses long-term stability, as the catalytic activity is not significantly different throughout the three times of recycle operation.

While the heterogeneous catalyst may be better if they possess the mesoporous structure, however, on the contrary De León et al. [60] figured out that the microporous support structure was preferable for the Methylene Blue degradation under photo-assisted Fenton system. In their work, natural montmorillonite clay was filtered into two parts, 250–450 μm particle size and <250 μm particle size, respectively. Both supports were then cation exchanged with Fe(III) complex ion, namely tri-nuclear ferric acetate complex ion, $[Fe_3(OCOCH_3)_7OH \cdot 2H_2O]^+$; the complex ion solution prepared by dissolved Ferric(III) nitrate in ethyl alcohol followed by the addition of acetic anhydride. Decolourization up to 93% was obtained for Fe–PILC for <250 μm (microporous) and only 85% decolourization for Fe–PILC between 250 and 450 μm of their particle size after 180 min.

In terms of the ability of certain clays as a better catalyst support to remove cationic dyes Orange II and Acid Light Yellow G, Chen et al. [74–76] have concluded that hydroxyl-Fe pillared bentonite (H-Fe-P-B) have good photosensitivity and that catalyst reactivity came from hydroxyl-Fe between the sheets rather than Fe^{3+} or Fe^{2+} in tetrahedral or octahedral sheets of bentonite. The catalyst also showed stable catalytic activity from pH 3.0 to 9.5, the assumption was made on the fact that the catalyst possesses strong surface acidity and the electronegativity of H-Fe-P-B, which made the wide range of pH for heterogeneous UV-Fenton system. Almost 100% discoloration and more than 60% TOC removal of Orange II could be achieved after 120 min treatment [74]. Also, it accounted for more than 98% decolourization and 65% TOC removal of 50 mg/L Acid Light Yellow G and could be achieved after 120 min treatment using UVA as adiation source from pH 3.0–9.0 [76]. The iron leaching rates of H-Fe-P-B were all below 0.6% in three cycles runs in the degradation of Acid Light Yellow G.

Besides, Chen et al. [77] also compared the catalytic activity relationship for different iron configuration such as hydroxyl-Fe, α-Fe_2O_3 and α-FeOOH loaded into bentonite in the UVA photo-assisted Fenton system. The order of catalytic activity of Fe pillared bentonites for Orange II decolourization followed the trend α-Fe_2O_3-pillared bentonite (α-Fe_2O_3-P-B) > hydroxyl-Fe pillared bentonite (H-Fe-P-B) > α-FeOOH-pillared bentonite (α-FeOOH-P-B). For the dye mineralization, the trend was found to follow the order α-Fe_2O_3-P-B = H-Fe-P-B $\gg$ α-FeOOH-P-B under their optimum conditions [77]. Chen et al. [77] suggested that iron leaching during the reaction was caused by the present of highly acidic intermediates such as 2-carboxybenzeneacetic acid, phthalic acid, oxalic acid formed in solution. The authors also suggested that UV light wavelength and temperature strongly influence the degradation of Orange II for photo-assisted Fenton process [75]. The rate constants of Orange II degradation in various photo-assisted Fenton systems were positive relative to the temperature of reaction solution. However, this finding were found to be contradictory to the outcome of Feng et al. [64], where temperature were found insensitive towards the degradation of basic dye Orange II under photo-assisted Fenton process by using Fe pillared bentonite as a heterogeneous catalyst based on the low reaction activation energy at 9.94 kJ/mol during decolourization rate of dyes at high temperature [78].

Halogen lamp had been employed as visible radiation light source to degrade reactive brilliant orange X-GN by using iron-pillared montmorillonite via conventional pillaring preparation method [79]. The results after 140 min of irradiation showed that there was over 98% colour removal for heterogeneous photo-Fenton process while TOC removal was just 52.9%. But for visible light/H_2O_2/Fe^{3+} process, TOC removal of X-GN was effectively lowered, and only 40.7% removal was attained [79].

For the researchers using the visible light radiation source ($\lambda > 420$ nm) for clay based catalyst, it is also interesting to share here that there is a type of organic ions, namely tris(2,2′-bipyridine) iron(+2), Fe (bpy_3^{2+}), intercalated laponite clay found to have higher effectiveness to degrade cationic pollutants for dye Rhodamine B and N,N-dimethylaniline which belongs to phenyl group in neutral pH but inactive toward anionic organic compounds such as Orange II and sulforhodamine-B [80]. In their experimental result, it took longer time about 450 min to mineralize up to 41% for the dye Rhodamine B.

3.2. Mechanism involved using clay based catalyst

Higher activity could be driven by two heterogeneous mechanisms using the clay based Fe; first mechanism is based on Fe^{3+} on the surface of the support for reaction Eqs. (1), (2) and (3) while the second mechanism is based on the Fe_2O_3 as active site on the support in reaction Eq. (4) and (5) which is the change in interaction between dye and Fe_2O_3 in laponite clay based Fe nanocomposite [61,62].

$$Fe^{3+}\text{on the surface of Fe} - \text{Lap} - \text{RD} + h\nu \rightarrow Fe^{2+}\text{on the surface of Fe–Lap–RD} \tag{1}$$

$$Fe^{2+}\text{on the surface of Fe} - \text{Lap} - \text{RD} + H_2O_2 \rightarrow Fe^{3+}\text{on the surface of Fe} - \text{Lap} - \text{RD} + {\bullet}OH + OH^- \tag{2}$$

$$\text{Fe} - \text{lap} - \text{RD} - \text{dye} + {\bullet}OH \rightarrow \text{Reaction intermediates} \rightarrow CO_2 + H_2O \tag{3}$$

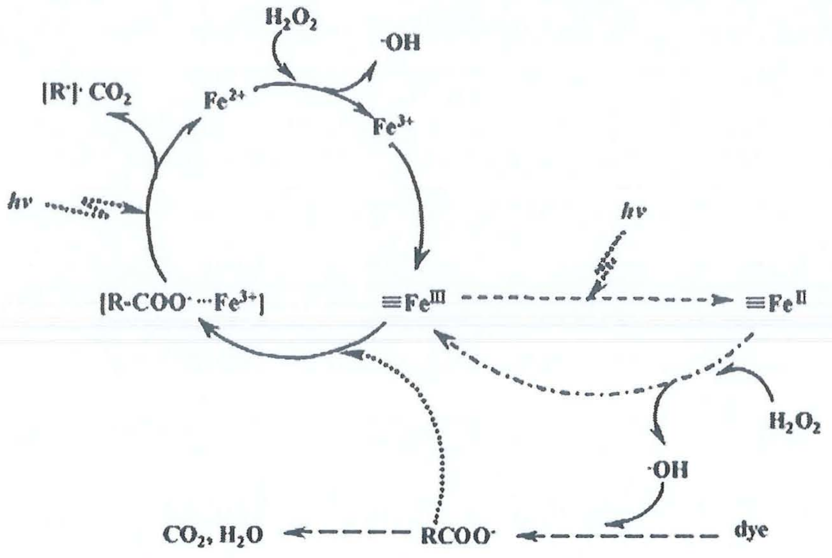
$$Fe_2O_3\text{in Fe} - \text{Lap} - \text{RD} + \text{dye} + h\nu \rightarrow [\text{dye}^{*}\ldots Fe_2O_3]\ \text{in Fe} - \text{Lap} - \text{RD} \rightarrow \text{dye}^{\bullet +} + Fe_2O_3\text{in Fe} - \text{Lap} - \text{RD} + e^-_{cb} \tag{4}$$

$$\text{dye}^{\bullet +} \rightarrow \text{Reaction intermediates} \rightarrow CO_2 + H_2O. \tag{5}$$

On the other hand, catalytic activities were also contributed from homogenous and heterogeneous processes in the reaction. The Fe^{2+} in solution was obtained through the photoreduction of the $\equiv Fe^{3+}$ under UV radiation. Meanwhile Fe^{3+} in solution was also produced when $\equiv Fe^{2+}$ is oxidized by H_2O_2, possible catalytic mechanism proposed for surface and solution reactions as shown in Scheme 1 [77].

4. Zeolite based catalyst for synthetic dye removal

Zeolites are crystalline aluminosilicate materials [81] with a three-dimensional framework and four-connected framework structure built from tetrahedra [82]. It is consist of robust, crystalline silica (SiO_2) and neutral frameworks. At some places in the framework Al^{3+} replaced Si^{4+} and the framework carries a negative charge [82]. This Si/Al ratio controls total acidity as well as acid site strength. Loosely held cations that sit within the cavities preserve the electroneutrality of the zeolite. Those cations are amenable to cation exchange capacities up to several milliequivalents per kilogram and are able to reversibly interact with polar molecules [83]. These properties have contributed significantly to the commercial success of zeolites to have excellent cation-exchange capability [84] but only a small number of zeolites are suitable for used as support in catalysis for synthetic dye removal under acidic condition. One major limitation of using common zeolite as support for dye wastewater pollutants is that it is exhibiting shape-selective molecular sieves in microporous structure; where active sites are specific to only a few reactants and product molecules. Relatively few works describe the use of zeolite based catalyst for catalytic abatement of synthetic dye removal, see Table 3. As of now, majority of these studies dealt with the use of the zeolites types such as ZSM5, HY and MCM-41 immobilize with metal active species for wastewater abatement. Zeolites are prefer by added into AOPs system to enhance the adsorption efficiency through combination of physical and chemical oxidation for dye removal rather than chosen as support by immobilizing it with other metal ions [85–87].



Scheme 1. Proposed photodegradation mechanism of Orange II including Fe cycling under UV light irradiation. [77].
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Table 3
Effects of zeolite/alumina/carbon/fly ash based catalysts applied in Fenton system for dye removal.

Dye	Catalyst/support	Decolourization conversion	Mineralization conversion	Conditions	Ref
Zeolite based catalyst					
Procion Marine H-EXL	Fe-exchanged Y zeolite	~100% in 120 min	42.73% in 120 min	pH 5.0; 1.0 g/L catalyst; 100 mg/L dye; 20 mmol/L H_2O_2; 50 °C	[7]
Reactive Yellow 84	Fe-Y zeolite (11.5 wt.% Fe)	96.90% in 60 min	34.52% in 60 min	pH 5.0; 1.0 g/L catalyst; 100 mg/L dye; 20 mmol/L H_2O_2; 50 °C	[88]
Congo Red	Fe-exchanged Y zeolite	97% in 4 h	na	pH 7.0; 1.0 g/L catalyst; 0.6 mL of H_2O_2 in 350 mL solution; 90 °C	[89]
Orange II	Fe/MCM-41 by MOCVD	na	85% in 90 min	pH 3.0; 1.0 g/L catalyst; 0.3 mM dye; 14.4 mM H_2O_2; 8 W UVC	[92]
Orange II	Bimetallic FeCu/MCM-41 by MOCVD	na	78%–93% in 120 min	pH (3.0–7.0); 1.0 g/L catalyst; 0.3 mM dye; 14.4 mM H_2O_2; 8 W UVC	[92]
Reactive Orange 16	Fe(III)-exchanged natural zeolite	100% in 120 min	~90% in 120 min	pH 5.2; 1.0 g/L catalyst; 50 mg/L dye; 15 mmol H_2O_2; 35 °C, UVA	[84]
Acid Blue 74	Fe-ZSM5 synthetic zeolite	>99% in 10 min	57.1% in 120 min	pH 5.0; 0.5 g/L catalyst; 8.56×10^{-5} mol/L dye; 21.4 mmol/L H_2O_2; 15 W UVC	[49]
Acid Red 14	Fe-ZSM5	na	~76.0% in 120 min	pH 7.0; 0.5 g/L catalyst; 40 mg/L dye; 20 mmol/L H_2O_2; 15 W UVC	[95]
Reactive Brilliant Blue KN-R	Fe-$ZSM5_{co}$	90%. in 20 min	na	pH 2.5; 4.0 g/L catalyst; 250 mg/L dye; 30 mmol/L H_2O_2	[96]
Reactive Brilliant Blue KN-R	Fe-Y_{ie}	~90%. in 30 min	na	pH 2.5; 4.0 g/L catalyst; 250 mg/L dye; 50 mmol/L H_2O_2	[96]
Alumina based catalyst					
Orange II	Iron oxide-Al_2O_3 beam (commercial grade)	70.0% in 4 h	45.0% in 4 h	pH 7.0; 5.0 g/L catalyst; 55 mg/L dye; 29.4 mmol/L H_2O_2; 5.0 mM $NaClO_4$, 15 W UVA	[101]
Acid Violet 7	Fe-Al_2O_3 (commercial grade)	70% in 60 min	45% in 60 min	pH 3.0; 1.0 g/L catalyst; 50 mg/L dye; 10 mmol/L H_2O_2; 6×8 W UVA	[104]
Carbon based catalyst					
Orange II	Fe-carbon aerogel	100% in 4 h	90% in 4 h	pH 4.0; 0.2 g/L catalyst; 100 mg/L dye; 6 mmol/L H_2O_2	[97]
Orange II	Fe-activated carbon	100% in 4 h	90% in 4 h	pH 4.0; 0.2 g/L catalyst; 100 mg/L dye; 6 mmol/L H_2O_2	[97]
Ash based catalyst					
Reactive Black 5	Fe-fly ashes	100% in 195 min	na	pH 2.8; 1.0 g/L catalyst; 60 mg/L dye; 5.5 mmol/L H_2O_2	[106]

4.1. Preparation methods and surface morphology towards dye degradation

The catalyst Fe-exchanged Y zeolite has been reported as a possible system for the pretreatment of simulated dye bath in the presence of reactive azo dye Procion Marine H-EXL, dye auxiliaries and dissolved salts by wet peroxide oxidation [7]. This zeolite Y support was obtained commercially with its surface area as high as 730 m^2/g. It then exchanges the Fe^{3+} for its cation support using simple ion exchange methods. For 100 mg/L simulated dye concentration, complete decolourization was achieved in less than 60 min under the optimum condition pH 5.0; 50 °C; 1 g/L Fe-Y; 20 mmol H_2O_2/L. This catalyst exhibited a poor catalytic activity because after 120 min reaction, the total organic carbon (TOC) still remains at a high level with only 42.73% mineralization. It is believed that the presence of several dye auxiliaries and dissolved salts inhibited the mineralization. The effect of dealumination of iron(III)-exchanged Y zeolites on oxidation of Reactive Yellow 84 azo dye in the presence of hydrogen peroxide was further studied by Neamtu et al. [88]. After the 60 min and under the same conditions, using Fe-Y-5 catalyst, 99.93% of colour removal, more than 74.14% of COD and 64.21% of TOC removal were obtained. By using HPICE analysis (a type of chromatograph), the peak showed that acetate, nitrate, formate, malanate and oxalate are present as main end products after 60 min. The authors suggested that bio-luminescence test could be used as pre-screening test for the toxicity evaluation and their result showed the product is more toxic than precursor compounds during the treatment at first 15 min.

Azo dye (Congo Red) was studied by Kondru et al. [89] using commercial Na-Y zeolite cation exchange with iron nitrate in solution. The surface area of Fe exchange Y zeolite is 423 m^2/g and account 9.74 wt.% Fe composes in their catalyst. The effect of temperature, initial solution pH, hydrogen peroxide concentration, and catalyst loading in catalytic wet peroxide oxidation was then studied. The percentage removals of dye at neutral pH, when temperature is 90 °C with 0.6 mL of H_2O_2 in 350 mL solution and 1 g/L catalyst, it was 97% in 4 h. Leaching of Fe cations out of zeolites depends strongly on pH of the solution, where, 7.8 ppm of iron was detected at solution of pH 2.0 however no leaching was observed at neutral pH [89].

Most of the zeolite based catalyst studied in the past were using a commercial grade type but in recent times, modification of the catalyst support to increase the surface area in order to enhance the catalytic activity start to pay the interest among researchers. Modification of natural zeolites or synthetic zeolites can be done in several methods such as acid treatment, ion exchange, and surfactant functionalisation, making the modified zeolites capable of achieving higher adsorption capacity [90]. Later several immobilization methods have been developed for the wastewater pollutants removal with the main goal to minimize the metal leaching and the capability to degrade the dye pollutants under broad range of pH. Lam and Hu [91], after their first catalyst communication for *in situ* oxidation for stabilization of Fe/MCM-41 catalyst prepared by metal organic chemical vapour deposition (MOCVD), in which the oxygen atoms was intercalated into the framework of both siliceous and ferric oxides via strong Fe–O–Si and Fe–O–Fe bonds, reported the better heterogenization version of the zeolite catalyst support. The immobilization iron catalyst by binding the oxygen atom was achieved by its strong adsorption to porous solid substrate MCM-41 channel molecular sieve yielding mineralization efficiency of orange II dye by ~85% and an extremely low iron leaching concentration of ~0.17 mg/L in acid medium throughout four runs.

In order to further improve the catalytic performance under wide range of pH, same methodology was applied with addition of bimetallic iron–copper catalyst supported on MCM-41[92]. They modified their catalyst to a high surface area about 1000 m^2/g, which is large enough to be used as catalytic materials. In this case, CuFe/MCM-41 was tested, the activity increases to 93% at acidic medium, and perform efficiently for the Orange II degradation with their mineralization achieved at the range of 78%–93% over a wide pH range (pH 3.0–7.0). The mechanism responsible for the enhanced reactivity and the atomic structure with bimetallic combinations is still unclear and a likely limitation to the full-scale application of bimetallic combinations to textile dye remediation is deactivation of the catalytic surface either by poisoning with sulfide or by formation of thick oxide films due to corrosion.

Zeolite catalyst prepared by *in situ* chemical vapour deposition method seems more stable towards leaching at acidic medium than other conventional methods of simple cation exchange, as well as to give the high degradation conversion. It is noted that under pH 5.5, the mineralization efficiency was still kept constant around 80% for all the ten runs; proven that there is strong bonding between the metal catalyst and the porous support. However, the major drawback is that the methodology was complicated and time consuming when applied to the epoxidation of ferric acetylacetonate inside a tubular rotating reactor under vacuum and transported to targeted substrate MCM-41 by an oxygen flow at temperature of 280 °C and then treated at the calcination temperature at 550 °C [91,92] .

Concurrently, natural zeolite sample obtained from Bigadiç region in Turkey was studied by Tekbas et al. [84] in photo-assisted Fenton oxidation using Remazol Brilliant Orange 3R (Reactive Orange 16) as a dye model pollutant. The Zeolite sample is mainly consists of clinoptilolite, which microporous structure framework. Zeolite based iron catalyst was prepared by simple ion exchange method. By the UVA irradiation, the optimal operational parameters were found as follows: 35 °C, solution pH 5.2, 15 mmol H_2O_2 dosage, 1 g/L catalyst loading and lead to more than 90% decolourization in 60 min. About 0.5 mg/L iron concentration in solution where leached from 28 mg/g iron concentration on the exchanged zeolite during the first run.

Within the same time frame, Kasiri et al. [49] used Fe-ZSM5 to degrade the Indigoid dye Acid Blue 74. The Fe-ZSM5 was synthesized in the presence of fluoride ions in order to solubilize the silica and iron sources. Under preparation temperature of 90 °C for Fe-ZSM5, it was found that bigger crystal size is more efficient compared with synthesis temperature at 170 °C, as shown in Fig. 5. Characterization of Fe-ZSM5 at 90 °C showed 187 m^2/g surface area with 38.95 Å, and XRF on the Fe-ZSM5 showed the chemical compound consist of SiO_2, SO_3, MnO and Fe_2O_3. The authors suggested that the addition of the zeolite did not enhance the decolourization efficiency but would enhance the mineralization of the pollutants and when their result was compared without zeolite addition, they concluded that adsorption of the dye molecules into zeolite particles did not play significant role [49].

Optimization studies using same model pollutants was carried out by same authors and concluded that the dye mineralization process was mainly influenced by pH and the initial concentration of the dye, whereas the other factors such as concentration of the catalyst, molar ratio of initial concentration of H_2O_2 to that of the dye showed lower effects [93,94]. The catalyst obeys the pseudo-first order kinetic and three consecutive experiments do not showed significant drop of the catalyst mineralization efficiency indicating that the catalyst has long-term stability with negligible deactivation due to leaching [95].

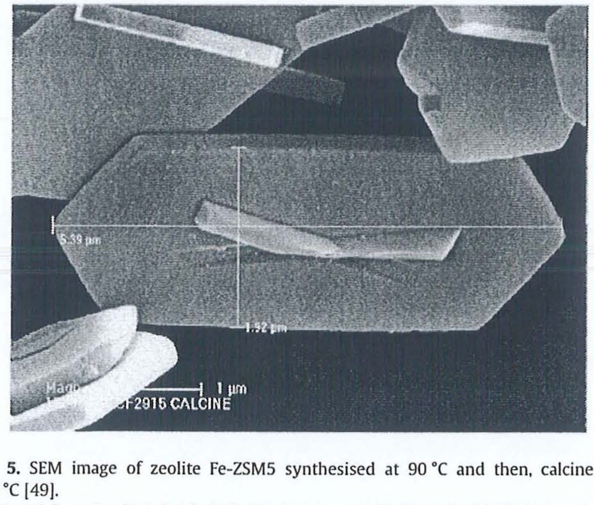

Fig. 5. SEM image of zeolite Fe-ZSM5 synthesised at 90 °C and then, calcined at 550 °C [49].
Reprinted from Applied Catalysis B: Environmental, 84, M. B. Kasiri, H. Aleboyeh and A. Aleboyeh, Degradation of Acid Blue 74 using Fe-ZSM5 zeolite as a heterogeneous photo-Fenton catalyst, Copyright (2008), with permission from Elsevier.

Fe-ZSM5 and the Fe-Y were also studied by the Chen et al. [96] to decolourize anthraquinone dye Reactive Brilliant Blue KN-R. The catalysts were prepared by co-precipitation and ion exchange methods, respectively. The catalytic activities follow the order of $\text{Fe-ZSM5}_{co} > \text{Fe-Y}_{ie} > \text{Fe-ZSM5}_{ie} > \text{Fe(II)} > \text{Fe-Y}_{co}$ (the alphabet in the subscript represent the synthesis methods, where 'co' represent the co-precipitation and 'ie' represent ion exchange). FeZSM-5_{co} has the highest KN-R decolourization capacity, which is four times higher than homogeneous Fenton reactions catalyzed by 15 mg/L Fe(II) ions. The synthesis methods which give rise to their composition and frame structure are the important factor for the catalytic activities and stability. In terms of the stability, Fe-Y_{ie} calcined at 350 °C was much better than Fe-ZSM5_{co} calcined at 450 °C with low iron leaching. Both catalysts also reported high iron leached from support at the first run, which account 11.0–12.0 mg/g leached from 65 mg/g of the Fe-loading contents in FeZSM-5_{co} and Fe-Y_{ie}.

Overall, in the experiment, the optimum pH for anthraquinone dye degradation was observed to be in the range 2.5 to 3.5. Most of the researchers using zeolite as a support on the Fenton reaction to degrade synthetic dyes in the pH range of (5.0–7.0) [94] except for anthraquinone dye in which the optimum was at pH 2.5 to 3.5 [96]. Further investigation on influence of pH of different categories of dyes using zeolite based catalyst is needed to explain the phenomena in future.

5. Activated carbon or carbon based catalyst for synthetic dye removal

Carbon materials are unique and have undeniable catalyst performance in their industrial applications. Carbon materials can be activated by tuning its porosity and increase its surface area to tailor into the specific reaction. Activated carbons that are derived from either synthetic materials or from low cost waste materials have been recognized not only as a good absorbent but also as catalysts and catalyst supports in many wastewater treatments. Ramirez et al. [97] have studied the surface chemistry based on the carbon based catalysts which are obtained from agricultural by-product (Olive stone) and carbon aerogels. Carbon aerogel was prepared by sol–gel methods and carbonization of an organic resorcinol–formaldehyde polymer in aqueous solution meanwhile olive stone was calcined at 1123 K to obtain the low cost activated carbon as end product. Both carbons were then impregnated with ferrous acetate in aqueous solutions. The SEM image of both catalyst structures is postulated in Fig. 6. Better catalytic activity with 90% TOC removal was reported for carbon aerogel-Fe compared to activated carbon-Fe, see Table 3. The authors explained that the lower catalytic activity of activated carbon-Fe, as it has a macroporous structure (150 nm) that cause the lower external surface area (55 m^2/g) for active sites to disperse thus adsorption capacity reduced. Whereas, carbon aerogel have bigger external surface area (337 m^2/g) and mesopores with 5 nm of radius which facile the iron catalyst dispersed nicely on the surface and yet better catalytic performance was achieved. In practice, carbon aerogel is still not a better choice as the catalyst support due to the high cost of chemical usage. Additionally, three consecutive experiments performed with the carbon aerogel-Fe sample showed some activity decay, which is due to both iron leaching and catalyst deactivation.

To minimize the leaching issue, similar study was also conducted by their group members, Duarte et al. [98], where the textural characteristics prepared from two synthesis methods were examined. The active sites and pore systems are tailored by well-known methods

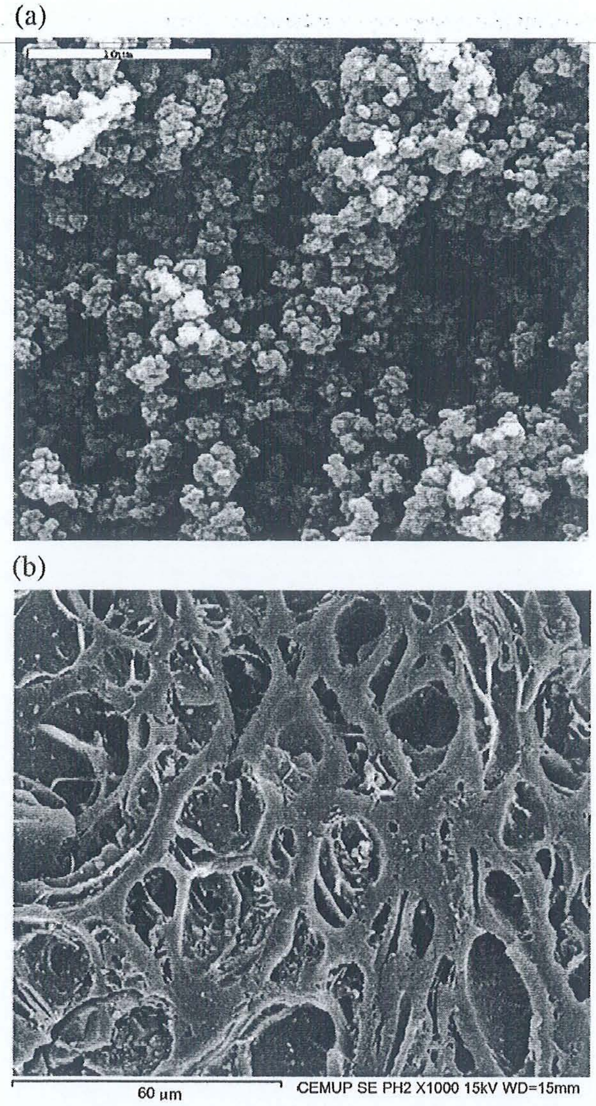

Fig. 6. SEM images of the carbon aerogel-Fe (a) and activated carbon-Fe (b) catalysts [97]. Reprinted from Applied Catalysis B: Environmental, 75, J. H. Ramirez, F. J. Maldonado-Hódar, A. F. Pérez-Cadenas, C. Moreno-Castilla, C. A. Costa and L. M. Madeira, Azo-dye Orange II degradation by heterogeneous Fenton-like reaction using carbon-Fe catalysts, Copyright (2008), with permission from Elsevier.

where they make use of the different transition metal salts namely Fe, Co, Ni doped into carbon aerogels by metal doping and impregnation methods, respectively. It was found that carbon aerogel based iron possessed the higher catalytic activity followed by carbon based Co and carbon based Ni almost inactive for both synthesis methods. The catalytic performance concluded by them mainly depends on the type of salts present. Catalytic activity can be enhanced by increasing their external surface area to mesoporous in order to permit the development of small nanoparticles and simultaneously decrease the mass transfer resistance for the reactants to access the carbon surface. However too high surface area (microporous), metal particles cannot be formed inside micropores, and thus sintering is favoured on the small external surface area that provides the large macropore volume, blocking some micropores. Meanwhile, macrostructure can be used to avoid metal leaching by its macropore volume which presents very low external surface area but the carbon matrix encapsulates some metal particles, avoiding the contact with the reactants.

Fenton-like degradation on dye pollutants Methylene Blue by activated carbons based iron was also studied by Castro et al. [99]. Iron metal salts were impregnated into both activated carbons, which were obtained from used coffee grounds and another one from commercial grade. From their results, it was found that activated carbon obtained from used coffee grounds showed more catalytic activity compared to commercial activated carbon based iron although the mechanism involved is unclear. Moreover, the activated carbon obtained from used coffee grounds have shown high stability which does not show iron leaching throughout the leaching test and can be recycle up to four times of usage.

6. Alumina based catalyst for synthetic dye removal

Alumina family in the form of catalyst support have a wide range of surface areas (from micropore to mesopore) but rather a few numbers of researchers used it as solid catalyst in Fenton system. It is commonly characterized by strong alkalinity and ion exchange capacity due to the presence of aluminum (+3) in their framework. One limitation of the alumina as catalyst support is that their synthesis method is rather cumbersome to get the higher purities of end materials; therefore, researchers employ commercial grade alumina material in Fenton process.

Catalytic activity by using iron oxide supported on alumina in degrading the Reactive Black 5 dye solution in a batch photoreactor has been reported by Hsueh et al. [100–102]. The interesting aspect of this study is that the authors recycled iron oxide-composite material which accumulated from FBR-Fenton process earlier to coat onto the activated alumina support. Activated alumina support used in the study has a high surface area beads as shown in Fig. 7. The catalyst greatly promotes not only the total removal of the colour under the pH range of 5.0–9.0 but also 45% mineralization in 240 min of Reactive Black 5 at neutral pH under the optimum conditions by 29.4 mM H_2O_2, 5.0 g/L of catalyst and 15 W UVA. Higher consumption of the H_2O_2 is required in this case, although, it can be reacted under neutral pH. In order to understand the catalyst absorption and desorption capacity, the authors further studied the catalyst behavior and revealed that interaction of dye, Reactive Black 5, when adsorbed by catalyst is an endothermic spontaneous process described by pseudo-second-order rate kinetic model.

Heterogeneous phase of photocatalytic degradation of azo dye Acid Violet 7 using UVA irradiation has been reported by Muthuvel and Swaminathan [103,104]. To immobilize the iron complex ion into alumina, potassium ferrioxalate or ferricnitrate was mixed with alumina in the pre-calculated ethanol/water mixture ratio. 5×10^{-4} M of Acid Violet 7 was almost completely decolourized in 60 min in the optimum condition of 1 g/L catalyst with 25 wt.% Fe and 20 mM H_2O_2 under pH 3.0. solution and solar irradiation. By comparison of UV and solar light process, the authors found that degradation rate was more effective in the presence of solar light than in UV light due to production of •OH radicals by visible light sensitized dye [103]. Recycling study revealed that the catalytic activity was achieved at 98% at the first run and reduced to 77% at the third run due to iron leaching from catalyst; subsequence runs maintained their efficiency at 77%.

Apart from the Acid Violet 7, two azo dyes namely, Direct Red 23 and Reactive Orange 4 respectively, were also studied in detail using Fe(II) loaded Al_2O_3 as a heterogeneous catalyst in the presence of H_2O_2 irradiated by UVA light. By comparing the different precursors in the alumina support, the catalyst ferrioxalate-Al_2O_3 showed to be more efficient than ferricnitrate-Al_2O_3 in the presence of UVA photo-assisted Fenton system [105]. Direct Red 23 undergoes easy degradation when compared to Reactive Orange 4 due to the presence of stable triazine ring system in Reactive Orange 4. Their optimum conditions for higher efficiency are: i) pH 2.0 for Direct Red 23 and pH 3.0 for Reactive Orange 4 and ii) H_2O_2 concentration-10 mmol/L for Direct Red 23 and 15 mmol/L for Reactive Orange 4 [105].

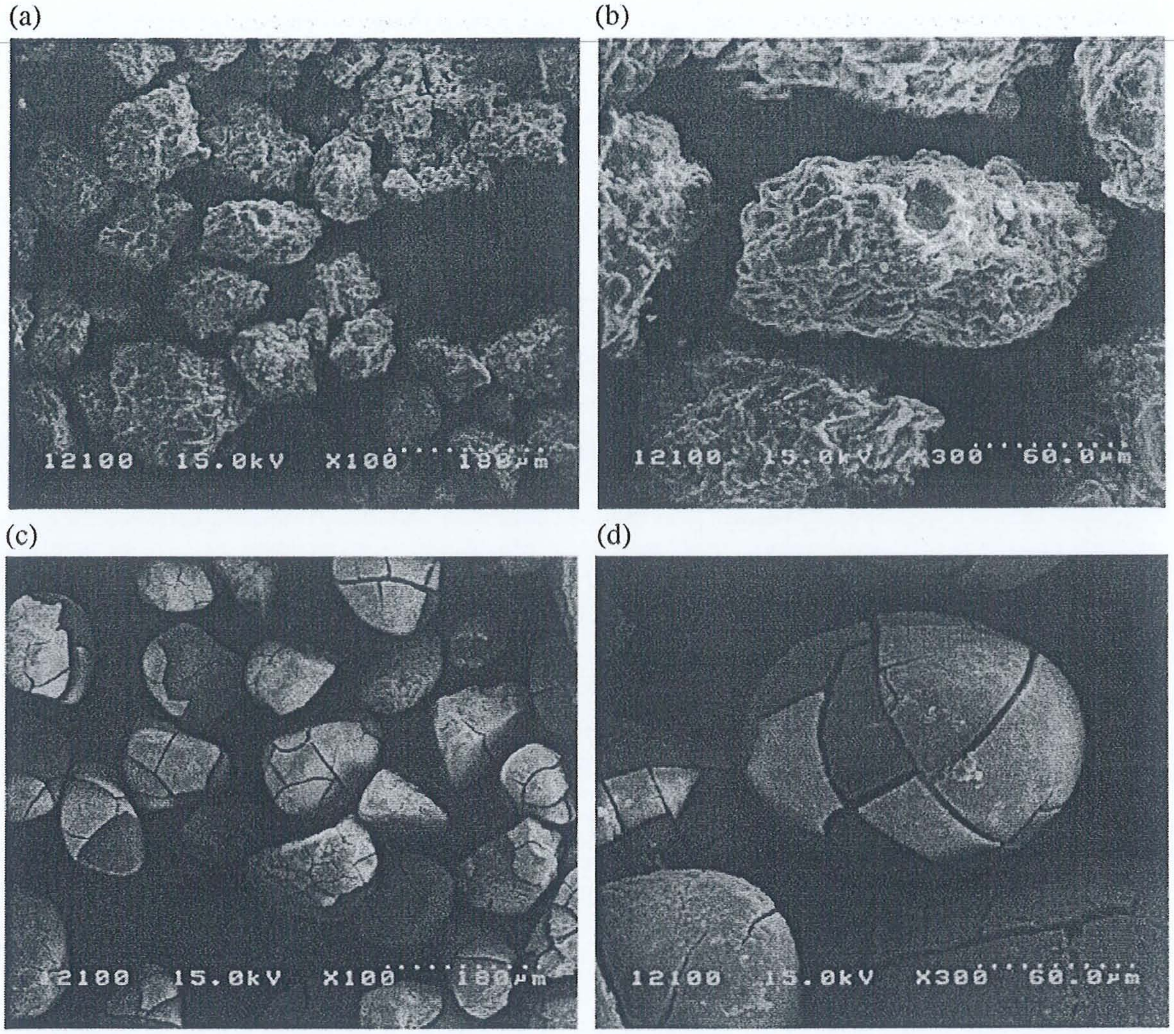

Fig. 7. Scanning electron micrographs of original activated alumina grain support: (a) 100×; (b) 300× and iron oxide: (c) 100×; (d) 300× [101].
Reprinted from Journal of Molecular Catalysis A: Chemical, 245, Chan-Li Hsueh, Yao-Hui Huang, Cheng-Chien Wang and Chuh-Yung Chen, Photoassisted Fenton degradation of nonbiodegradable azo-dye (Reactive Black 5) over a novel supported iron oxide catalyst at neutral pH, copyright (2006), with permission from Elsevier.

Based on their above discussion, alumina based iron catalyst exhibit higher degradation efficiency in acidic pH as reported by Muthuvel et al. [103–105]. Notwithstanding, this excludes the research done by Hsueh et al. [100,101] where pH range of 5.0–9.0 was reported. However, it was agreed that alumina based irons have the higher activities under near solar irradiation Fenton system for acid dyes, direct dyes and reactive dyes. Although, the chemistry and nature of the alumina based catalyst under *near* solar irradiation remained largely unknown.

7. Fly ashes based catalyst

The iron containing fly ashes have been studied by some researches to remove the wastewater pollutants such as arsenic removal, and heavy metals. Fly ash is a waste material originating in large quantities from a coal thermal power plant that can cause disposal problem [106,107]. Thus, attempts have been made to minimize the impact on the environment by utilizing fly ashes as a low cost absorbent for several pollutants removal [108–112], but in general, it needs a large amount of fly ashes to remove the pollutants. And in recent times, fly ashes have changed their role as catalyst support for dye removal under Fenton system [106]. The nature of metal ions such as Ca, K, Mg, Ti contained in the fly ash make them simple using the ion exchanged methods to prepared fly ash based iron [106]. Furthermore, with proper synthesis method and hydrothermal treatment, the thermally treated fly ashes can turn to zeolite [108]. Flores et al. [106] prepared five different amounts of immobilized iron mix and heated together in an aqueous solution until evaporation. The residue was treated at 100 °C overnight and then calcined at 500 °C for four hours. The experimental results show that it is possible to oxidize 0.061 mM Reactive Black 5 (in a media 0.05 M Na_2SO_4, $\approx$pH 2.8 adjusted with H_2SO_4) using a stoichiometric amount of H_2O_2. After two hours of treatment, the reaction solutions were found to become colourless completely and 80% of the original chemical oxygen demand was removed. The advantage thereof by using fly ashes is its lightweight and can prevent clogging of an electrochemical flow-cell if applied in a more realistic experiment.

8. Other heterogeneous catalysts for synthetic dyes removal

Green rust or Fe(II)–Fe(III) hydroxyl salts which have been known as an effective catalyst to treat the inorganic contaminants and dechlorination has also started to shift attention towards the treatment of organics contaminant through their first degradation evaluation on Methyl Red dye using Fenton process at neutral pH [113]. Kone et al. [113] suggested that poorly crystallized goethite badly crystallized iron oxide might form when green rust and hydrogen peroxide are oxidized leading to deactivation of the process. The results showed that green rust could be used to promote the reduction/oxidation reaction of organic pollutants.

It can be said that almost all the iron based heterogeneous catalysts such as carbon nanotubes, carbon nanofibers, activated carbon, hydrotalcite-like materials, mesoporous silica (MCM 41), silica, silica xerogel, sepiolite, and zeolite USY have been tested in their degradation activities of Acid Orange II towards its decolourization, Total Organic Carbon content, Chemical Oxygen Demand removal, and toxicity have also been reported [114]. Amongst the tested catalysts, Rodriguez et al. [114] concluded that the best catalyst belongs to iron supported on sepiolite for Orange II dye removal.

Reports [115] show that natural polymers such as chitosan have been used in the decolourization of Rhodamine B, Methylene Blue and Acridine Orange. Collagen fiber has also been used to remove Orange II and Malahite Green [116,117] and reports show that they are capable to degrade the dye pollutants up to certain extent. However, investigation revealed that those natural based catalysts are usually very selective and their catalytic activity in general are not good when compared to others and most often, research on the subject is still at the identification and conceptualization stage due to incomplete basic concept of the foundations, unsophisticated methodologies and inconsistent research findings. Sharing this information and experimental results with other researchers in similar fields help to gain insight into their work and provide guidance on which areas are more suitable to embark on replacements and modification of the synthesis methods on the prepared catalysts. Successful results are also helpful to know whether the system could be used to promote the reduction/oxidation reaction of organic pollutants.

9. Major causes of catalysts deactivation in heterogeneous Fenton system

The causes of catalyst deactivation in heterogeneous catalytic Fenton process have been observed by authors. Nevertheless, catalyst deactivation may occur due to diversity of factors, as pointed out by Moulijn et al. [118] and Guo et al. [119]. Among these include attrition by reduction of the catalyst specific surface area, poisoning of the catalytic agents by compounds formed during oxidation, surface deposition and strong adsorption on a polymeric carbon layer, and most commonly the leaching by the dissolution of some metal oxides from catalysts into the acidic reaction medium under Fenton system. Accumulation of toxic intermediate in the form of the acetic acid, halogen-, sulfur- or phosphorus-containing compounds can cause poisoning during dye degradation process [30]. Fig. 8 shows a schematic representation of the deactivation phenomena inside a catalyst particle.

It is worth mentioning that catalyst deactivation can be prevented with proper characterization of the support by knowing their nature, the chemistry involved in the reaction and control of the properties of the active sites to distribute homogenously on the support. A part from this, good research practice can also take into consideration the need to prevent catalyst deactivation for the dye removal by using the Fenton process. For example i) purification of the support especially for natural support materials; ii) optimizing the reaction condition especially the effect of the pH; iii) introducing the buffer solution to maintain the pH when effect of pH is crucial; and iv) doping with other metal precursors on the support to create bimetallic catalysts. In many ways, bimetallic catalysts can overcome the weaknesses of the single catalyst alone.

10. Future prospect on dye removal using heterogeneous catalytic Fenton process

Comprehensive effort aiming at the development of new catalytic processes, mesostructured catalyst will constitute a major part. But this part led to conspicuous innovation, and this is because the chemical engineering aspect of catalyst industrial development was considered simultaneously with the basic science aspects and the development of the whole process [120]. Since the surface of the catalyst support have shown a remarkable effect for the active site to promote the reaction with the reactants, the challenge in future is to increase the surface area by appropriate synthesis methods either by modifying the structure or properties of supports [52], to dope with other elements making up the catalyst to contain several elements homogeneously distributed on the support and in order to have better reaction rate to explore a new and effective catalyst. Table 4 summarized the main advantages and drawbacks of the different catalysts discussed in this review.

11. Conclusions

The efforts on heterogeneous Fenton system have showed great improvement on the progress of catalyst development by using a lesser amount of oxidizing agent, wide range of reaction pH, higher catalytic activities and encouraging kinetic rate compared to homogenous catalyst. Various preparation methods from simple ion exchange, impregnation, pillaration to complex chemical vapour decomposition followed by calcination have been developed to strengthen the active sites to stick on the supports. Furthermore the heterogeneous catalyst has successfully demonstrated its capabilities to operate under a broad range of pH from (2.0–9.0) as compared to homogenous catalyst only under narrow acidic conditions. Among the catalysts discussed above, pillared clay based catalyst has been studied heavily by the researchers as it offers promising stability in performance compared to other catalysts. Other catalysts should be given the chance to explore their capabilities or for optimization through the design of future synthetic methods. Moreover, bimetallic catalyst incorporated into the support and the development of the mesoporous structure supports through the modification of their synthesis method were also successfully demonstrated with ignorable leaching under their optimum reaction conditions; although, it is just few cases reported. Nevertheless, excellent performance was reported through design of solid metal nanoparticles based catalyst compared to homogenous catalysts in Fenton process for synthetic dye abatement.

Nomenclature

AOP	advanced oxidation process
BOD	biological oxygen demand
COD	chemical oxygen demand
FBR	Fluidized bed reactor
≡Fe	Fe deposited on the surface of the support
Fe0	Zero valent iron
$h\nu$	ultraviolet radiation
PILC	pillared interlayered clay
•R	organic radical
TOC	total organic carbon
TSS	total suspended solid

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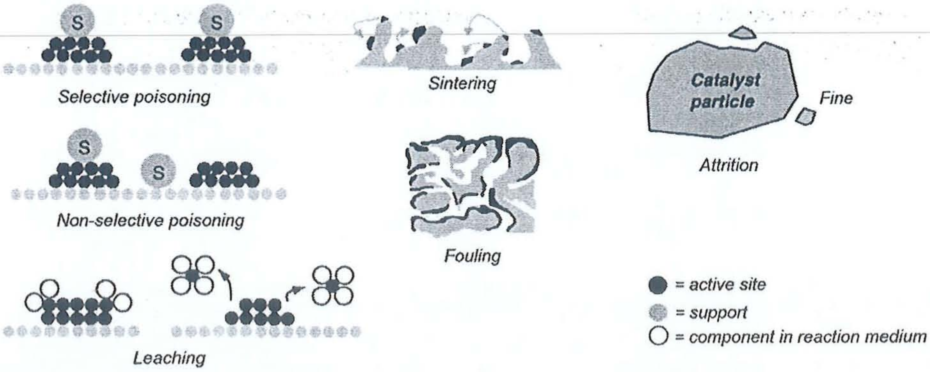

Fig. 8. Major causes of deactivation in heterogeneous catalysis [118].
Reprinted from Applied Catalysis A: General, 212, J.A. Moulijn, A. E. van Diepen, F. Kapteijn, Catalyst deactivation: is it predictable?: What to do? Copyright (2001), with permission from Elsevier.

Table 4
Summary of advantages and drawbacks for various heterogeneous Fenton catalysts.

Catalyst type	Advantages	Drawbacks
Clay based catalyst	- Possess catalytic activity in the wide range of pH (3.0-9.5) [74–76]. - Possess catalytic activity under visible light irradiation [79,80]. - Consist of iron minerals naturally [37] with exception of synthetic clay [61]. - Acid activated clay and catalyst coated film can minimize leaching [66]. - Remain at high efficiency up to ten runs [92].	- Leaching of active phases could result after the formation of acid intermediates in solution [77]. - Bimetallic catalyst is easily leached into solution at pH<3.0 [72]. - Under visible light irradiation, it takes longer time to mineralize the dyes [80].
Zeolite based catalyst	- Easily prepared by ion exchanged with commercial grade zeolite [7,84]. - Catalytic activity is commonly optimized at pH range 5.0–7.0 [49,84,95]. - Incorporation of bimetallic catalyst on the support showed better performance in stability and insensitivity towards pH [92]. - Possess catalytic activity under UVA irradiation [84].	- High hydrogen peroxide consumption [49,96,101].
Carbon based catalyst	- Mesoporous catalyst possesses higher catalytic activity when compared to microporous and marcoporous [98].	- Leaching of active phase from catalyst after several runs resulted in activity decay [97].
Alumina based catalyst	- Possess catalytic activity under UVA irradiation [100,101,103–105]. - Possess catalytic activity at neutral pH [100,101].	- Only commercial grade alumina/alumina beads is use in the Fenton system, modification of the alumina has not been reported so far [100,101,103–105]. - High hydrogen peroxide consumption [100,101]. - Longer degradation time [101].
Fly ash based catalyst	- Easily prepared by ion exchanged with fly ash from bituminous coal [106].	- It can only be optimized under acidic medium [106]. - Non- recyclable [106]. - Only stable in heterogeneous phase up to 6 h [106].

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Short communication

Fenton-like oxidation of reactive black 5 solution using iron–Montmorillonite K10 catalyst

N.K. Daud, B.H. Hameed*

School of Chemical Engineering, Engineering Campus, Universiti Sains Malaysia, 14300 Nibong Tebal, Penang, Malaysia

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ABSTRACT

Decolorization of reactive azo dye, reactive black 5 (RB5), was conducted using Fe(III) immobilized on Montmorillonite K10 (MK10) as a catalyst in the presence of H_2O_2 using Fenton-like oxidation process. The effect of different parameters such as iron ions loading on supported catalyst, catalyst dosage, initial pH of dye solution, initial concentration of H_2O_2 and dye and reaction temperature on the decolorization efficiency of the process were studied. The results indicated that by using 12 mM of H_2O_2 and 3.50 g L^{-1} of the 0.11 wt.% Fe(III) oxide on MK10 catalyst at pH of 2.5, 99% of decolorization efficiency was achieved within 150 min in a batch process.

1. Introduction

Fenton reaction wastewater treatment process is known to be very effective in the removal of many hazardous organic pollutants and dyestuff from water. Fenton's reagent was discovered about 100 years ago but its application as an oxidizing process for destroying toxic organics was not applied until the late 1960s [1]. The Fenton reaction causes dissociation of the oxidant with the formation of highly reactive hydroxyl radicals that attack and destroy the organic pollutants [2]. However, it should be pointed out that the homogeneous Fenton process has a significant disadvantage. Homogeneously catalyzed reactions need up to 50–80 mg L^{-1} of iron ions in solution, which is well above Environmental Act 1974 directives that allow only 5 mg L^{-1} of iron ions in treated water to be dumped directly into the environment. In addition, the removal and treatment of the sludge-containing iron ions at the end of the wastewater treatment is expensive and needs large amount of chemicals and manpower [3].

To overcome these drawbacks, much attention has been focused on the development of heterogeneous catalyst for Fenton process in recent years [4]. Selection of catalyst support is equally important during preparation of the heterogeneous catalyst. The use of heterogeneous solid Fenton catalysts such as iron (III) oxide immobilized on Montmorillonite K10 (Fe–MK10) can be an alternative. The Fenton-like processes have been used as a powerful source of hydroxyl radicals with H_2O_2 in the presence of metal cations under controlled reaction conditions [4,5]. For example, when iron salts are adsorbed onto the surface of MK10, the reduction–oxidation reactions between Fe(III)/Fe(II) take place in the presence of hydrogen peroxide which promote the formation of reactive components such as the hydroxyl ($^{\bullet}OH$) and the hydroperoxyl ($^{\bullet}OOH$) radicals. The radicals generated by the decomposition of hydrogen peroxide can oxidize organic compounds adsorbed over the catalyst or degrade soluble organic compounds in the vicinity of iron active ions present at both the catalyst surface and in the bulk liquid phase. Thus, the formed Fe^{2+}/Fe^{3+} complexes on the surface of catalyst can then react with H_2O_2 thus allowing iron ions to participate in the Fenton catalytic cycle [6–8].

The main goal of this study was to investigate the applicability of iron (III) oxide immobilized on Montmorillonite K10 as heterogeneous Fenton catalyst for decolorization of reactive black 5 (RB5) solutions as a model for real textile wastewater. The effects of different parameters such as iron ions loading on supported catalyst, catalyst amount, initial concentrations of H_2O_2 and dye, including initial pH of the dye solution on the decolorization efficiency of the process would be assessed.

2. Experimental procedures

2.1. Materials

The reactive dye, reactive black 5 (Fig. 1) (CAS number = 17095-24-8, Synonyms = Remazol Black B, empirical formula = $C_{26}H_{21}N_5Na_4O_{19}S_6$, molecular weight = 991.82, and

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* Corresponding author. Tel.: +60 45996422; fax: +60 45941013.
E-mail address: chbassim@eng.usm.my (B.H. Hameed).

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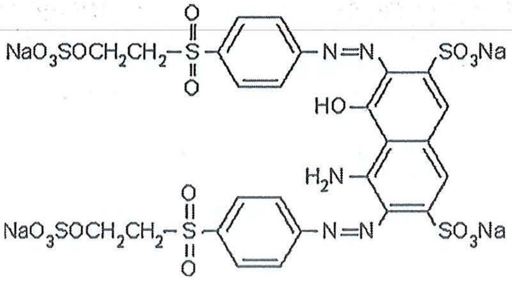

Fig. 1. The structure of RB5.

λ_{max} = 597 nm) was provided by Sigma–Aldrich, Malaysia and used without purification. Hydrogen peroxide solution (30%) and Montmorillonite K10 powder were of analytical grade and purchased from Merck Chemicals, Malaysia. Distilled water was used throughout the experiments. The initial pH of the solution was adjusted using 1.0 M NaOH or 1.0 M H_2SO_4 to explore the effect of the pH.

The Fe–MK10 catalyst was prepared by the incipient impregnation method [9], in which distilled water is used to solubilize the $Fe(NO_3)_3{\cdot}9H_2O$ (Merck). Then, MK10 was added to this aqueous solution and was stirred constantly in the water-bath until all water was evaporated. After impregnation, the sample was dried at 105 °C for 12 h, followed by calcination at 500 °C for 4 h in a muffle furnace, ground to 200-mesh and named as Fe–MK10.

2.2. Catalytic activity

All experiments were carried out in 250-mL stoppered glasses (Erlenmeyer flask) placed in a thermostated water-bath with an agitation of 130 rpm for 150 min. Each experimental run was performed by taking an appropriate amount of stock dye solution followed by dilution with distilled water to 200 mL. Predetermined amounts of impregnated catalyst were then added to the flask. Also, initial solution pHs were adjusted to the desired values by using prepared 1.0 M H_2SO_4 or 1.0 M NaOH solution. The reactions commenced when measured amounts of H_2O_2 solution were added to the flask. Thereafter, 3 mL volume of samples were withdrawn periodically and analyzed using a UV–Vis spectrophotometer (Shimadzu, model UV 1601, Japan) with the maximum absorbance wavelength for RB5 at 597 nm. At each stage, the samples withdrawn were returned into the conical flask to prevent any loss of contents. Thus, the concentration of dye in the reaction mixture at different reaction times was determined by measuring the absorption intensity at λ_{max} = 597 nm and with a calibration curve. Prior to the measurement, a calibration curve was obtained by using the standard RB5 solution with a known concentration. The decolorization efficiency of RB5 is defined as follows:

$$\text{Decolorization efficiency (\%)} = \left[1 - \frac{C_t}{C_o}\right] \times 100 \qquad (1)$$

where C_o (mg L^{-1}) is the initial concentration of RB5 and C_t (mg L^{-1}) is the concentration of RB5 at reaction time, *t* (min).

The total iron concentration in the solution was determined using Atomic Absorption Spectrophotometer (AAS) model Shimadzu AA 6650 with the maximum absorbance wavelength (λ_{max}) of iron ion obtained at 248.35 nm. Similarly, prior to the measurement of the iron concentration, a calibration curve was obtained by using the standard iron ion solution in 0.10 M HNO_3 solution with a known concentration. Finally, when the decolorization of RB5 was completed, the samples were analyzed to determine the total iron ion leached from the catalyst.

3. Results and discussion

Decolorization of RB5 solutions by Fenton-like process using Fe–MK10 as a catalyst was studied based on six different parameters: effect of iron ions loading on supported catalyst, effect of catalyst dosage, effect of pH, effect of initial concentration of hydrogen peroxide, effect of initial concentration of dye and effect of reaction temperature. The detailed results of these parameters are presented in Table 1.

The effect of iron ions loading on MK10 was investigated by varying the ferric ions concentration from 0.030 to 0.14 wt.%. The decolorization efficiency increases with increase in iron ions loading, reaching a maximum value of 0.11 wt.% of ferric ions on MK10 and then a decrease was observed. This is equivalent to 99% decolorization in 150 min of reaction. Hence, 0.11 wt.% of iron (III) oxide loading on MK10 was found to be quite good for maximum efficiency. Since, an increase of the amount of iron ions involved in the process resulted to an increase in the number of $^{\bullet}OH$ radicals significantly.

It was also observed that the efficiency of the process increased with an increase in the amount of catalyst. The highest value of 3.5 g L^{-1} of catalyst was reached before a decline was noticed. The fact that higher decolorization efficiency was achieved at the highest catalyst dosage was mainly attributed to the higher production of $^{\bullet}OH$ with more ferric ions in Fenton-like reaction [10]. In the present work, 3.5 g L^{-1} of catalyst dosage was considered to be a suitable dosage for the decolorization of RB5.

The effect of initial pH value of solutions on the decolorization of RB5 by Fenton-like process was studied in the pH range of 1.5–5.0. A direct influence of initial pH on the decolorization of RB5 could be observed and the best decolorization efficiency was obtained at pH of 2.5. An important observation here revealed that at initial pH of 4.0 and 5.0, the decolorization of RB5 could not be established in 150 min of reaction. This is principally due to the formation of ferrous/ferric hydroxide complexes leading to catalyst deactivation, and this resulted in the amount of $^{\bullet}OH$ radicals generated to be very small [11,12]. However, when the initial pH was decreased from 5.0 to 2.5, the decolorization efficiency of RB5 increased significantly within 150 min from 8.47% to 99%. Also, the decolorization efficiency of RB5 was reduced to 68.35% with a further decrease of the initial pH from 2.5 to 1.5. This could be explained by the formation of oxonium ion ($H_3O_2^+$), which enhanced the stability of H_2O_2 and restricted the generation of $^{\bullet}OH$ at low pH conditions (pH < 2.5) [13]. In addition, the scavenging of $^{\bullet}OH$ by the excess of H^+ is also another reason for the lowering of the decolorization efficiency of RB5 at pH 1.5 [11,14].

The effect of initial concentration of H_2O_2 on the decolorization of RB5 was examined by varying the initial concentration of H_2O_2 from 4 to 32 mM. It would be observed that increasing the dosage of H_2O_2 from 4 to 12 mM enhanced the decolorization of RB5. However, when further increase in the dosage above 12 mM was used, there was no observed improvement in the decolorization but rather a sharp drop. In fact, the decrease in the decolorization efficiency of RB5 at high dosage of H_2O_2 was mainly caused by the scavenging effect of excess H_2O_2 to $^{\bullet}OH$. In addition, the recombination of $^{\bullet}OH$ also contributed to the decline in the decolorization efficiency of RB5 [10].

The efficiency of Fenton-like process as a function of initial concentration of the dye was evaluated. As the lifetime of hydroxyl radicals is very short (only a few nanoseconds), they can only react where they are formed. Increasing the quantity of RB5 molecules per volume unit logically enhances the probability of collision between organic matter and oxidizing species, leading to an increase in the decolorization efficiency [15].

The effect of temperature on the decolorization of RB5 was studied at different temperatures of 30, 40 and 50 °C. As can be seen

Table 1
Effects of six parameters on the decolorization of RB5 at different reaction conditions.

Fe^{3+} loading on MK10 (wt.%)	Catalyst dosage ($g L^{-1}$)	pH	$[H_2O_2]$ (mM)	$[RB5]_o$ ($mg L^{-1}$)	Temperature (°C)	Decolorization efficiency (%) at reaction time, *t* (min)				
						30 min	60 min	90 min	120 min	150 min
0.030	2.0	2.5	4	50	30	19.09	31.06	55.07	81.76	99.74
0.060	2.0	2.5	4	50	30	16.21	30.59	61.28	90.51	99.45
0.080	2.0	2.5	4	50	30	15.36	29.35	59.70	90.34	99.81
0.11	2.0	2.5	4	50	30	20.93	46.12	86.16	99.77	99.93
0.14	2.0	2.5	4	50	30	17.88	39.41	78.36	98.66	98.68
0.11	0.50	2.5	4	50	30	13.75	28.80	47.13	71.97	85.75
0.11	1.0	2.5	4	50	30	12.69	29.62	56.50	89.47	98.19
0.11	1.50	2.5	4	50	30	12.90	29.38	61.55	92.94	99.65
0.11	2.0	2.5	4	50	30	17.49	49.49	85.86	97.79	99.77
0.11	2.50	2.5	4	50	30	20.98	48.23	89.79	98.96	99.24
0.11	3.0	2.5	4	50	30	19.26	47.63	85.73	98.76	97.84
0.11	3.50	2.5	4	50	30	26.00	62.18	96.86	98.34	99.53
0.11	4.0	2.5	4	50	30	24.27	58.12	96.19	98.15	98.10
0.11	4.5	2.5	4	50	30	25.32	60.43	96.65	98.09	98.16
0.11	5.0	2.5	4	50	30	25.82	61.24	96.50	98.21	98.25
0.11	3.5	1.5	4	50	30	15.77	27.16	45.78	68.35	79.13
0.11	3.5	2.0	4	50	30	16.58	46.81	88.83	96.89	98.82
0.11	3.5	2.5	4	50	30	24.00	69.41	97.20	99.30	99.39
0.11	3.5	3.0	4	50	30	20.42	51.72	78.45	95.47	98.89
0.11	3.5	3.5	4	50	30	9.19	22.57	37.28	54.72	69.50
0.11	3.5	4.0	4	50	30	4.23	8.00	7.76	17.70	23.11
0.11	3.5	5.0	4	50	30	3.88	4.83	6.18	8.47	11.13
0.11	3.5	2.5	4	50	30	29.52	73.45	96.65	98.79	99.02
0.11	3.5	2.5	8	50	30	32.98	76.39	96.66	98.29	98.43
0.11	3.5	2.5	12	50	30	34.42	80.21	97.57	99.07	99.60
0.11	3.5	2.5	16	50	30	22.79	60.60	95.13	98.29	98.23
0.11	3.5	2.5	20	50	30	28.71	70.19	98.81	98.84	98.13
0.11	3.5	2.5	24	50	30	24.82	60.49	96.61	98.91	98.23
0.11	3.5	2.5	28	50	30	22.71	52.03	92.15	98.68	98.09
0.11	3.5	2.5	32	50	30	25.16	65.86	93.94	98.89	98.22
0.11	3.5	2.5	12	25	30	24.89	44.70	73.88	97.87	99.32
0.11	3.5	2.5	12	50	30	24.64	50.17	84.81	98.59	99.31
0.11	3.5	2.5	12	75	30	27.78	52.27	84.70	98.89	99.89
0.11	3.5	2.5	12	100	30	31.93	55.47	86.37	98.49	99.90
0.11	3.5	2.5	12	50	30	34.42	80.22	97.57	98.07	99.60
0.11	3.5	2.5	12	50	40	41.75	95.70	98.17	99.62	99.79
0.11	3.5	2.5	12	50	50	79.12	99.95	99.20	99.63	99.81

from Table 1, raising the temperature has a positive impact on the decolorization of RB5. The decolorization efficiency within 60 min of reaction increased from 80.22% to 99.95% as the temperature is increased from 30 to 50 °C. Furthermore, the period of time required for the decolorization of RB5 was much shorter at higher temperature. This can be explained that the Fenton-like reaction, as other reactions, is accelerated by raising temperature which improved the generation of $^{\bullet}OH$ radicals and therefore enhanced the decolorization of RB5 [10].

Leaching and stability tests were carried out to check the potential and the stability of the catalyst itself. In all of the experiments, concentration of iron ions was below $5\,mg\,L^{-1}$ and this conforms to the standard of Environmental Quality Act 1974. This shows that the catalytic activity is mainly due to the heterogeneous catalyst (Fe–MK10) and not to the leached iron ions, even though a small amount of iron was found in the aqueous solution. In order to test the long-term stability of the catalyst, Fe–MK10 was recovered by filtration from the solution after the treatment, washed with distilled water, dried at 105 °C for 12 h and then tested again under the same reaction conditions in four consecutive cycles. A reduction in catalytic activity was observed. This might be due to the iron loss rather than its active component. Other authors reported similar results, but they attributed the loss of activity to poisoning of the active catalytic sites due to adsorbed organic species [15].

4. Conclusions

The results revealed that the iron (III) immobilized MK10 catalyst obtained through incipient impregnation method could serve as a very active heterogeneous catalyst for the decolorization of RB5. The optimum condition process of 0.11 wt.% Fe–MK10, $3.5\,g\,L^{-1}$ dosage of catalyst, pH 2.5, 12 mM of H_2O_2 gave 99% decolorization efficiency of solution containing $50\,mg\,L^{-1}$ of RB5 in just 150 min of reaction in a batch process. Leaching tests indicated that the activity of the catalyst is not due to the leached iron ions, although a small amount of these ions was found in the aqueous solution. Significantly lower concentration of iron ions obtained from the solution after the treatment could give this system, Fe–MK10/H_2O_2, a great advantage over the homogeneous Fenton-type system.

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Decolorization of Acid Red 1 dye solution by Fenton-like process using Fe–Montmorillonite K10 catalyst

N.K. Daud, M.A. Ahmad, B.H. Hameed*

School of Chemical Engineering, Engineering Campus, Universiti Sains Malaysia, 14300 Nibong Tebal, Penang, Malaysia

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ABSTRACT

In this work, the decolorization of Acid Red 1 (AR1) dye was conducted using Fe(III) oxide immobilized on Montmorillonite K10 (Fe–MK10) catalyst in the presence of hydrogen peroxide (H_2O_2) in batch process. The effects of different parameters such as iron loading (Fe^{3+}) on Montmorillonite K10 (MK10), catalyst dosage, solution pH, initial concentration of H_2O_2 and AR1 and reaction temperature on the decolorization efficiency of the process were studied. The results indicated that by using $5.0\,g\,L^{-1}$ catalyst dosage of 0.14 wt.% Fe–MK10 at pH 2.5 and 16 mM of H_2O_2, 99% of the $50\,mg\,L^{-1}$ of AR1 was decolorized within 150 min. Leaching test indicated that the leached iron from the catalyst was less than $5\,mg\,L^{-1}$.

1. Introduction

Water pollution is a major problem in the global context. Chemical process industries, such as oil refineries, petrochemical units, dye and dye intermediate manufacturing industries, textile units, among others, are typical industries that dump toxic organic compounds to the nearer water courses, thus causing sever pollution [1]. Amongst them, the dye and dye intermediate manufacturing and textile industries stand out as they produce a large amount of effluents which can cause serious environmental problems as they contain colored compounds resulting from dyes unfixed to fibers during the dyeing process [2].

The effluents discharged from these industries are usually strongly colored, and the direct release of the wastewater into receiving water body will cause damage to both aquatic life and human beings due to their toxic, carcinogenic and mutagenic effects [3,4]. Actually, the removal of dyes from wastewater is a challenge to the related industries, because the synthetic dyes used are stable compounds and difficult to destroy by common treatments. Physical, chemical, and biological methods are presently available for the treatment of wastewater discharged from various industries [5]. However, physical methods such as liquid–liquid extraction, ion-exchange, adsorption, air or steam stripping, etc., are ineffective on pollutants which are not readily adsorbable or volatile, and have further disadvantages because they simply transfer the pollutants to another phase rather than destroying them [6].

Acid dyes are a type of azo dyes, that are characterized by the presence of one or more azo groups (–N=N–) bound to aromatic rings and the largest and most important class of synthetic organic dyes. It has been estimated that more than 50% of all dyes in common use are azo dyes because of their chemical stability and versatility [7,8]. The complex molecular structures of most azo dyes make them resistant to biological or even chemical degradation. This also renders the conventional physical, chemical, and biological treatment methods insufficient and costly for their removal from water [9].

Advanced oxidation processes (AOPs) have been widely proposed, as they operate at temperature near ambient and atmospheric pressure [10]. Hydroxyl radicals ($^\bullet OH$), highly reactive species generated in sufficient quantities by these systems, have the ability to oxidize the majority organic constituents in industrial effluents [11,12]. Common AOPs involve Fenton and photo-Fenton processes, ozonation, electrochemical oxidation, photolysis with H_2O_2 and O_3, high-voltage electrical discharge process, TiO_2 photocatalysis, radiolysis, water solution treatment by electronic beams or γ beams and various combinations of these methods [13–15].

Fenton reaction employed in wastewater treatment processes are known to be very effective in the removal of many hazardous organic pollutants from water [16,17]. Fenton's reagent was discovered about 100 years ago, but its application as an oxidizing process for destroying toxic organics was not applied until the late 1960s [18]. The key step in the Fenton type reaction is the formation of hydroxyl radicals ($HO^\bullet$) from H_2O_2 and Fe(II). It is known that the systems of Fenton type are responsible for oxidation of different organic materials, but their usage as catalysts induces an additional pollution [19–21].

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* Corresponding author. Tel.: +60 45996422; fax: +60 45941013.
E-mail address: chbassim@eng.usm.my (B.H. Hameed).

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To overcome the disadvantages of homogeneous Fenton process, heterogeneous Fenton and Fenton-like catalysts have recently received much attention [19]. In a previous work [22,23] we reported the decolorization of Acid Red 1 and reactive black 5 using rice husk-based catalyst and iron–Montmorillonite K10 catalyst, respectively. The objective of this work was to investigate the applicability of Fe(III) oxide contained Montmorillonite K10 (MK10) as heterogeneous Fenton catalyst for decolorization of Acid Red 1 (AR1). The effects of different parameters such as different loading of ferric iron on Montmorillonite K10 (MK10), catalyst dosage, initial concentration of dye and H_2O_2 and initial pH and temperature on the decolorization efficiency of the process were studied.

2. Materials and methods

2.1. Chemicals and reagents

The azo dye, Acid Red 1 (AR1) was obtained from Sigma–Aldrich as commercially available dye and used without further purification. Hydrogen peroxide (H_2O_2) (30%, w/w) and Montmorillonite K10 (MK10) were purchased from Sigma–Aldrich (M) Sdn Bhd, Malaysia. Distilled water was used throughout this study.

2.2. Preparation of Fe–MK10 catalyst

The Fe–MK10 catalyst was prepared by the impregnation method [24], in which distilled water is used to solubilize the ferric nitrate nonahydrate ($Fe(NO_3)_3{\cdot}9H_2O$) (Merck). Then, MK10 was added to this aqueous solution and was stirred constantly in the water-bath until all water was evaporated. After impregnation, the sample was dried at 105 °C for 12 h, followed by calcination at 500 °C for 4 h in a muffle furnace [23].

2.3. Catalyst characterization

Elemental chemical analyses were performed using Energy Dispersive X-ray (EDX) spectroscopy to determine the composition of the original clay and the exact amount of iron in the final catalyst. The morphology of the MK10 was studied using scanning electronic microscopy (SEM) (SEM-JEOL-JSM6301-F) with an Oxford INCA/ENERGY-350 microanalysis system. Fourier Transform Infrared (FT-IR) spectra were recorded in the 4000–400 cm^{-1} region with a PerkinElmer 1730 FT-IR spectrometer, using a He–Ne laser source in KBr pellet (1 mg sample with 300 mg KBr) and 15 scan per minute to improve the signal-to-noise ratio.

Brunauer–Emmett–Teller (BET) specific surface area was determined by adsorption of nitrogen at 77 K using a Micromeritics, ASAP 2020 surface area and porosity analyzer. The X-ray diffraction (XRD) patterns of the catalyst (before and after impregnation) were measured with SIEMENS XRD D5000 equipped with Cu Kα radiation.

2.4. Experimental procedure

Experimental runs were carried out in batch mode using conical flasks filled with 200 mL of the AR1 solution at a given concentration (25–100 mg L^{-1}). In a typical run, the reaction suspension was prepared by adding a given amount of catalyst into solution which has been adjusted to the desired pH value by NaOH or H_2SO_4. The reactions commenced when predetermined amounts of H_2O_2 solution were added to the flasks. Thereafter, samples were withdrawn periodically and analyzed using a UV–vis spectrophotometer. After filtration through 0.42 μm Millipore membrane filters to remove suspended particles. At each stage, the samples withdrawn were returned into the conical flasks.

Table 1
Chemical compositions of MK10 and Fe–MK10 determined by EDX.

Element	Concentration (wt.%)	
	MK10	Fe–MK10
O	40.42	40.46
Fe	8.26	8.48
Al	11.50	10.57
Si	39.82	40.49

2.5. Analytical methods

The concentration of AR1 was analyzed on UV–vis spectrophotometer (Shimadzu, model UV 1601, Japan) with its adsorption at 532 nm, which is the maximum absorption wavelength of AR1. Because the reaction continued after sampling, the measurement of absorbance of reaction solution was done within one min. The decolorization efficiency of AR1 is defined as follows:

$$\text{decolorization efficiency}(\%) = \left[1 - \left(\frac{C_t}{C_0}\right)\right] \times 100 \qquad (1)$$

where C_0 (mg L^{-1}) is the initial concentration of AR1 and C_t (mg L^{-1}) is the concentration of AR1 at reaction time, t (min).

The total Fe in the solution was determined using Atomic Absorption Spectrophotometer (AAS) model (Shimadzu AA 6650) with the maximum absorbance wavelength (λ_{max}) of iron ion (III) of 248.35 nm. After the decolorization of AR1 was completed, the samples were analyzed to determine the total iron ion leached from the catalyst [23].

3. Results and discussion

3.1. Catalyst characterization

The chemical composition of the 0.14 wt.% Fe–MK10 and MK10 were measured by EDX and are the results are presented in Table 1. The results show that the major elements in MK10 and impregnated MK10 are Si, O, Fe and Al and revealed that the Fe concentration of the Fe–MK10 catalyst is 8.48 wt.%, while it is only 8.26 wt.% in MK10. The distinction of percent by weight of Fe in impregnated MK10 is about 0.22%. Fe was introduced into the clay layers after impregnation method. Slight variations are noticed between the expected and the determined iron content of the samples, which is due to the high hydration degree of the solids at the stages of the preparation procedure, thus making it difficult to obtain the targeted iron contents. The experimental error of the results was determined and represents about 2.6% of uncertainty. Whereas for Si, O and Al, the changes of composition by weight percent occurred about 0.67 wt.%, 0.040 wt.% and 0.93 wt.%, respectively due to the agglomeration of components because of the impregnation of MK10. The reason for using the best loading assayed (0.14 wt.%) was due to the limitation of the iron ions leaching from the support of catalyst that followed the Environmental Quality (Sewage and Industrial Effluents) Regulation 1979 (must below than 5 mg L^{-1}).

Fig. 1 shows the SEM images of MK10 and 0.14 wt.% Fe–MK10. The card-like pattern of the clay mineral layers is seen and not much change on the morphology can be visualized although after MK10 was impregnated with Fe.

FT-IR spectra (4000–400 cm^{-1}) of the MK10, 0.14 wt.% Fe–MK10 and 0.14 wt.% Fe–MK10 after decolorization of AR1 are presented in Fig. 2. Comparing the spectrum of pure MK10 with the spectrum of Fe–MK10, two peaks were depressed at 3629 cm^{-1} and 526 cm^{-1} and one new peak emerged at 1384 cm^{-1} [25]. The former was the $NO_3{}^-$ stretching mode, which showed that there was some redundant positively charged iron aggregates outside the interlayer space of Fe–MK10 [26], while the latter was the FeOOH bending vibra-

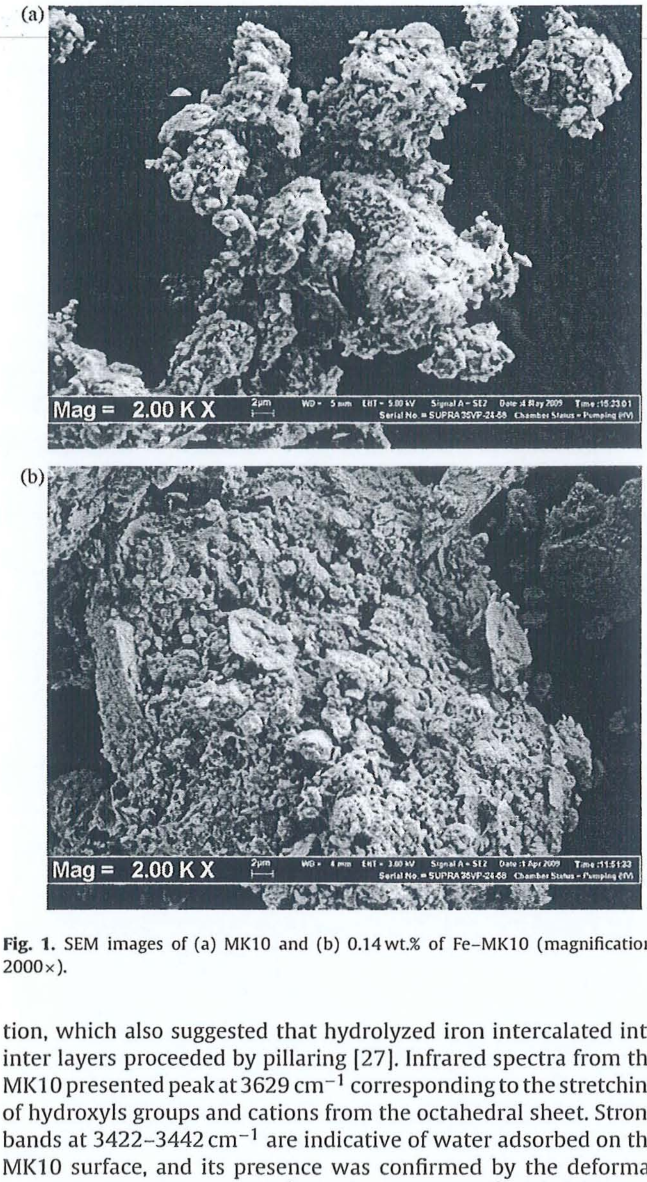

Fig. 1. SEM images of (a) MK10 and (b) 0.14 wt.% of Fe-MK10 (magnification: 2000×).

tion, which also suggested that hydrolyzed iron intercalated into inter layers proceeded by pillaring [27]. Infrared spectra from the MK10 presented peak at 3629 cm^{-1} corresponding to the stretching of hydroxyls groups and cations from the octahedral sheet. Strong bands at 3422–3442 cm^{-1} are indicative of water adsorbed on the MK10 surface, and its presence was confirmed by the deformation band at 1637–1635 cm^{-1}. Bands at 1055 cm^{-1} and 1047 cm^{-1} can be assigned to stretching vibrations of silica–oxygen tetrahedrons as (Si–O–Si). The band at 470 cm^{-1} can be attributed to the bending (Si–O) and stretching (M–O) vibrations. The shift of band at 1047 cm^{-1} and disappear and/or decrease in the intensities of bands of deformation of Al_2OH at 800–900 cm^{-1} and 500–700 cm^{-1} (Si–O), (M–O) and Si–O–Al (octahedral Al) can be indirect evidence of the incorporation of Fe^{3+} into clay [28,29].

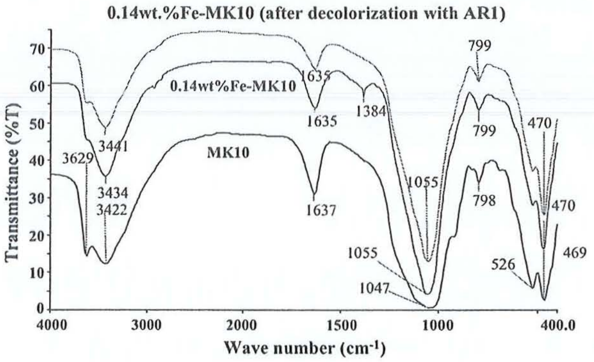

Fig. 2. FT-IR spectra of the samples.

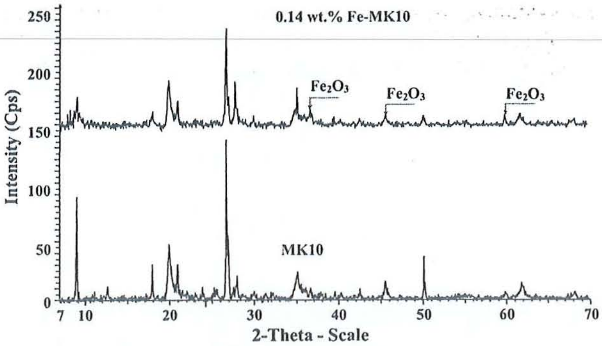

Fig. 3. XRD diffractograms of the samples.

BET surface area, pore volume and pore size of 0.14 wt.% Fe-MK10 are 185.434 $m^2\,g^{-1}$, 0.274 $cm^3\,g^{-1}$ and 59 Å, respectively.

Fig. 3 shows the XRD diffractograms of MK10 and impregnated MK10. It can be seen that the impregnated MK10 maintains the layered structure in crystalline form with sodium and quartz-rich elements, but with a remarkable loss of ordering if compared to the MK10 itself. This catalyst, once calcined at 500 °C, show a weak diffraction peaks at $2\theta = 9°$, 18° and 50°. On the other hand, it may be underlined that no peaks due to iron phases are observed in the diffractograms [30]. However, small peaks of anhydrous (Fe_2O_3) oxides were formed after calcinations of the impregnated MK10 by the removal of the organic moieties [31]. This component is indicative of the presence of iron in the impregnated catalyst.

3.2. *Role of catalyst support*

Before the study on parameters that influence the decolorization process, it is important to evaluate the AR1 decolorization process, i.e., if decolorization occurs through adsorption, through a catalytic reaction or through both processes. The first run was a blank, carried out to evaluate the ability of H_2O_2 or iron ion to decolorize AR1 in aqueous solutions without the addition of any heterogeneous catalyst. Fig. 4 shows the efficiency of AR1 decolorization due to hydrogen peroxide or iron ion is almost negligible (<4% within 150 min), and could be attributed to its low oxidation potential as compared to hydroxyl or perhydroxyl radicals [32]. To determine the influence of the adsorption processes, experiments without H_2O_2 were also carried out. Fig. 4 shows that MK10 as a catalyst support has a low adsorption capacity (6.2% decolorization of dye within 150 min of reaction).

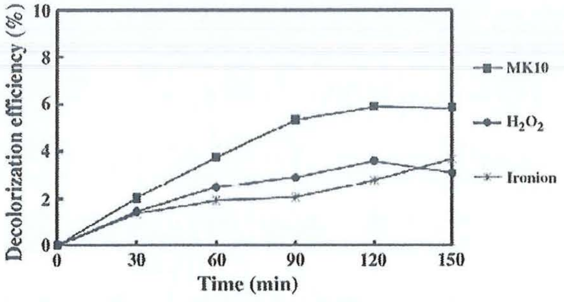

Fig. 4. Un-catalyzed AR1 dye solutions removal by H_2O_2 (4 mM), iron ion (0.05 mM) and adsorption on MK10 (2.0 g L^{-1}).

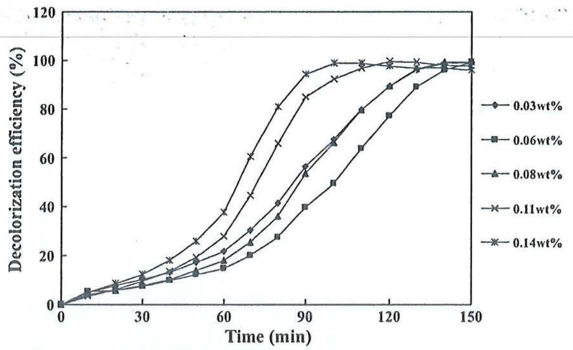

Fig. 5. Effect of iron loading on MK10 on the decolorization of AR1. *Reaction conditions*: initial concentration of AR1, $[AR1]_0 = 50\,mg\,L^{-1}$; initial concentration of hydrogen peroxide, $[H_2O_2]_0 = 4\,mM$; pH 2.5; dosage of catalyst = $2.0\,g\,L^{-1}$; temperature = 30 °C; and agitation speed = 130 rpm.

3.3. Effects of different parameters

Fig. 5 shows the effect of iron loading on MK10. The most fast decolorization efficiency was 0.14 wt.% of Fe^{3+} loading with a value of 99% observed within 150 min reaction. Hence, 0.14 wt.% of Fe^{3+} loading was selected to be the best loading assayed for maximum efficiency. It is important to remark that all decolorization curves in Fig. 5 show a sigmoidal profile, which is typical for autocatalytic or radical reactions. Basically two regions can be identified, the initial one representing the induction period, and the second one after the inflection point representing the steady state [31].

The influence of the catalyst dosage on decolorization efficiency against time is presented in Fig. 6. The efficiency of decolorization within 150 min was 99% with a dosage of $2\,g\,L^{-1}$ until $5\,g\,L^{-1}$ but the kinetics of decolorization was better with high concentration of catalyst. An increase of the concentration of catalyst will increase the amount of Fe ions involved in the process, which in turn increase the number of hydroxyl radical significantly.

The influence of initial pH of the dye solution on the Fe–MK10/H_2O_2 process efficiency was studied using seven solutions with initial pH of 1.5, 2.0, 2.5, 3.0, 3.5, 4.0 and 5.0 and without any modifications or control of pH during the process. Fig. 7 shows the decolorization of dye as a function of the initial pH of the solution at various reaction times. The results indicate that the decolorization of AR1 was significantly influenced by the solution pH and the best solution of pH assayed was observed at 2.5. A similar result was reported in literature [22].

Fig. 8 shows the decolorization of dye as a function of the H_2O_2 concentration of the solution at various reaction times and the results showed that 8 mM was the best concentration of H_2O_2 assayed when the initial concentration of AR1 was $50\,mg\,L^{-1}$ and the initial pH 2.50. The reaction went more slowly when the concentration was lower (4 mM) or higher (32 mM). At low concentration, H_2O_2 cannot generate enough $HO^{\bullet}$ radicals and the oxidation rate is logically slow. The increase of the oxidant concentration from 4 to 8 mM leads to an increase in the reaction rate, as expected, because more radicals will be formed. Nevertheless, for a very high H_2O_2 concentration (32 mM), the performance decreases.

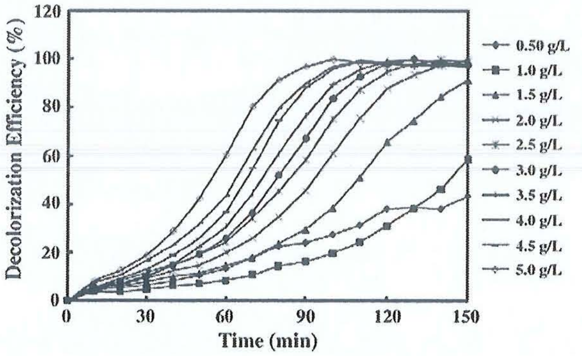

Fig. 6. Effect of dosage of catalyst on the decolorization of AR1. *Reaction condition*: initial concentration of AR1, $[AR1]_0 = 50\,mg\,L^{-1}$; initial concentration of hydrogen peroxide, $[H_2O_2]_0 = 4\,mM$; pH 2.5; 0.14 wt.% of iron ions in catalyst; temperature = 30 °C; and agitation speed = 130.

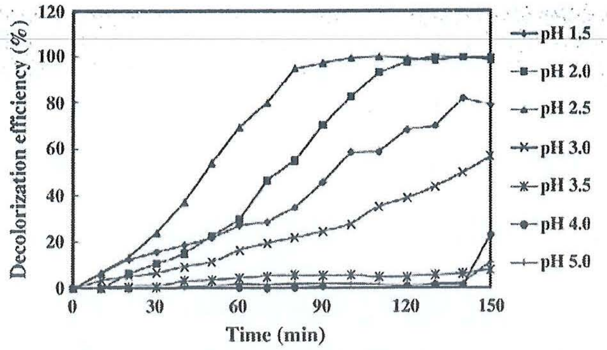

Fig. 7. Effect of pH on the decolorization of AR1. *Reaction conditions*: initial concentration of AR1, $[AR1]_0 = 50\,mg\,L^{-1}$; initial concentration of hydrogen peroxide, $[H_2O_2]_0 = 4\,mM$; dosage of catalyst = $5.0\,g\,L^{-1}$ with 0.14 wt.% of iron ions in catalyst; temperature = 30 °C; and agitation speed = 130 rpm.

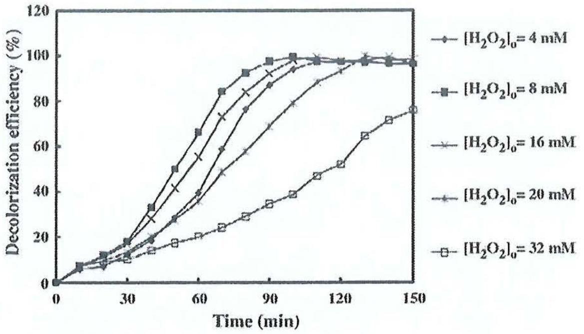

Fig. 8. Effect of initial concentration of H_2O_2 on the decolorization of AR1. *Reaction conditions*: initial concentration of AR1, $[AR1]_0 = 50\,mg\,L^{-1}$; dosage of catalyst = $5.0\,g\,L^{-1}$ with 0.14 wt.% of iron ions in catalyst; temperature = 30 °C; agitation speed = 130 rpm; and pH 2.5.

Fig. 9 shows the effect of initial concentration of AR1 on the decolorization efficiency of AR1. It was observed that the higher

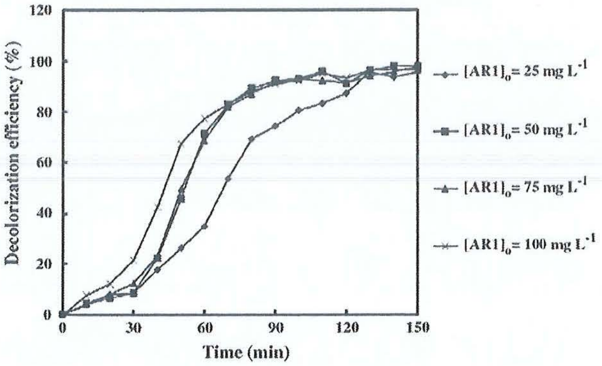

Fig. 9. Effect of AR1initial concentration on the decolorization of AR1. *Reaction conditions*: initial concentration of hydrogen peroxide, $[H_2O_2]_0 = 16\,mM$; dosage of catalyst = $5.0\,g\,L^{-1}$ with 0.14 wt.% of iron ions in catalyst; temperature = 30 °C; agitation speed = 130 rpm; and pH 2.5.

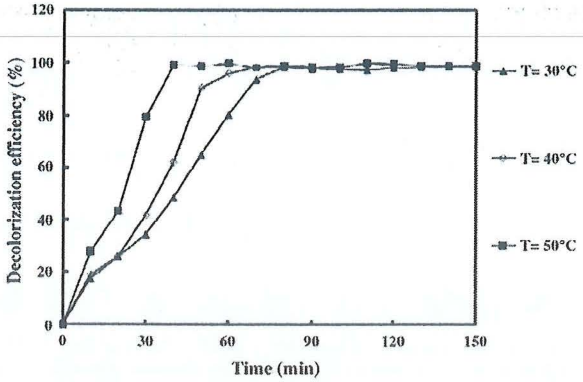

Fig. 10. Effect of temperature on the decolorization of AR1. *Reaction conditions*: initial concentration of AR1, $[AR1]_0 = 50\,mg\,L^{-1}$; initial concentration of hydrogen peroxide, $[H_2O_2]_0 = 16\,mM$; dosage of catalyst = $5.0\,g\,L^{-1}$ with 0.14 wt.% of iron ions in catalyst; agitation speed = 130 rpm; and pH 2.5.

the concentration of dye, the shorter is the reaction period needed to decolorize AR1 completely. As the lifetime of hydroxyl radicals is very short (only a few nanoseconds), they can only react where they are formed. Increasing the quantity of AR1 molecules per volume unit logically enhances the probability of collision between organic matter and oxidizing species, leading to an increase in the degradation efficiency [32].

The results obtained for the AR1 decolorization at three different temperatures (30 °C, 40 °C and 50 °C) are shown in Fig. 10. The results show clearly that the reaction rate increases with increase in temperature. This is because higher temperature increased the reaction rate between H_2O_2 and any form of ferrous/ferric ion, thus increasing the rate of generation of oxidizing species such as $^{\bullet}OH$ radical or high-valence iron species. Similar results have been reported [33] where similar performances were achieved at higher temperatures due to the accelerated decomposition of H_2O_2 into oxygen and water.

3.4. Spectral changes of AR1 during decolorization process

The changes in the absorption spectra of AR1 solution during the decolorization process at different reaction times are shown in Fig. 11. As can be seen from the spectra, before the treatment, the UV–vis spectrum of AR1 was characterized by one main band in the visible region, with its maximum absorption at 532 nm, and by two bands in the ultraviolet region located at 322 nm and 354 nm. Different structural units and groups in the dye molecules have different absorbance peaks, the main conjugates of AR1 include azo linkage (–N=N–), benzene and naphthalene ring. The chromophore containing azo linkage has absorption in the visible region, while benzene and naphthalene ring have it in the ultraviolet region, and naphthalene ring's absorption wavelength is higher than that of the benzene ring [33]. It was clearly observed that the absorption peak at 532 nm diminished very fast and almost completely disappeared under 150 min of reaction. This indicated a rapid decolorization of AR1, a complete decolorization of $50\,mg\,L^{-1}$ AR1 can be achieved in 150 min in the presence of 16 mM H_2O_2 and $5.0\,g\,L^{-1}$ of catalyst. The ultraviolet band at 322 nm and 354 nm was also observed to gradually diminish but at a lower rate than that of visible band, which indicated the destruction of the benzene and naphthalene rings. Therefore, $^{\bullet}OH$ radical first attacks azo groups and opens –N=N– bonds, destructing the long conjugated π systems and consequently causing decolorization [34].

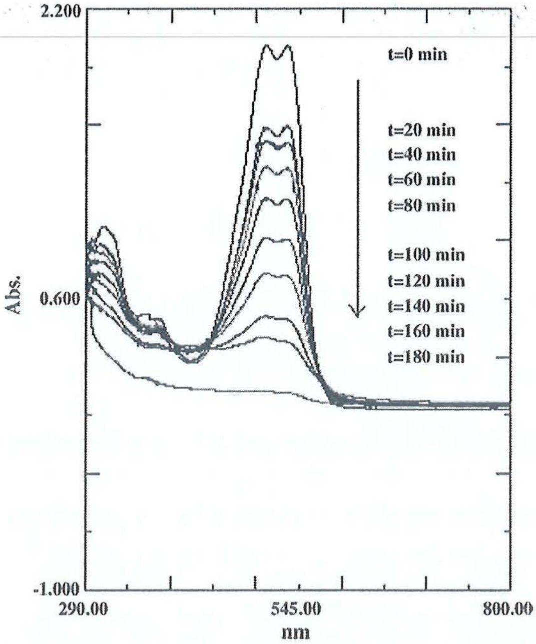

Fig. 11. Absorbance spectra. *Reaction conditions*: initial concentration of AR1, $[AR1]_0 = 50\,mg\,L^{-1}$; initial concentration of hydrogen peroxide, $[H_2O_2]_0 = 16\,mM$, dosage of catalyst = $5.0\,g\,L^{-1}$ with 0.14 wt.% of iron ions in catalyst, agitation speed = 130 rpm; temperature = 30 °C; and pH 2.5.

3.5. Catalyst stability and leaching test

Fig. 12 shows the performance reached in terms of AR1 decolorization in four consecutive cycles. To recover the catalyst, the final effluent was filtered. After the first cycle, and in order to check if the leached iron was responsible for the catalytic activity, both AR1 and H_2O_2 were added to the solution in the same concentrations at the beginning of the experiment. Fig. 12 shows that in these conditions AR1 decolorization is only a very small fraction of that recorded in the presence of the Fe-MK10. Although a homogeneous catalytic contribution also exists, as a consequence of the iron leaching, the process is essentially heterogeneous. For subsequent cycles, the filtered catalyst was dried overnight between consecutive runs. Even though slight activity decay was observed, this might be due to the iron loss, AR1 decolorization decreases from 99 to 64% in fourth cycles, i.e., 12 h of operation. Other authors reported similar results, but they attributed the loss of activity to poisoning of the active catalytic sites due to adsorbed organic species [30]. Leaching tests

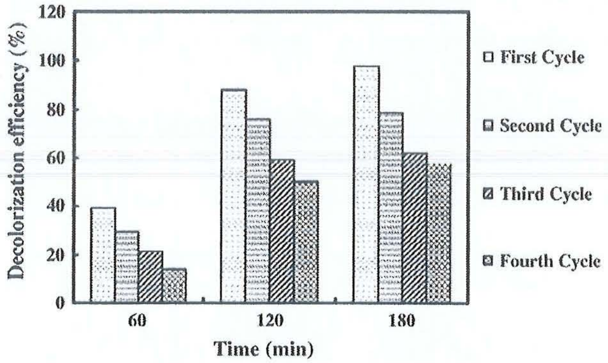

Fig. 12. Reusability test of the Fe-MK10. *Reaction conditions*: initial concentration of AR1, $[AR1]_0 = 50\,mg\,L^{-1}$; initial concentration of hydrogen peroxide, $[H_2O_2]_0 = 16\,mM$; dosage of catalyst = $5.0\,g\,L^{-1}$ with 0.14 wt.% of iron ions in catalyst; agitation speed = 130 rpm; temperature = 30 °C; and pH 2.5.

were carried out to check the potential of leaching of iron ions from MK10. In all of the experiments, concentration of the Fe ion was below 5 mg L^{-1} and this conforms to the standard of Environmental Quality (Sewage and Industrial Effluents) Regulation 1979.

4. Conclusion

In this study it was demonstrated that the Fe–MK10 obtained through impregnation method served as a reactive Fenton-like heterogeneous catalyst for the decolorization of AR1. Under the best conditions (0.14 wt.% Fe–MK10, 5.0 g L^{-1} dosage of catalyst, pH 2.5, 16 mM of H_2O_2), 99% decolorization of solution containing 50 mg L^{-1} AR1 could be removed within 150 min in a batch process. The Fe–MK10 catalyst exhibit not only good catalytic activity but also reasonable small iron leaching (below the Environmental Quality (Sewage and Industrial Effluents) Regulation 1979 values), indicating that the active phases are strongly fixed to the support (possibly iron strongly bonded to the surface of MK10 or engaged in small oxide clusters dispersed in the solid, inside or outside the porosity). Consecutive reaction cycles carried out with this sample showed a minor deactivation, which is possibly due to some iron leaching, thus evidencing the possibility of being used in continuous processes.

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Fe-ball clay as effective heterogeneous Fenton type catalyst for the decolorization of Reactive Blue 4

H. Hassan, B. H. Hameed*

School of Chemical Engineering, Engineering Campus,
University of Science Malaysia, 14300 Nibong Tebal, Penang, Malaysia
Corresponding author. e-mail: chbassim@eng.usm.my (B. H. Hameed)
Fax: + 6045941013

Abstract

Heterogeneous Fenton type processes using Fe-ball clay (Fe-BC) catalyst were investigated for the decolorization of model pollutant, Reactive Blue 4 (RB4) in water. Experimental results demonstrated that the RB4 decolorization increased by increasing Fe-BC dosage and initial H_2O_2 concentration, and by decreasing pH, respectively. Comparative studies indicated that RB4 decolorization were much higher in the presence of Fe-BC and H_2O_2 than those in presence of H_2O_2, raw natural clay or Fe-BC only and raw BC and H_2O_2 jointly. Adsorption and heterogeneous Fenton reaction were proposed as mechanism that governed the fast decolorization of RB4. The optimal reacting conditions were found to be 0.80 wt.% iron (II) oxide loading on BC, dosage of catalyst = 5.0 g L^{-1}, initial pH = 3.0, $[H_2O_2]_0$ = 8 mM, $[RB4]_0$ = 25 mg L^{-1} at temperature 30 °C. Under optimal conditions, 99% decolorization efficiency of RB4 was achieved within 140 min reaction time.

Keywords: Fe-ball clay, Reactive Blue 4, Heterogeneous Fenton, Decolorization