

SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO	
RAD: 13-264131- -2	FECHA: 2014-12-04 17:35:46
DEP: 2020 DIRECCION DE NUEVAS CREACIONES	EVE: 1 REGISTRO/DEPOSITO/CONCESION/DEPOSITO
TRA: 2 PATENTES DE INVENCION	FOLIOS: 8
ACT: 519 PRESENTACION	

DIRECCIÓN DE NUEVAS CREACIONES

2020
Bogotá, D.C.,

Abogado(a)/Señor(a)
JUAN SEBASTIAN CARO GARCIA
MOISES CAMILO CARO GARCIA

Asunto: Radicación: 13-264131- -2
 Trámite: 2
 Evento: 1
 Actuación: 519
 Oficio: 15161
 Folios: 8

Patente de Invención	X			Patente de Modelo de Utilidad	
Vía Nacional	X				
Vía PCT (Fase Nacional)		Capítulo I		Capítulo II	
No. Solicitud Internacional					
Fecha de Presentación Internacional					

Como resultado del Examen de Fondo realizado, con fundamento en el Artículo 45 de la Decisión 486 de la Comisión de la Comunidad Andina, se comunica:

1. Documentos estudiados

Descripción:	Radicado No. 13-264131-00000-0000	08/Noviembre/2013
Reivindicaciones:	Radicado No. 13-264131-00000-0000	08/Noviembre/2013

2. Objeto de la invención

De acuerdo con lo establecido en el numeral 1.2.2.2 del capítulo primero del Título 10 de la Circular Única para efectos del examen de patentabilidad, se tendrá en cuenta la tasa pagada por el solicitante al momento de comenzar el examen para las reivindicaciones adicionales; esto es que cuando la solicitud contenga más de diez (10) reivindicaciones y no se haya pagado la tasa complementaria, sólo se estudiarán las cubiertas por la tasa pagada. En el presente caso se tiene en cuenta la totalidad del capítulo reivindicatorio.

Título de la solicitud: “Composición cosmética con activos de origen natural para tinturar fibras queratínicas”.

El problema planteado en esta solicitud consiste en la necesidad de suministrar una composición cosmética para la tinción permanente de las fibras queratínicas más segura y amigable con el usuario y con el medio ambiente.

Para resolver este problema técnico la solicitud en estudio proporciona una composición cosmética para tinturar fibras queratínicas que comprende:

- a) Un agente de acoplamiento de origen natural;
- b) Un intermediario de reacción;
- c) Un alcalinizante; y

Un vehículo cosméticamente aceptable.

El objeto de la presente solicitud se relaciona con la clasificación internacional de patentes (CIP): A61K8/30; A61K8/33; A61K8/40; A61Q5/10

Reivindicaciones (Art 30 D 486, Art 22 PCT)

La reivindicación 1 no es concisa porque reclama una composición donde sus componentes se identifican por su función (un agente de acoplamiento, un intermediario de reacción, un agente alcalinizante y un vehículo) y no por su nombre químico, lo cual no permite establecer con precisión el alcance de la solicitud. Se recuerda a los solicitantes que una composición se debe caracterizar por sus componentes y las proporciones de los mismos en la composición. Se sugiere modificar la reivindicación de tal manera que se identifiquen claramente las posibilidades de agentes de acoplamiento, intermediarios de reacción y agentes alcalinizantes, de acuerdo a lo efectivamente soportado en la descripción.

La reivindicación 1 no es concisa porque no identifica claramente las posibilidades de alcaloides, taninos, xantinas, isotianinas y antocianinas incluidas en el alcance de la solicitud de acuerdo a lo soportado en la descripción. Se sugiere identificar de forma clara cada una de las posibilidades de agentes de acoplamiento de origen natural de tal forma que sea posible determinar el alcance de la solicitud.

Las reivindicaciones 2 y 3 no se encuentran enteramente soportadas en la descripción porque la solicitud solo presenta composiciones que comprenden salvigenina y quinina como agentes de acoplamiento. Adicionalmente, la reivindicación 2 no es concisa porque establece que el agente de acoplamiento pertenece a la familia de los alcaloides, taninos, xantinas, isotianinas, antocianinas, sin establecer cuáles son las posibilidades para cada uno de éstos de acuerdo a lo soportado en la descripción. b

Las reivindicaciones 5 y 6 no se encuentran totalmente soportadas en la descripción porque no se encuentra en la descripción alguna composición que comprenda agentes de acoplamiento sintético y que pueda ser tomada como soporte de la materia reclamada.

La reivindicación 12 no es concisa porque caracteriza los componentes adicionales de la composición por su función y no por su nombre químico, lo que no permita determinar claramente el alcance de la solicitud. Se recuerda al solicitante que una composición debe ser caracterizada por sus componentes y las proporciones de los mismos. Adicionalmente, no se encuentra soporte descriptivo para la composición reclamada.

La reivindicación 13 no es concisa porque no establece las posibilidades de agentes oxidantes de acuerdo a lo soportado en la descripción. La descripción solo soporta el uso de peróxido de hidrógeno.

La reivindicación 14 no se encuentra enteramente soportada en la descripción porque no se encuentra en la descripción ninguna composición que comprenda peróxido de úrea, bromatos de metales alcalinos, perboratos, persulfatos, perácidos, peroxidasas, oxigenasas y lacasas.

La reivindicación 17 no es concisa, ni se encuentra totalmente soportada en la descripción porque se caracterizan los componentes por su función y no por su nombre químico, y adicionalmente, tampoco se establece claramente cuál es la composición del kit, es decir no establece la composición de las partes del kit y las cantidades de cada componente. Por otro lado, no se encuentra en la descripción ningún kit que comprenda la composición de las reivindicaciones 1 – 16, agentes oxidantes, agentes cuaternizados, agentes hidratantes, hidrolizados de elastina y queratina, agentes reparadores y agentes humectantes, por lo tanto el kit reclamado no cuenta con soporte descriptivo. No es posible efectuar un análisis de patentabilidad para el kit reclamado debido a que dicho kit se refiere a una agregación de componentes indeterminados y en una forma indeterminada ya que no es claro si se refiere a la combinación de una, dos, tres o varias composiciones, o como se conforma el mencionado kit, lo cual impide adelantar un estudio de patentabilidad al no poder determinar de forma clara el objeto de la reivindicación.

3. Determinación del Estado de la Técnica

El estado de la técnica se determinó con base en la fecha de presentación de la solicitud de patente nacional: Noviembre 8 de 2013, y se encontraron los siguientes documentos que anticipan el objeto de esta solicitud:

Ítem	Documento	Título	Fecha de Publicación
D1	WO2011076647	Inverse emulsion for treating the hair comprising a particular fatty substance and an alkaline agent	30/Junio/2011
D2	EP2301520	Oxidative dye	30/Marzo/2011

D1 http://worldwide.espacenet.com/publicationDetails/biblio?CC=WO&NR=2011076647A2&KC=A2&FT=D&ND=3&date=20110630&DB=EPODOC&locale=en_EP

Divulga una composición en emulsión para el cabello caracterizada porque comprende: (a) al menos 35% en peso de una o más sustancias grasas seleccionadas de hidrocarburos líquidos, ésteres grasos líquidos, siliconas líquidas, y alcoholes grasos insaturados líquidos; y (b) uno o más agentes basificantes (resumen). El documento también reclama un dispositivo que comprende dos compartimentos, el cual comprende por un lado: a) una emulsión inversa que comprende: al menos 35% de sustancias grasas y uno o más agentes basificantes para el tratamiento del cabello; y por otro lado b) una composición conteniendo uno o más agentes oxidantes (Pág. 2, lín. 23). El documento menciona que la composición comprende tintes oxidantes generalmente seleccionados de bases oxidantes y agentes de acoplamiento (Pág. 2, lín. 25), entre las bases de oxidación menciona para-fenilendiamina, para-aminofenoles, derivados de pirazol, 4,5-diamino-1-(β-hidroxietil)pirazol, entre otros (Pág. 13, lín. 28, 39 y pág. 14 lín. 34), y señala también que la composición puede comprender colorantes directos como lawsona, juglona, alizarina, purpurina, el ácido carmínico, ácido quermésico, purpurogalina, protocatechaldehído, el índigo, la isatina, la curcumina, espinulosina, apigenidina, hematoxilina, hemateína, brasilina, brasileína y orceínas (Pág. 20, lín. 3 – 9) o por ejemplo indigoid (Pág. 16, lín. 34). Además, la anterioridad menciona que se pueden usar agentes de acoplamiento adicionales como α-naftol (pág. 16, lín 5) y 2-amino-3-hidroxipiridina (Pág. 16, lín. 6 y 7).

D2 <http://www.google.com/patents/EP2301520A2?cl=en>

Divulga composiciones para el teñido oxidante de fibras de queratina, en particular cabello humano, que comprende (Párr. [0009]): un colorante natural obtenido de diferentes partes de plantas (Párr. [0082]) tal como salvigenina (Pág. 15, lín. 40 – 50), un componente desarrollador tal como p-fenilendiaminas (Párr. [0045]) y p-aminofenoles (Párr. [0049]), medio alcalino usando trietanolamina (Párr. [0035]) o una combinación de amoniaco y trietanolamina (Párr. [0037]) y un vehículo cosméticamente aceptable (Párr. [0009]).

4. Examen de Patentabilidad (Art 14 D486)

Novedad (Art 16 D486)

La reivindicación 1 consiste en una composición cosmética para tinturar fibras queratínicas que comprende:

- a) Un agente de acoplamiento de origen natural;
- b) Un intermediario de reacción;
- c) Un alcalinizante; y

Un vehículo cosméticamente aceptable.

Comparación de las características técnicas **esenciales**, con las del estado de la técnica:

Características esenciales	D1	D2
Una composición cosmética para tinturar fibras queratínicas que comprende:	Emulsión para tratar el cabello que comprende (resumen):	Composiciones para el teñido oxidante de fibras de queratina, en particular cabello humano, que comprende (Párr. [0009]):
a) Un agente de acoplamiento de origen natural;	Entre los colorantes directos naturales que se pueden utilizar según la invención, puede hacerse mención de lawsona, juglona, alizarina, purpurina, el ácido carmínico, ácido quermésico, purpurogalina, protocatecaldehído, el índigo, la isatina, la curcumina, espinulosina, apigenidina, hematoxilina, hemateína, brasilina, brasileína y orceínas (Pág. 20, líns. 3 – 9) por ejemplo indigoid (Pág. 16, lín. 34). También menciona que se pueden usar agentes de acoplamiento adicionales como α-naftol (pág. 16, lín 5), 2-amino-3-hidroxipiridina (Pág. 16, líns. 6 y 7).	La composición comprende un colorante natural obtenido de diferentes partes de plantas (Párr. [0082]) tal como salvigenina (Pág. 15, líns. 40 – 50)
b) Un intermediario de reacción;	Bases de oxidación como: para-aminofenoles (Pág. 13, lín. 28 y 29), derivados de pirazol (Pág. 13, lín. 39), para-fenilendiaminas (Pág. 13, líns. 11 – 19)	Componente desarrollador tal como p-fenilendiaminas (Párr. [0045]) y p-aminofenoles (Párr. [0049])
c) Un alcalinizante; y	La emulsión comprende un agente basificante como amoniaco, hidróxido de sodio, hidróxido de potasio (Pág. 9, líns. 33 – 36) y alcanolaminas como trietanolamina (Pág. 10, lín. 24).	Medio alcalino usando trietanolamina (Párr. [0035]) o una combinación de amoniaco y trietanolamina (Párr. [0037])
Un vehículo cosméticamente aceptable.	Un vehículo cosméticamente aceptable (Ejs. 1 – 8)	Un vehículo cosméticamente aceptable (Párr. [0009])

Las características **esenciales** de la composición de la reivindicación 1 habían sido divulgadas previamente en el documento D1, el cual enseña una composición en emulsión para el cabello caracterizada porque comprende: (a) al menos 35% en peso de una o más sustancias grasas seleccionadas de hidrocarburos líquidos, ésteres grasos líquidos, siliconas líquidas, y alcoholes grasos insaturados líquidos; y (b) uno o más agentes basificantes (resumen). El documento también reclama un dispositivo que comprende dos compartimentos, el cual comprende por un lado: a) una emulsión

inversa que comprende: al menos 35% de sustancias grasas y uno o más agentes basificantes para el tratamiento del cabello; y por otro lado b) una composición conteniendo uno o más agentes oxidantes (Pág. 2, lín. 23). El documento menciona que la composición comprende tintes oxidantes generalmente seleccionados de bases oxidantes y agentes de acoplamiento (Pág. 2, lín. 25), entre las bases de oxidación menciona para-fenilendiamina, para-aminofenoles, derivados de pirazol, 4,5-diamino-1-(β -hidroxietil)pirazol, entre otros (Pág. 13, lín. 28, 39 y pág. 14 lín. 34), y señala también que la composición puede comprender colorantes directos como lawsona, juglona, alizarina, purpurina, el ácido carmínico, ácido quermésico, purpurogalina, protocatechaldehído, el índigo, la isatina, la curcumina, espinulosina, apigenidina, hematoxilina, hemateína, brasilina, brasileína y orceínas (Pág. 20, líns. 3 – 9) o por ejemplo indigoid (Pág. 16, lín. 34). Además, la anterioridad menciona que se pueden usar agentes de acoplamiento adicionales como α -naftol (pág. 16, lín 5) y 2-amino-3-hidroxipiridina (Pág. 16, líns. 6 y 7).

Las características **esenciales** de la composición de la reivindicación 1 habían sido divulgadas previamente en el documento D2, el cual enseña composiciones para el teñido oxidante de fibras de queratina, en particular cabello humano, que comprende (Párr. [0009]): un colorante natural obtenido de diferentes partes de plantas (Párr. [0082]) tal como salvigenina (Pág. 15, líns. 40 – 50), un componente desarrollador tal como p-fenilendiaminas (Párr. [0045]) y p-aminofenoles (Párr. [0049]), medio alcalino usando trietanolamina (Párr. [0035]) o una combinación de amoníaco y trietanolamina (Párr. [0037]) y un vehículo cosméticamente aceptable (Párr. [0009]).

En consecuencia, la reivindicación 1 carece de novedad, según lo divulgado en los documentos D1 y D2 de forma independiente.

Las reivindicaciones dependientes 2 – 16 no mencionan alguna característica que haga nueva a la composición de la reivindicación 1, por lo cual se considera que no son nuevas.

Nivel Inventivo (Art18 D486)

La reivindicación 1 consiste en una composición cosmética para tinturar fibras queratínicas que comprende:

- a) Un agente de acoplamiento de origen natural;
- b) Un intermediario de reacción;
- c) Un alcalinizante; y

Un vehículo cosméticamente aceptable.

Comparación de las características técnicas **esenciales**, con las del Estado de la Técnica:

Características esenciales	D1	D2
Una composición cosmética para tinturar fibras queratínicas que comprende:	Emulsión para tratar el cabello que comprende (resumen):	Composiciones para el teñido oxidante de fibras de queratina, en particular cabello humano, que comprende (Párr. [0009]):
a) Un agente de acoplamiento de origen natural;	Entre los colorantes directos naturales que se pueden utilizar según la invención, puede hacerse mención de lawsona, juglona, alizarina, purpurina, el ácido carmínico, ácido quermésico, purpurogalina, protocatechaldehído, el índigo, la isatina, la curcumina, espinulosina, apigenidina, hematoxilina, hemateína,	La composición comprende un colorante natural obtenido de diferentes partes de plantas (Párr. [0082]) tal como salvigenina (Pág. 15, líns. 40 – 50)

Características esenciales	D1	D2
	brasilina, brasileína y orceínas (Pág. 20, líns. 3 – 9) por ejemplo indigoid (Pág. 16, lín. 34). También menciona que se pueden usar agentes de acoplamiento adicionales como α -naftol (pág. 16, lín 5), 2-amino-3-hidroxipiridina (Pág. 16, líns. 6 y 7).	
b) Un intermediario de reacción;	Bases de oxidación como: para-aminofenoles (Pág. 13, lín. 28 y 29), derivados de pirazol (Pág. 13, lín. 39), para-fenilendiaminas (Pág. 13, líns. 11 – 19)	Componente desarrollador tal como p-fenilendiaminas (Párr. [0045]) y p-aminofenoles (Párr. [0049])
d) Un alcalinizante; y	La emulsión comprende un agente basificante como amoniaco, hidróxido de sodio, hidróxido de potasio (Pág. 9, líns. 33 – 36) y alcanolaminas como trietanolamina (Pág. 10, lín. 24).	Medio alcalino usando trietanolamina (Párr. [0035]) o una combinación de amoniaco y trietanolamina (Párr. [0037])
Un vehículo cosméticamente aceptable.	Un vehículo cosméticamente aceptable (Ejs. 1 – 8)	Un vehículo cosméticamente aceptable (Párr. [0009])

Los documentos D1 y D2 se consideran el estado de la técnica cercano a la invención definida en la reivindicación 1 porque:

El documento D1 enseña una composición en emulsión para el cabello caracterizada porque comprende: (a) al menos 35% en peso de una o más sustancias grasas seleccionadas de hidrocarburos líquidos, ésteres grasos líquidos, siliconas líquidas, y alcoholes grasos insaturados líquidos; y (b) uno o más agentes basificantes (resumen). El documento también reclama un dispositivo que comprende dos compartimentos, el cual comprende por un lado: a) una emulsión inversa que comprende: al menos 35% de sustancias grasas y uno o más agentes basificantes para el tratamiento del cabello; y por otro lado b) una composición conteniendo uno o más agentes oxidantes (Pág. 2, lín. 23). El documento menciona que la composición comprende tintes oxidantes generalmente seleccionados de bases oxidantes y agentes de acoplamiento (Pág. 2, lín. 25), entre las bases de oxidación menciona para-fenilendiamina, para-aminofenoles, derivados de pirazol, 4,5-diamino-1-(β -hidroxietil)pirazol, entre otros (Pág. 13, lín. 28, 39 y pág. 14 lín. 34), y señala también que la composición puede comprender colorantes directos como lawsona, juglona, alizarina, purpurina, el ácido carmínico, ácido quermésico, purpurogalina, protocatechaldehído, el índigo, la isatina, la curcumina, espinulosina, apigenidina, hematoxilina, hemateína, brasilina, brasileína y orceínas (Pág. 20, líns. 3 – 9) o por ejemplo indigoid (Pág. 16, lín. 34). Además, la anterioridad menciona que se pueden usar agentes de acoplamiento adicionales como α -naftol (pág. 16, lín 5) y 2-amino-3-hidroxipiridina (Pág. 16, líns. 6 y 7).

El documento D2 enseña composiciones para el teñido oxidante de fibras de queratina, en particular cabello humano, que comprende (Párr. [0009]): un colorante natural obtenido de diferentes partes de plantas (Párr. [0082]) tal como salvigenina (Pág. 15, líns. 40 – 50), un componente desarrollador tal como p-fenilendiaminas (Párr. [0045]) y p-aminofenoles (Párr. [0049]), medio alcalino usando trietanolamina (Párr. [0035]) o una combinación de amoniaco y trietanolamina (Párr. [0037]) y un vehículo cosméticamente aceptable (Párr. [0009]).

La diferencia entre la invención, definida en la reivindicación 1 y las composiciones divulgadas en el documento D1 consiste en que el documento D1 no divulga una composición específica que comprenda un agente de acoplamiento de origen natural.

No se evidencia alguna ventaja o efecto superior de la composición reclamada frente a la composición divulgada en el documento D1 porque la anterioridad sugiere el mismo tipo de componentes de las composiciones reclamadas y no se encuentra en la

descripción de la solicitud algún ensayo que demuestre alguna ventaja de las composiciones específicas de la presente solicitud frente a las divulgadas previamente.

Por lo tanto, el problema técnico objetivo que pretende resolver esta invención se puede formular así: “cómo modificar las composiciones divulgadas en el documento D1 para obtener composiciones alternativas”.

Sin embargo, el documento D2 divulga composiciones donde un colorante natural siempre es incluido y las cuales mejoran el cuidado del cabello (Párrs. [007] y [009]).

En consecuencia, la persona del oficio normalmente versada en la materia, que conoce la información divulgada en el documento D2, el cual sugiere el uso de colorantes naturales (dentro de los colorantes naturales es conocido ampliamente el uso de la quinina¹), se vería motivada a incluir dichos colorantes en las composiciones divulgadas en el documento D1 (que comprende los componentes de uso común en éste tipo de composiciones) con la expectativa razonable de encontrar composiciones para teñir fibras queratínicas mejorando el cuidado del cabello.

Conclusión:

La reivindicación 1 no cumple el requisito de novedad (Art. 16), y tampoco cumple con el requisito de nivel inventivo (Art. 18).

5. Conclusión

Los requisitos de Patentabilidad de la presente Solicitud están afectados así:

Ítem	Documento	Reivindicaciones afectadas	Requisito que afecta
D1	WO2011076647	1 – 17	Novedad y Nivel Inventivo
D2	EP2301520	1 – 17	Novedad y Nivel Inventivo

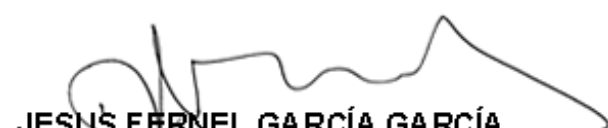
¹ <http://pr.hec.gov.pk/Thesis/996S.pdf> (Pág. 5, tercer Párr.)

En cumplimiento del artículo 45 de la Decisión 486 de la Comisión de la Comunidad Andina, se le indica que debe dar respuesta dentro del término de sesenta (60) días contados a partir del día siguiente de la fecha de notificación de la presente comunicación. En caso de no dar respuesta al presente requerimiento, o si a pesar de la respuesta subsistieran los impedimentos para la concesión, se denegará la patente.

Se invita al solicitante se sirva indicar, si así lo considera, su renuncia al término faltante de sesenta (60) días para dar respuesta a este requerimiento y presentarla por escrito.

Finalmente, se le recuerda al solicitante que si como respuesta a este requerimiento llegara a modificar el capítulo reivindicatorio y éste contenga más de diez (10) reivindicaciones, no pagará la tasa de modificación voluntaria pero sí la correspondiente al pago por reivindicación adicional.

Notifíquese el presente oficio conforme a lo dispuesto en el numeral 5.2, literal e), del capítulo quinto del título primero de la Circular Única No. 10 de 2001.



JESÚS FERNEL GARCÍA GARCÍA
Director de Nuevas Creaciones (E)

El anterior requerimiento fue notificado por fijación en lista, de fecha 2014-12-09

Elaboró: Juanita Catalina Rico Valbuena
Revisó: Gloria Jacqueline Alfonso Roza

Degradation of Industrial Organic Compound - RB 19



By

Maria Siddique

SP05-R07-004

PhD Thesis

COMSATS Institute of Information Technology
Islamabad- Pakistan
March, 2011



COMSATS Institute of Information Technology

**Degradation of Industrial Organic Compound - RB
19**

A Thesis Presented to

COMSATS Institute of Information Technology, Abbottabad

In partial fulfillment
of the requirement for the degree of

**PhD
(Environmental Sciences)**

By

Maria Siddique

CIIT/SP05-R07-004/ATD

March, 2011

Degradation of Industrial Organic Compound - RB 19

A Post Graduate Thesis submitted to the Department of Environmental Sciences
as partial fulfillment of the requirement for the award of Degree of PhD.

Name	Registration Number
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Supervisor

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Lahore, Campus.
March, 2011

Final Approval

This thesis titled

Degradation of Industrial Organic Compound - RB 19

By

Maria Siddique

Has been approved

For the COMSATS Institute of Information Technology, Abbottabad

External Examiner: _____

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Dean: _____

Prof. Dr. Arshad Saleem Bhatti

Dean (Faculty of Sciences), Islamabad

Declaration

I Maria Siddique hereby declare that I have produced the work presented in this thesis, during the scheduled period of study. I also declare that I have not taken any material from any source except referred to wherever due. If a violation of HEC rules on research has occurred in this thesis, I shall be liable to punishable action under the plagiarism rules of the HEC.

Date: _____

Signature of the student:

(Maria Siddique)
(CIIT/SP05-R07-004/ATD)

Certificate

It is certified that Miss. Maria Siddique has carried out all the work related to this thesis under my supervision at the Department of Environmental Sciences, CIIT Abbottabad.

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Submitted through:

Prof. Dr. Arshid Pervez
Head, Department of Environmental Sciences
CIIT, Abbottabad

Prof. Dr. Ishtiaq Jadoon
Chairman, Department of Environmental Sciences
CIIT, Abbottabad

***DEDICATED
TO
MY PARENTS***

For their endless love and support

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Maria Siddique

ABSTRACT

DEGRADATION OF INDUSTRIAL ORGANIC COMPOUND

- RB 19

Reactive dyes are the largest group of dyes used in textile industry and difficult to eliminate by conventional wastewater treatment plants. Different kinds of physico-chemical processes are being used for the degradation of reactive dyes. These techniques were used to decolorize and degrade dyes. Unfortunately, most of them were frequently plagued mainly due to process inefficiencies and persistence in nature. The textile effluent containing reactive dyes are potentially toxic and mutagenic compounds. Therefore, in the present study different techniques for dye degradation and decolouration were studied. The techniques used were electrochemical, sono-electrochemical, thermal pressure hydrolysis, photocatalysis, and sono-photocatalysis. In each method, effects of different operational parameters were investigated on dye degradation. The results demonstrated that sonoelectrochemical degradation was three times more effective than the individual effects of ultrasonic and electrochemical treatment. In hydrolysis process it has been found that hydrolysis of RB 19 was enhanced at high temperature (120 °C) and pressure (2 atm) as compared to normal conditions of temperature and pressure. Further enhancement in dye degradation was observed when optimum amount of hydrogen peroxide oxidant was used at high temperature and pressure. In sonophotocatalysis process the rate of RB 19 degradation under UV light and TiO₂ catalyst was found to be maximum under acidic conditions with 300 mgL⁻¹ TiO₂ and 100 mgL⁻¹ dye concentration. The further increase in the degradation of RB 19 was achieved by combining photocatalysis and ultrasonic process. The dye degradation mechanism for different techniques resulted in the formation of small molecular weight products e.g. acetic acid, benzoic acid, oxalic acid, etc. All these techniques were found to follow first order reaction with successful reduction in half life. It is concluded that sonoelectrochemical degradation technique was found to be more efficient as compared to other treatment techniques in term of dye decolorization, degradation, reduction of TOC, half life and electrical energy consumption.

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LIST OF ABBREVIATIONS

AOPs	Advance oxidation processes
ANOVA	Analysis of variance
BOD	Biological oxygen demand
C.I	Color index
COD	Chemical oxygen demand
C ₀	Initial concentration
C _t	Concentration at time t
DC	Direct current
EC	Energy consumption
eV	Electron volt
GC-MS	Gas chromatography-mass spectrometry
H ₂ O ₂	Hydrogen peroxide
hν	Photon
IC	Inorganic carbon
k	Rate constant
KW h	Kilo watt hour
kHz	Kilo hertz
LC-MS	Liquid chromatography with MS
L	Liter
λ _{max}	Maximum absorption wavelength
mg	Milligram
Min	Minute
m/z	mass to charge ratio
·OH	Hydroxyl radical
P	Pressure
RB 19	Reactive blue 19 dye
R ²	Regression coefficient
T	Temperature
TC	Total carbon
TiO ₂	Titanium dioxide
TOC	Total organic carbon
SEF	Sonoelectrochemical Fenton process
UV	Ultraviolet light
UV-Vis	Ultraviolet-visible
US	Ultrasound

Chapter 1

Introduction

Water is one of the vital requirements for existence of life. Addition of some foreign material from different sources like agricultural and surface runoff, commercial and industrial effluents and chemical spills may lead to its contamination (Tariq et al. 2008). These effluents contain a wide variety of complex, biodegradable and non-biodegradable organics like, pesticides, herbicides and dyes (Ligrini et al. 1993) with concentration levels and types varying to a great extent (Alinsafi et al. 2007). Textile industry uses large amount of water for dyeing and preparing fabric, and is considered as major water consumer as well as the largest dye consumer sector. Effluents from textile industry contain large amount of dyestuff that is usually a complex organic compound and is used to impart desired color. A number of different industries e.g., pharmaceutical, plastics, leather, pulp/paper and food are using dyes. Dyes are classified into different categories including anthraquinone, azo, acidic, basic, reactive, direct, neutral and disperse dyes. Among these, the anthraquinone and azo dyes are most commonly used and more than 60% of them are reactive (Siddique et al. 2009). Textile industry is extensively using the reactive dyes, due to its strong covalent bonding between the fabric and reactive group in dye molecules. However, the low affinity of reactive dyes with fabric fibers is posing the main problem. Therefore, their concentrations in textile wastewater are significantly high and in dyeing process almost 15% of dye residues are going into effluents (Galindo et al. 2001). Large number of dyes and chemicals used are released directly in to receiving waters without much effective treatment. The dye discharge into the environment poses serious threat to sustainability of ecosystems because they are highly resistant to natural degradation. They are persistent to environment and prove to be toxic and mutagenic to aquatic life even at 5.2 mgL^{-1} of the dye concentrations (Weisburger, 2002; Nilratnisakorn et al. 2007; Siddique et al. 2009). Moreover, aquatic ecosystems can be disturbed by dyes due to hindrance in oxygen exchange and penetration of light into water bodies (Epolito et al. 2005). Further, the bioaccumulation of these dyes may also present a risk to aquatic life (Ozer et al. 2005; Khalaf, 2008).

Therefore, elimination of such dyes from textile effluents is of considerable interest and importance. Hence the textile effluents should be effectively treated before final disposal.

Here in the present study different techniques for Reactive Blue 19 dye (RB 19) degradation and decolorization were investigated. The techniques were electrochemical, sono-electrochemical, thermal pressure hydrolysis, photocatalytic, and sono-photocatalytic degradation. Operational parameters like pH, dye concentration, ultrasonic irradiation power, reaction time, temperature, pressure and impact of catalyst concentration were studied and optimized where possible. UV-Visible spectrophotometer, TOC analyzer and GC-MS were used for analysis of dyestuff.

1.1 Significance of the Study

The reactive dyes are commonly used in Pakistan. A number of techniques are being used with the addition of chemicals for the treatment of these dyes, creating more problems to the environment. Hence this study is beneficial for degrading the reactive dyes of textile effluents in order to remediate its adverse effects. The main significances of the research are:

1. The methods adapted for study are simple and safe.
2. The methods are cost effective.
3. The treated water can be discharged after the degradation of dye.

1.2 Objectives of the Study

1. To breakdown the environmentally persistent RB 19 by sono-electrochemical, thermal pressure hydrolysis and sono-photocatalysis techniques in to simpler compounds.
2. To determine the rate of reaction and chemical kinetics.
3. To determine the degraded products and reaction mechanism.

Chapter 2

Literature Review

Treatment of textile wastewaters is of great importance because of their lethal and aesthetic impacts on water channels. Although numerous investigations have been carried out to treat reactive dyes containing wastewaters by developing efficient treatment technologies. There is not even a single solution which is adequate for remediating the wide range of textile effluent. The government has been impelled by ecological and human health concerns to treat textile wastewater in order to reduce the color intensity and dyes concentrations. In spite of having knowledge about the problem, several textile industries are failed to effectively remove reactive dye compounds from their effluents (Lewis, 1999). Prior to the development of efficient effluent treatment technologies, it is very important to reduce the effluent discharge by improving the dye fiber bonding process.

2.1 Back Ground History of Dyes

Synthetic dyes were manufactured in 1856, by William Henry Perkin an English chemist. He did remarkable effort in the synthesis of quinine-a bluish substance known as aniline purple having excellent dyeing properties. In this way the fresh dyes started to come into the market. Further, up till to 19th century the dyes were obtained from natural resources for using. The organic dyes especially used in textiles are usually originated from plants, fungi and lichens and are aromatic in nature (Matsui et al. 1981; Babuna et al. 1998; Uygur and Kok, 1999; Georgiou et al. 2003; Yasar et al. 2006).

2.2 Dye Classification

Among all aromatic compounds, colored compounds absorb light with wavelengths only in the visible range (350-700 nm) in electromagnetic spectrum. Dyes have *chromophores* and *auxochromes*, former is delocalized electron system with double bonds in conjugation e.g. -C=O, -C=N-, -NO₂-, N=N-, -C=C-, quinoid rings and later is electron-leaving/giving component for increasing the chromophore color by changing electron system whole energy e.g. -OH, -COOH-, -NH₃, and SO₃H. Owing to the chemical structure and the presence of chromophore, dyes can be classified into 20-30 different groups and the most significant groups are azo, triarylmethane, phthalocyanine, and anthraquinone dyes. On applications basis, dyes are categorized

into different classes. But frequently used dyes in textile industry are acidic, basic, disperse, direct, mordant, sulfur, reactive, vat, and azoic dyes (Wilcock, 1992). The concentrations of these dyes discharged in the wastewater depend upon their ability to fix with the fabric. (Table 2.1). The chemical structures of these dyes are illustrated in Table 2.2 (Uygur, 1997).

Table 2.1: Concentrations of different Classes of dyes in Wastewaters

Dye	Waste dye (%)
Direct	10
Disperse	5
Basic	2
Acid	5
Reactive	30

Society of Dyers and Colorists developed the CI number i.e., *Color Index*, in 1924 for the classification of dyes. A color index number with five digits is allotted to dye compound on the basis of their chemical structure. The classification and the shade or hue of the dye is also given with the CI number. For example, CI Basic Violet 2 (CI 42520) is the violet dye color with basic type (Table 2.2) (Ganesh et al. 1994).

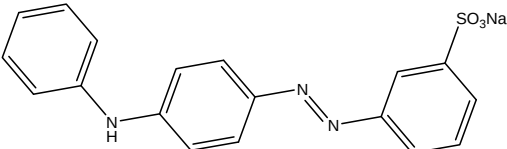
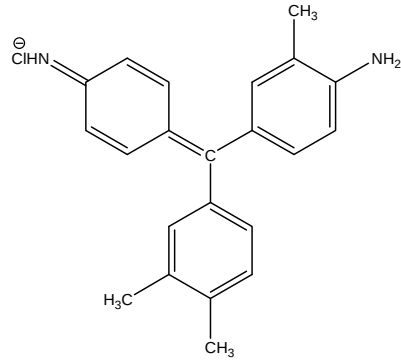
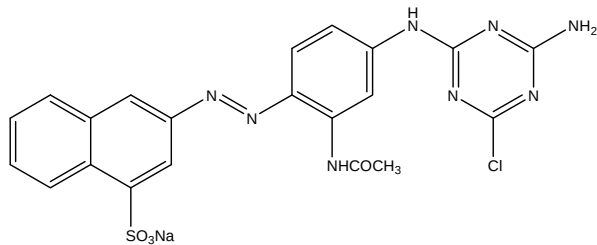
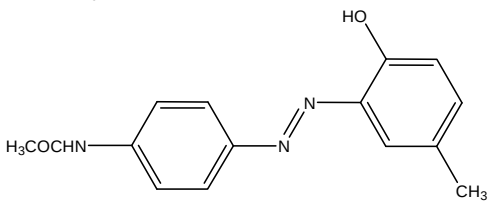
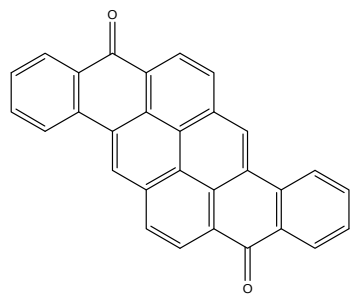
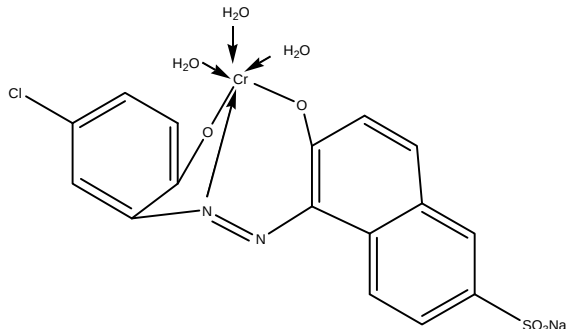
2.2.1 Acidic Dyes

Acidic dyes are anionic and soluble in water having different color-bearing groups as chromophores, and using the nitro, sulfonic and carboxyl as acidic functional groups. Sulfonic group addition makes the dye water soluble (Wilcock, 1992).

2.2.2 Basic Dyes

Basic dyes bear amino groups as chromophores and they are mostly cationic dyes. The mostly used basic dyes are triarylmethane, anthraquinone, diarylmethane or azo compounds. Among dyes the basic dyes contains approximately 5% (Wilcock, 1992).

Table 2.2: Some examples of commercial dyes

Names	Structure
Acidic Dyes	
Acid Yellow 36	
Basic Dyes	
Basic Violet 2	
Reactive Dyes	
Reactive Yellow 3	
Disperse Dyes	
Disperse Yellow 3	
Vat Dyes	
Vat Orange 9	
Metal Complex dyes	
Acid Violet 56	

2.2.3 Direct Dyes

Direct dyes are salts of sulfonic acid of azo dyes. They are highly water soluble and comparatively larger molecules having high attraction for textile fibers. Their binding to the fiber is by Van der Waals forces (Wilcock, 1992).

2.2.4 Reactive Dyes

Reactive dyes are water soluble dyes having anionic nature. They have strong binding ability to the textile fibers by covalent bonding. Few examples of reactive dyes are anthraquinone, dichlorotriazine and phthalocyanine (Wilcock, 1992).

2.2.5 Disperse Dyes

These dyes are rarely dissolveable and can go into man-made fibers (polyamide, acryl, polyester and cellulose acetate). This phenomena requires fiber swelling, either by a chemical softeners or by raising temperature up to 120 °C. With the fine disperse solutions of these dyes, dyeing process occurs in dye baths. These dyes are having an important position in the Color Index. They are normally nitro (yellow to red or azo compounds), metal complex azo (all colors) or anthraquinone (green and blue) compounds (Kaur, 2007).

2.2.6 Vat Dyes

These dyes are generally designed for dyeing cellulose fibres and are water insoluble dyes. The vat dyes in its reduced form are used in dyeing method. They can impregnate the fabric in their reduced form by sodium dithionite. Next, the insoluble form of dye can be formed again by oxidation. All vat dyes mostly consist on indigoids or anthraquinones (Wilcock, 1992; Kaur, 2007).

2.2.7 Sulphur Dyes

These dyes are complex aromatics consisting of a polymer with heterocyclic S-containing rings. Unlike vat dyeing, sulphur dyeing involves redox reactions. Cellulose fibers are mainly dyeing with sulphur dyes (Wilcock, 1992).

2.2.8 Mordant Dyes

These dyes are used as a chemical (mordant) that are combining the dye to the fiber and fix both together. They can be used for dyeing cellulose fibres, leather, wool, paper and silk (Wilcock, 1992).

2.2.9 Pigment Dyes

Pigment dyes are non ionic, insoluble compounds that maintain their crystalline structure through out their application. For printing different fabrics these dyes can be used with thickeners.

2.2.10 Metal Complex Dyes

These dyes normally do not belong to any particular application dye class. But they are included in many application classes of dyes, i.e., they are present in reactive, acid and direct dyes. These are strong complexes of one or two dye molecules and one metal atom (usually chromium, copper, nickel or cobalt), respectively i.e., 1:1 and 1:2 metal complex dyes. 1:1 and 1:2 metal complexes are formed when a single metal atom is coordinated with one dye molecule or two dye molecules respectively. These dyes are usually azo in nature (Kaur, 2007).

2.3 Dyes as Environmental Pollutant

The textile dyes with high aromaticity and low biodegradability have appeared as major environmental pollutants and up to 15% of the unfixed dye is lost in the process of dyeing and is entered in the wastewater (Kaur, 2007). This is mainly true for reactive dyes as the hydrolyzed form does not fixed to textile fibers. Reactive vinyl sulfone group ($-\text{SO}_2-\text{CH}=\text{CH}_2$) is formed by reactive dyes, that impregnate the fabrics under alkaline conditions. Further hydrolysis of this vinyl sulfone group forms hydrolyzed byproduct which does not form a bond with fabrics. Therefore, about 30% of hydrolyzed form reactive dyes may discharge in the wastewater (Steenken et al. 1992; Gahr et al. 1994; Hao et al. 2000) showing considerably high values of color as compare to the desired values set by National Environmental Quality Standards (NEQs) (National Environmental Quality Standards, 1999). The discharge of highly

colored wastewaters with residuals of unfixed dyestuff in natural water represent a significant problem to the surface water (Matsui et al. 1981; Babuna et al. 1998; Yasar et al. 2006) which impose negative impacts on communities using this resource containing reactive dye wastes. The lack of adequate finances for treatment is likely to cause significant threat to life forms. The photosynthetic activity of aquatic plants hindered due to accumulation of color that hampers sunlight penetration and ultimately the whole ecosystem is threatened (Georgiou et al. 2003). Most of the dyes are composed of non-biodegradable products and under anaerobic conditions they are cleaved by microorganisms to form carcinogenic aromatic amines (Uygur and Kok, 1999).

Among variety of textile dyes, anthraquinone is the 2nd major class among textile dyes after azo and have been acknowledged as the best dyestuff of dye-complex because it has been widely used for multi-purpose in water and various organic solvents (Baughman and Weber, 1994; Tawabini, 2003). Anthraquinone reactive dyes are utilized for cotton fibers but the toxicity of these dyes is relatively greater as compared to other types of dyes used because of having fused aromatic structure that is more resistant to degradation and hence remain colored in the wastewater for an indefinite period. These dyes give variety of colors in the visible region, but most frequently used colors are blue, green and violet (Christie, 2001; Fontenot et al. 2002). The chromophores of these dyes have combined with different types of reactive groups e.g., chlorotriazine, vinyl sulfone, difluorochloropyrimidine, trichloropyrimidine. They are different from all other classes of dyes because of their strong covalent bond formation to the textile fibres. RB 19 is an anthraquinone based vinylsulphone dye, especially important in dyeing of cellulosic fibres. In different studies RB 19 was preferred as a model dye due to its low fixing ability (75-80%) on cellulose as the competition between the formation of reactive vinyl sulfone and 2-hydroxyethylsulfone occurs (Figure. 2.1). The later does not attach on the textile fiber (Webber and Stickney, 1993; Rajkumar et al. 2007). Without proper treatment, the dye may be persistent and can reside in the environment for a long time period; e.g., the half life of the hydrolyzed RB 19 is almost 46 years at 7 pH and 25 °C (Webber and Stickney, 1993). Due to the

dye stability, less biodegradation and chemical strength, a large number of techniques have been developed for their elimination from wastewaters to reduce their impact on the environment.

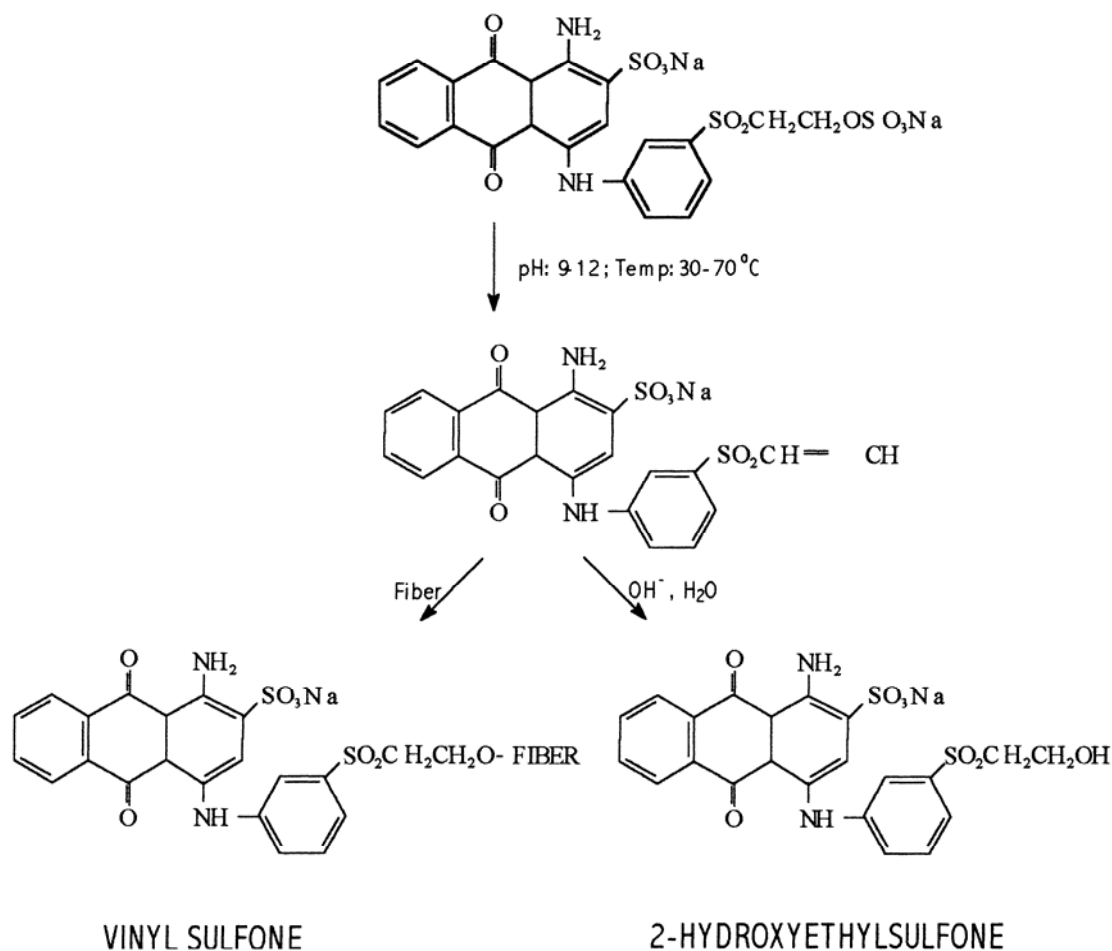


Figure 2.1: Competition between formation of reactive and hydrolyzed forms of RB 19 (Webber and Stickney, 1993)

2.4 Dye Removal Techniques

A number of chemical, biological and physical treatment techniques have been developed and used for treating textile wastewaters, such as flocculation, chemical coagulation, activated carbon adsorption or membrane separation (reverse osmosis, ultra filtration) etc. These processes have shown some limitations in sense of feasibility, practicability, reliability, cost, environmental impact, operational difficulty,

stability, pretreatment requirements, sludge production, the amount of the organic removal and possible toxic by products. It is observed that the application of an individual/alone process can not completely degrade and decolorize the colored compounds in wastewater. A particular form of wastewater can be decolorized successfully by some methods which sometimes are not appropriate to other types of colored wastewater (Swamy and Ramsay, 1999). The present achievements in water treatment methods are related through the oxidation of these refractory organic compounds which depends on the generation of highly reactive chemical species that degrade non-biodegradable molecules in to biodegradable compounds (Kaur, 2007).

In the present study, different techniques like sonochemical, electrochemical, thermal pressure hydrolysis and photocatalysis are used to find out the best possible option for the treatment of model effluent solution of RB 19. The details of the process are given below.

2.4.1 Ultrasonic Process

Ultrasound is sound of a frequency above human hearing, which in young adults stretches as far as 18 kHz. Power ultrasound used in chemistry, lies within the range of 20 kHz to 100 kHz. When sound passes through a medium it forms longitudinal waves that cause compression and rarefaction cycles. The decomposition of organic compounds is carried out by the irradiation of the ultrasound (called sonolysis) which oxidizes these compounds. This is a new harmless treatment process which attracts great attraction. More than last fifteen years a numbers of new intensification technologies have been developed which also includes sonochemical process (Peter et al. 1998).

Ultrasound is becoming popular for their use in the treatment of wastewaters. Degradation of textile dyes can considerably achieved using ultrasound in recent years, (Mason, 1990; Sangave and Pandit, 2004).

Sonochemical effects are based upon high power sound irradiation of aqueous solutions at frequencies that generate cavitations usually in 20-1000 kHz range. Cavitation process is based on formation of micro-bubbles, in which the increase and collapse of microbubbles happen in very short period of time i.e., microseconds releasing large degrees of energy (Vajnhandl and Marechal, 2005) (Figure 2.2).

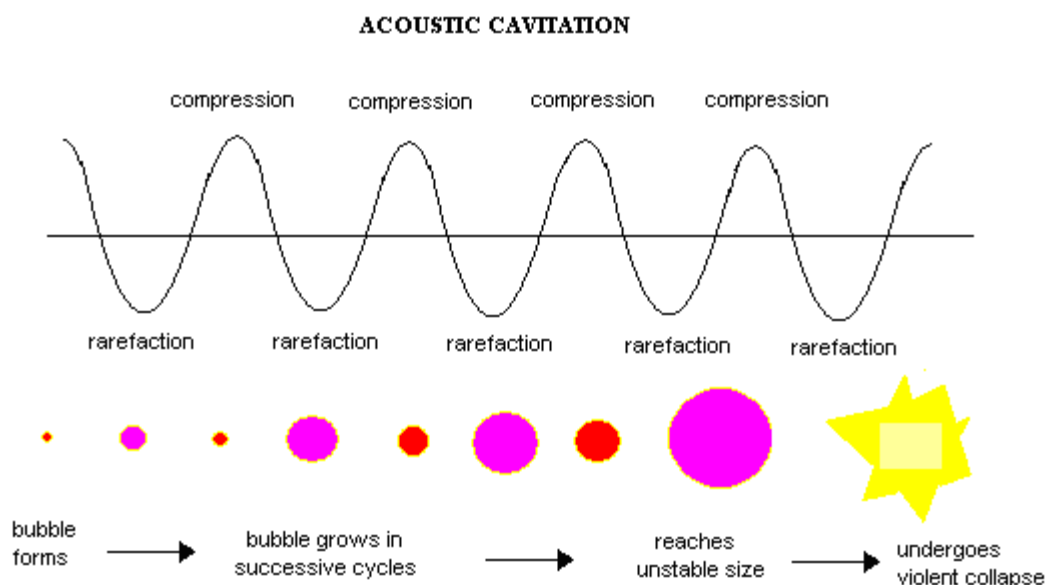


Figure 2.2: Generation of an acoustic bubble

During the bubble collision the release of high pressure and temperature breakup the gas molecules that are trapped in the micro bubbles into localized high concentrations of oxidizing radical species. These radicals can effectively degrade the pollutants in water after their migration, by recombining or reacting with gaseous molecules either in the cavity or in the liquid out side the cavity (Suslick, 1989; Mason et al. 1993; Suslick, 1999). The combined chemical and physical effect of cavitation permits the ultrasound application in water and effluent treatment. However, the complete mineralization of the pollutants in the case of ultrasound treatment is not cost effective in terms of dissipated power and the time scale. The ultrasound and other conventional treatment processes are found more effective when combined together as compare to individual process (Adewuyi, 2001).

2.4.2 Electrochemical Process

Electrochemical treatment which is an emerging technology has been applied to many kinds of waste water (Naumczyk et al. 1996; Simonsson, 1997) for the removal of organic and inorganic impurities. Electrochemical methods have been involved in different applications i.e., in the field of environmental engineering, ranged from water disinfection methods (Patermaragis and Fountoukidis, 1990) to the industrial wastewaters treatment as generated from pulp/paper industry, tanneries, metal plating and food processing plants (Kongsricharoern, 1994; Chiang et al. 1997; Vlyssides et al. 1997; Tubtimngam, 2001). In electrochemical methods the effluent is exposed to electrolysis, in which partial oxidation of the molecules takes place thus avoiding excessive power consumption. These processes do not require additional reagents as they are clean and operate at a low temperature (Legrand, 1993; Ochoa, 1995). Generally, the electrochemical decomposition of organics in wastewaters can be attained by oxidation that can occur at the anode directly and/or indirectly or due to the species generated by the anode (Sistiaga et al. 1994). The electrochemical treatment is a relatively new method with some advantages as it can be operated under normal pH conditions, less temperature and results in complete decolorization and significant decreases of chemical oxygen demand and biological oxygen demand. The electrochemical process reduces sludge production and it also favors the conversion of non-biodegradable organic compounds into biodegradable products i.e., CO_2 and H_2O , that normally be known as combustion or electrochemical mineralization (Comninellis, 1994). However, some times the electrolytes concentration, particularly sodium chloride is important for the production of high concentrations of hypochlorite anions, polychlorinated aromatic and free chlorine products, but these are not suitable for the environment (Naumczyk et al. 1996; Feng et al. 2000; Holcapek et al. 2001; Gonzalez and Pelaez, 2002; Rehorek et al. 2002). Further more an integrated approach of ultrasound and electrochemical process for treating wastewaters is found to be an advantage but has not received much attention until recently.

2.4.3 Thermal Pressure Hydrolysis

Hydrolysis is an important detoxification process and is used for degradation of organic compounds like pesticides. Under high pressure and temperature pure water unexpectedly converts into such form that reacts with organic compounds. Due to high pressure chemical reaction takes place in solution phase that alters its transition state, activation volume and molecular conformation resulting in enhanced chemical reactions thus converting harmful organic compounds into harmless final products (Gibson et al. 1939; Lowwitz et al. 1959; Shigeru et al. 1996, Siddique et al. 2009).

Water at high temperature provides a more favorable reaction medium than the water at atmospheric pressure for organic compounds. The water remarkably changes its chemical or physical properties at high temperatures, further the density and solubility parameter of water decreases and dissociation constant of water increases. The rise in temperature also decreases the dielectric constant of water that induced some changes in the physical properties thus changing the solvent properties of water. As a result the increase solubility of water increased the chemical reactions of organic compounds. The acid and base catalyzed reactions can be increased more by increasing dissociation constant in water as compare to the natural acceleration at high temperature. For different chemical reactions at the same time water perform as a reagent, catalyst and convenient solvent at high temperature and pressure that are normally accelerated by base or acid (Robina et al. 2002).

2.4.4 Photocatalytic Process

Photocatalytic process uses UV radiations to excite a semiconductor by light. The oxidizing species either free holes or hydroxyl radicals (bound) are generated under these conditions. The semiconductor may be attached on the support or in fine suspended particles in the water. The most energetic photocatalysts for this purpose is the TiO_2 because of its low cost, good performance, high stability and no self diffusion process (Andreozzi et al. 1999). The photocatalytic process starts by absorbing UV radiation that is equal or higher than the band gap energy onto the TiO_2 particles. This generates a photogeneration of electron pairs and holes in the semiconductor (Figure.

2.3). These excited electrons and holes can either recombine or can be used further in the oxidation and reduction process. The excited electrons and holes react with the adsorbed electron acceptor or donor species on the surface of semiconductor in these reactions (Bard, 1979).

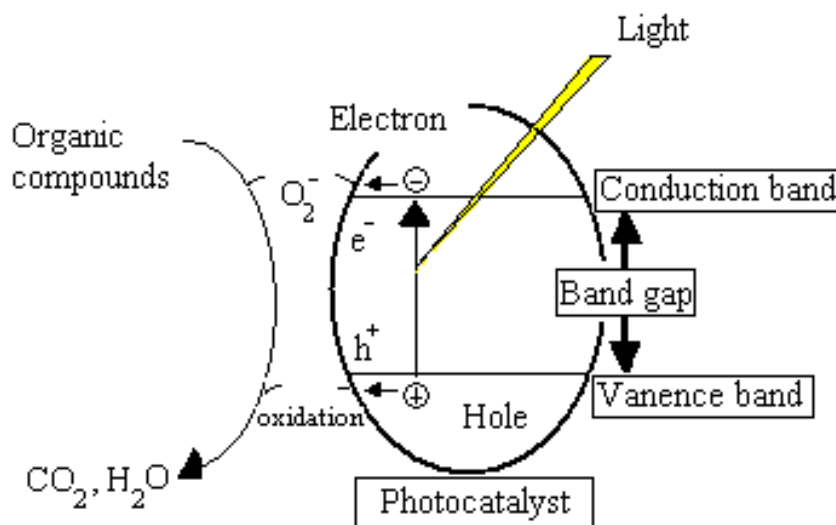
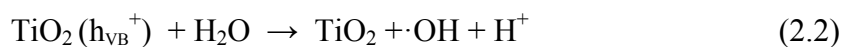
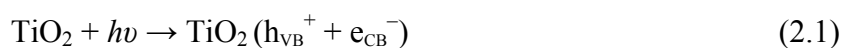
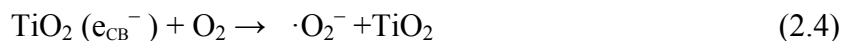


Figure 2.3: Mechanism taking place on the surface of semiconductor (Kaneko & Okura, 2003)

An electrical field is created at the semiconductor/liquid junction of the solid side that separates the electrons pairs/energized holes thus allowing the electron and holes to move in separate direction (Heller, 1981). In photocatalytic degradation the first step initiates by hole trapping with the production of short-lived and very reactive hydroxyl radicals. The hydroxyl radicals are produced either in the highly hydroxylated semiconductor surface or by direct oxidation of the organic pollutant in Ultraviolet radiations. At the same time, the reduction of adsorbed oxygen species takes place, derived either from dissolved oxygen molecules in the aqueous system or by other electron acceptors available in the aqueous system (Turchi and Ollis, 1990; Puma et al. 2008). The heterogeneous photocatalytic oxidation mechanism is shown below;





Various organic pollutants are attacked and oxidized by radicals formed according to the above mechanisms. Color and organic dyes removal by photocatalytic degradation is a promising and an efficient technique. The UV irradiation in titanium dioxide presence resulted in the decomposition of various organic compounds thus forming water, mineral acids or carbon dioxide (Kaur, 2007).

2.4.4.1 Photocatalysts

Research over the last three decades has not only confirmed the capability of sunlight for detoxification and disinfection but also has accelerated the natural process by the use of catalysts. The valence band (VB) oxidation potential must be higher than the material under investigation for occurring oxidizing reactions. The valence and conductance band redox potential ranged from -1.5 and +4.0 volts opposed to normal hydrogen electrode for different semiconductors. Therefore, variety of species can be treated by Advanced Oxidation Process (AOP) by selecting different semiconductor photocatalyst. Different types of semiconductor materials appropriate for photocatalytic purposes are metal oxides and sulphides. Some of the important semiconductors that are using in photocatalytic reactions, with the properties of the band gap energy, CB and VB potentials, and the wavelength required for the activation of catalyst producing this gap are listed in Table 2.3, the radiation must be of an equal or lower wavelength than that calculated by that Planck's equation (Eq. 2.10) (Kaur, 2007).

$$\lambda = hc / E_{\text{bg}} \quad (2.10)$$

where h = constant (Plank's 6.626×10^{-34} J s), λ = wave length, c = the speed of light and E_{bg} = band-gap energy of semiconductor.

In variety of environmental applications, TiO_2 is proved to be the most suitable semiconductor as compared to the listed semiconductors. Zinc oxide emerges also as an appropriate semiconductor but it cannot be used for practical applications due to its dissolution in acidic solutions. Other semiconductors (e.g. CdS) can form chemically activated surface-bond intermediates by absorbing larger portions of the solar radiations than TiO_2 , but unfortunately these catalysts can be degraded in heterogeneous photocatalysis during the repetitive cycles (Kaur, 2007).

Table 2.3: Band positions of some common semiconductor photocatalysts in aqueous solution (Kaur, 2007)

Semiconductor	Conductance band	Valance band	Band gap (eV)	Band gap wave length (nm)
TiO_2	-0.1	+3.1	3.2	390
SnO_2	+0.3	+4.1	3.9	318
ZnO	-0.2	+3.0	3.2	390
ZnS	-2.3	+1.4	3.7	336
CdS	-0.4	+2.1	2.5	497
CdSe	-0.1	+1.6	1.7	730

2.4.4.2 Titanium dioxide as an ideal catalyst

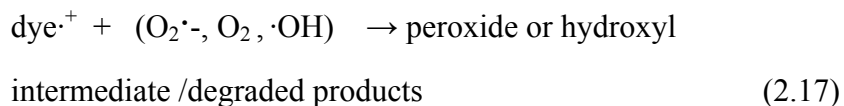
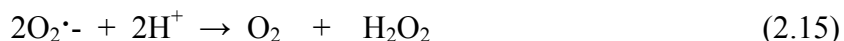
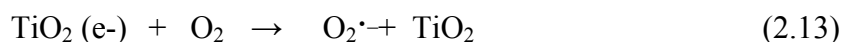
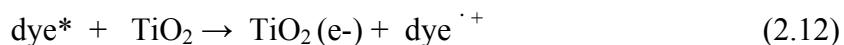
Titanium dioxide is close to being an ideal photocatalysts in several aspects. It is the most efficient semiconductor/photocatalysts and frequently used in sun blocks or in vitamin tablets as a builder, pigment and cosmetic. It is chemically and biologically inert, do not corrode during photochemical reactions and is cheap as compare to other catalysts. Brookite, rutile and anatase are the crystalline forms of titanium dioxide. Among three the rutile and anatase are commonly used forms and the latter is being used mostly in treating wastewaters. However, the rutile and anatase band gap energies are about 3.0 eV and 3.2 eV respectively but the oxidation dynamic strength is comparable. Rutile is more stable than anatase thermodynamically, but at low temperature (<600 °C) the anatase formation is kinetically favored that can clarify its high surface density for active sites with its surface area for catalysis and adsorption. Moreover, TiO_2 is of unique importance as it can absorb UV radiation from sun. This is

or the reason that titanium dioxide has a proper separation phenomenon among its different bands that can be exceeded via photons of solar energy (Kaur, 2007).

The conspicuous drawback of semiconductors is after excitation the photo-generated charge carriers depict a high rate of recombination. The electron-hole recombination declines the overall efficiency of the semiconductor by decreasing the quantum yield of the desired oxidation/reduction processes. The use of ultraviolet region of solar spectrum constitutes a subsequent problem because the earth receives only 4-6% of this excitation light. The said constraint is reduced by catalysts modification process, photosensitization and metal ions doping by various colored inorganic and organic compounds to cause a red shift in semiconductors light response (Kaur, 2007). Therefore, research on catalyst improvement has been done on the following points:

1. Physical and chemical modification of TiO₂ to improve the catalyst performance.
2. Dye sensitization to increase the useful wavelength range of the solar radiation.

The photo-sensitization mechanism of dye molecules by TiO₂ can be summarized as under:



The oxidation potential of sensitizer is higher as compare to the conductance band of titanium dioxide, and under the irradiation of visible light the adsorbed dye follows the preliminary excitation. The electron is than transferred from the dye's excited state to the titanium dioxide's conduction band. If the regeneration step is eradicated carefully than oxidative degradation of the dye can possibly be initiated. Different variety of dye

compounds have been studied as photosensitizers. Many recent reports showed the catalysts surface photo-excitation based decomposition is a significant method for treating dye containing wastewaters (Kaur, 2007).

2.5 Review of Treatment Techniques for RB 19 Removal

The treatment methodologies that are generally adopted to treat RB 19 can be categorized as: (i) physico-chemical and (ii) biological. The above mentioned categories of the methodologies are discussed briefly in following paragraphs. The technologies involve photocatalysis (Lizama et al. 2001; Lizama et al. 2002; Kurbus et al. 2002; Xia et al. 2008a; Rezaee et al. 2008a; Rezaee et al. 2008b; Rezaee et al. 2008c; Neval and Deniz, 2008; Xia et al. 2008b; Verma and Ghaly, 2008), sonolysis (Enes, 2006), electrochemical (Yang et al. 2005; Rajkumar et al. 2006; Lin and Peng, 2006; Andrade et al. 2007; Rajkumar et al. 2007), ozonation (Hsu et al. 2004; Fanchiang and Tesang, 2009), biological (Lee et al. 2004; Ramsay et al. 2005; Wang et al. 2007; Champagne and Ramsay, 2007; Kokol et al. 2007) and physical methods (Andrzejewska et al. 2004; Jesionowski et al. 2005; Andrzejewska et al. 2007; Ozcan et al. 2007; Hasan et al. 2008).

2.5.1 Physico-Chemical

2.5.1.1 Sonolysis

Sonolysis is the formation of radicals using ultrasound and has been applied for the decolorization and decomposition of dye molecules. The sonochemical method is generally induced upon the violent collapse of cavitations resulted in the formation of short-lived radical species. The studies on the decomposition of RB 19 using activated carbon, ultrasound and combined activated carbon/ultrasound confirmed that decolorization of dye using combined ultrasound/activated carbon was greater than the individual methods. The use of ultrasonic irradiation was found to be useful for decolorization of RB 19 by adsorption from aqueous solution (Enes, 2008).

Guyer et al examined the combination of ultrasonic irradiation with hydrogen peroxide and found that the combined procedure yielded 10-25% acceleration in color

degradation and significant enhancement in COD reduction (Guyer et al. 2004). The anthraquinone dyes degradation was investigated by Lall et al using three processes: ultrasound, ozonation and ultrasound-enhanced ozonation. The authors found that decolorization rates were enhanced under conditions of constant ultrasonic radiation and continuous gas application. Also increase in ultrasonic power resulted an increase in the mass-transfer coefficient (Lall et al. 2003).

2.5.1.2 Photocatalytic oxidation

The degradation and removal of organic contaminants by a photocatalytic oxidation process has been found as substitute or supplement method (Ollis et al. 1991; Muneer et al. 1997).

Xia et al studied the activity of $\text{La}^{3+}/\text{S}/\text{TiO}_2$ co-doped photocatalyst on photodegradation of RB 19 under irradiation of visible light. The results showed that the $\text{S}/\text{La}^{3+}/\text{TiO}_2$ photocatalyst showed highest absorption and activities in the visible range for degradation of RB 19 in sample (Xia et al. 2008). Decolorization of RB 19 is very efficient by advance oxidation process under hydrogen peroxide/UV and increasing hydrogen peroxide concentration the rate of decolorization increases (Rezaee et al. 2008c).

Rezaee et al reported photochemical oxidation processes ($\text{K}_2\text{S}_2\text{O}_8/\text{UV-A}$, $\text{K}_2\text{S}_2\text{O}_8/\text{UV-C}$) and chemical oxidation processes (dark/ $\text{K}_2\text{S}_2\text{O}_8$) for RB 19 decolorization and found that $\text{UV-C}/\text{K}_2\text{S}_2\text{O}_8$ is much more effective as compared to (dark/ $\text{K}_2\text{S}_2\text{O}_8$) and $\text{UV-A}/\text{K}_2\text{S}_2\text{O}_8$ processes (Rezaee et al. 2008a). Verma and Ghaly investigated the decolorization of Remazol Brilliant Blue dye in synthetic effluent by photo reactor, which consisted on; a UV lamp (low range) and a TiO_2 coated spiral coil. They tested the decolorization activity with separate techniques and then compared the results with combined techniques and concluded the result that this dye can better be degraded with combined techniques (Verma and Ghaly, 2008).

The photocatalytic discoloration of RB 19 was investigated in aqueous suspension of TiO_2 and ZnO (Lizama et al. 2002). The reactions were described in terms of pH

amount of catalyst and the dye concentration it was reported that ZnO has greater degradation activity than TiO₂. Lizama et al studied that the reactive dyes degradation (yellow 2, orange 16, red 2, and anthraquinone reactive blue 19) can best be obtained by the use of photo-assisted catalytic activity (Lizama et al. 2001).

2.5.1.3 Adsorption

Adsorption process is a known method for the treatment of textile effluents. It widely used in different purification and separation purposes in industrial processes. In terms of cost and ease of operation the adsorption method was also found to be very successful for color removal. Decolorization by adsorption is influenced by some chemical and physical factors like adsorbent surface area, dye-adsorbent interactions, particle size, time, pH and temperature (Anjaneyulu et al. 2005).

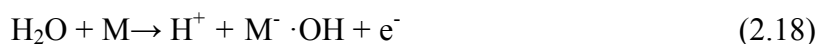
A wide range of adsorbents for the removal of RB 19 have been used for wastewaters treatments. Andrzejewska et al reported the decomposition of RB 19 dye by aminosilane-modified silica. It was observed that the application of aminosilane-modified silica proved to be very efficient as it can remove more than 90% of dye from solutions (Andrzejewska et al. 2004). It is inferred that using 3-aminopropyltriethoxysilane and N-2-(aminoethyl)-3-aminopropyltrimethoxy- silane in various solvents (CH₃OH, C₆H₅CH₃, CH₃OH and CH₃COCH₃:H₂O mixture) modify the surface of rutile titanium dioxide that resulted in the higher adsorption efficiency of RB 19 (Andrzejewska et al. 2004). Hasan et al investigated the RB 19 adsorbed on composite beads of oil palm ash and cross-linked chitosan. The result showed that in the acidic solutions dye uptake was higher than the alkaline and neutral solutions, i.e., pH 6 the maximum adsorption occurred. Thus, the low-cost adsorbents (composite beads of oil palm ash /cross-linked chitosan) were found efficient adsorbent for the removal of RB 19 (Hasan et al. 2008). The use of modified bentonite (clay minerals) (dodecyltrimethyl- ammonium bromide- DTMA) as an adsorbent with a cationic surfactant was carried out successfully by Ozcan et al to remove RB 19 by adsorption from the liquid solution. The result showed that in acidic conditions at pH about 1.5, the adsorption capacity of DTMA–bentonite is higher ($3.30 \times 10^{-4} \text{ mol g}^{-1}$) which is due

to the strong electrostatic interactions of dye anion and adsorption site (Ozcan et al. 2007).

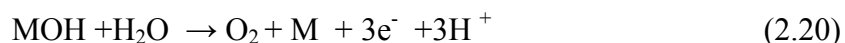
2.5.1.4 Electrochemical oxidation

Electrochemical process is based on effluent electrolysis. The process uses different electrodes and hydroxyl radicals are produced in solution by electrolysis, which chemically reacts with pollutants. The process very simply involves passing the waste between the electrodes across which a DC current is applied. Highly active species may produce in solution for the oxidation of organic compounds. The electrochemical oxidation of organic compounds in the solution usually follows two steps using the traditional anodes.

1. Water electrolysis at anode resulted in the generation of radicals species ($\cdot\text{OH}$) that can further adsorbed on to the electrode M (electrodes active sites) (Gutiérrez and Crespi, 1999).



2. The adsorbed hydroxyl radicals oxidize the organic pollutant R that further resulted in the formation of RO which is an oxidized organic product. That product can further be oxidized by repetitive radical species attack that is produced continuously by the anodic discharge of water. In this process the formation of oxygen is the main side reaction, which is again used in process reactions (Gutiérrez and Crespi, 1999).



According to literature, the electrochemical oxidation has been reported as an effective process for treating actual textile and synthetic runoff. (Mantzavinos and Psillakis, 2004; Meric et al. 2004). Electrochemical methods such as electrochemical coagulation and electrochemical oxidation have been used widely for treating reactive dyes and Chen, 2004 and Chatzisyseon, 2006 have been reviewed recently its several applications. Electrochemical oxidation has been used for the decontamination of

various reactive dyes by various electrodes, for instance the titanium dioxide, IrO₂, Pt, graphite anodes, some titanium based alloys and the diamond electrodes doped with boron using supporting electrolyte typically sodium chloride.

A number of current studies reported the use of electrochemical oxidation for treating aqueous solutions containing RB 19. Andrade et al investigated the electrochemical performance of F and Fe doped (separately or together) or pure Ti-Pt/b-PbO₂ electrodes for the oxidative treatment of the RB 19 containing wastewaters. The F and Fe doped PbO₂ electrodes showed good efficiency for the degradation of the RB 19 (Andrade et al. 2007). A minor advantage of a BDD/Nb anode was also found to degrade RB 19, as 82% TOC reduction and 95% decolorization efficiency were achieved for a 25 mg dm⁻³ dye solution with 0.5 M Na₂SO₄ treated at flow rate of 2.4 dm³ h⁻¹, 50 mA cm⁻² and 25 °C for 8 min after using up of only Q = 0.3 Ah dm⁻³ (Andrade et al. 2007). Rajkumar et al investigated the degradation of RB 19 by electrochemical process using titanium based anode. The effects of different parameters were also identified on treatment efficiency with further analysis of the major degraded intermediates and products (Rajkumar et al. 2007). The electrochemical oxidation of the RB 19 was investigated by Fryda et al using an Nb/BDD anode that achieved 90% dye decolorization and 82% TOC reduction after reaction time of 10 min and 2 h in the solution respectively (Fryda et al. 1999).

The photo/electrochemical oxidation of organic pollutants have been reviewed to improve the dyes removal efficiency (Vinodgopal et al. 1993; Hidaka et al. 1996; Kesselman et al. 1997). Fujishima et al suggested the use of a single crystal rutile titanium dioxide photo anode for photo electrolytic removal of reactive dyes (Wahl et al. 1995). The application of Ti/RuO₃TiO₇O₂ anode has also received much attention as it allows the passage of higher current density with larger stability. Ronaldo et al investigated electrochemically assisted photocatalytic degradation of RB 19 by Ti/RuO₃ TiO₇ O₂ electrode, dimensional stable anode (DSA) and reported higher than 95% decolorization and about 52% TOC removal during the reaction time of 2 h. Pelegrini et al performed the electrochemical oxidation study of RB 19 dye in a quartz cell in which three electrode were equipped with the anode at pH 11. Only 35% dye

decolorization and 9.6% TOC reduction was achieved after 120 min of electrolysis at $E_{\text{anod}} = 1.8 \text{ V}$ vs. AgCl/Ag (Pelegrini et al. 1999). The use of photoelectrochemical degradation process for treating RB 19 using TiO_2/Ti photo anode was also investigated and found that the method is more suitable when applied at the final stages of wastewater treatment when effluents have passed prior from some preliminary treatment (Zainal et al. 2007).

2.5.1.5 Ozonation

Ozonation has been used extensively for eliminating color and textile dyes and is therefore one of the most efficient methods (Slokar et al. 1998; Hao et al. 2000; Mondal, 2008). However the main drawback of ozonation in its gaseous state is its direct application, with the generation of large quantities of residues that need further disposal. Ozone, the strong oxidizing agent known with $E_0 = 2.07 \text{ V}$, and can produce the nonselective and highly active oxidant i.e. ($\cdot\text{OH}$, $E_0 = 3.06 \text{ V}$) at basic pH conditions (Gottschalk et al. 2000). Thus the complex aromatic rings of dyestuffs can effectively be breaking down, which results in the degradation/decolorization of the organic dye (Mondal, 2008). Ozone reaction with reactive type is more successful as compare to other dye classes i.e., disperse, sulfur and acidic dyes. The back ground literature showed that ozonation process carried out mostly on azo dyes (Shu and Huang, 1995; Liakou et al. 1997; Wu and Wang, 2001; Khare et al. 2007) and a few information is presented on anthraquinone reactive dyes treatment by ozonation (Perkowski and Ledakowicz, 2002; Liu et al. 2007). RB 19 representative reactive anthraquinone dye was investigated with a semi batch reactor by ozonation. The dye degradation and decolorization efficiencies of RB 19 were found about 83% and 97% by ozonation after reaction time of 10 min respectively (Fanchiang and Tesang, 2009). Similarly Hsu et al performed the decolorization study of RB 19 in a gas inducing reactor under constant process (Hsu et al. 2004).

For RB 19 removal several other combined methods have been used beside the individual ozonation process. Ozonation and ultrasonic irradiation (O_3/US) combination is another attractive process for the treatment of wastewater and has been

intensely applied from the past numerous years. He et al studied the decomposition of RB 19 in model solutions by coupling sonolysis with ozonation. The results showed that ultrasonic irradiation showed insignificant results when use alone, but O₃/US treatment showed higher degradation as compare to ozonation alone (He et al. 2008). Song et al studied the efficiency of the ozone enhanced electrochemical/coagulation process for RB 19 decolorization using iron electrodes in water. More than 96% of color removal and 80% TOC removal were found. It was also found that by applying a simultaneous ozonation process the efficiency of the electrochemical/coagulation process can be enhanced (Song et al. 2008). Further study was conducted using enzymatic, photochemical and ozonation methods for RB 19 removal. Each process showed specific attributes; the ozonation process resulted into complete decolorization at a very less period of time; however significant dye degradation was not achieved. The enzymatic process showed the quick decolorization of the dye but the highest decolorization rates was 30% which is insignificant relatively to decolorization rates attained by the other methods. The photocatalytic process showed significant results. The titanium dioxide or zinc oxide photocatalysts allows complete dye degradation and decolorization at about 60 min of reaction times (Zamora et al. 1999).

2.5.2 Biological Process

Different biological processes have been applied for the degradation and decolorization of RB 19. A large variety of microorganisms including yeasts, fungi and bacteria have been studied in live or dead forms, under aerobic and anaerobic conditions and for the biosorption of dye. The biological methods have been found effective for dye degradation and is considered more cost effective alternative as compared to physico chemical processes (Donmez, 2002; Aksu and Donmez, 2003; Aksu, 2003).

Besides the individual treatment techniques used for RB 19 degradation, furthermore, integrated approaches have also been reviewed.

2.6 Ultrasound and Electrochemical Process

Electrochemical treatment of wastewaters discharged by the textile industry could be less effective due to the recalcitrance of the commonly used dyes. Combination of ultrasound and electrochemical processes is an attractive option for reducing treatment cost for wastewaters containing toxic and non-biodegradable pollutants.

The use of electrochemical oxidation for treating aqueous model solutions containing a variety of dyes has been reported by several studies. The influence of different operating parameters on the decomposition of Basic Brown and Acid Blue was investigated by a lead / lead oxide anode while on Acid Orange 7 degradation by diamond anode doped with boron respectively (Awad and Galwa, 2005; Fernandes et al. 2004). Reactive Black 5 and Basic Yellow 28 were used as samples for comparing the performance of a diamond electrode vs conventional metal electrode i.e., aluminum, copper and iron (Rivera et al. 2004), while for determining the degradation efficiency of 29 different industrial dyes use of an activated carbon electrode in electrochemical method was investigated (Shen et al. 2001). Further for treating RB 5 a number of advanced oxidation methods like titanium dioxide photocatalysis, UV/hydrogen peroxide, electro/Fenton and combined UV/electro/Fenton were compared and studied about their effectiveness (Kusvuran et al. 2005).

Although the electrochemical decomposition of dyes with different model aqueous solutions have been presented in different research papers, but the literature regarding textiles actual effluent treatment is also exists. Different continuous methods e.g., activated sludge; coagulation and electrochemical oxidation were investigated by Lin and Peng for processing of industrial waste. Further the effect of variable parameters i.e., solution pH, concentration of coagulant, number of electrodes, current density, reaction times in biological and electrochemical reactors were carefully investigated and optimized conditions were reported for the treatment efficiency (Lin and Peng, 1996). The electrochemical oxidation of industrial wastewater by Pt-Ti electrode at different chloride concentrations is reported. The results showed that the real effluent was efficiently degraded by electrochemical treatment and biodegradation (as

concluded by the chemical oxygen and biological oxygen demand ratio) was also enhanced (Vlyssides et al. 1999). The electrochemical degradation and decolorization rate of textile effluent over three titanium electrodes coated by various metals were compared and major degraded by products were also identified (Naumczyk et al. 1996). Sakalis et al established a small size continuous electrochemical reactor that was efficient enough to achieve 90% dye color removal for the textile effluent at 40 minutes time interval (Sakalis et al. 2005).

The combination of ultrasound and electrochemistry comprises a booming field due to the combined chemical (possible change in the mechanisms) and mechanical effects (the liquid/solid mass transfer and the activation of the electrodes surface) of ultrasound. Usually it involves the mixed system consisted of a solid and a liquid i.e., electrode and electrolyte. In ultrasonic process, a liquid jet can be generated by the collision of cavitation bubbles at or near to the surface of electrode, targeted at the surface. Almost any electrochemical process can be enhanced by the application of power ultrasound mainly due to this jet (Mason, 1990). Generally electrochemical process is a complex process but it is safe to consider it a transfer of ions across the surface of electrodes. A thin layer generate at the border of an aqueous solution when an electrode is dipped into it. As electrochemistry involved the movement of ions across the layer so disturbance in this layer influence the electrochemical process. The ultrasonic cavitations on collapse produced micro jet that will further reduce the diffusion layer thickness and support diffusion across the surface of electrode which is frequently a rate controlling step (Mason, 2000). Several useful sonoelectrochemical effects includes the surface effects, changed adsorption events, enhanced mass transport, electrode fouling reduction, production of altered product distributions, manipulation of reaction mechanism, increase in current efficiencies and yields, required less amount of cell power and increasing the limiting current in analytical applications. Sono-electrochemistry thus offers significant benefits for a variety of different applications (Walton and Phull, 1996). The combined ultrasound and electrochemical process may form an interesting technique for treating wastewater but

the literature studies showed that this combination is not yet explored extensively for organic dyes degradation.

Foord studied the electrochemical characteristics of Procion Blue at boron doped diamond electrodes in combination with ultrasound (Foord, 2001). Lorimer et al conducted study on the degradation of dyes using sonoelectrolysis, which showed its potential for the dyes removal and decolorization (Lorimer et al. 2001). Mamdouh et al reported the degradation of an organic dye molecule (specifically meldola blue, MDB) under the influence of power ultrasound in combination with electrochemically generated hydrogen peroxide (Mamdouh et al. 2002). Yakov et al used a combined electrochemistry/ultrasound waves/Fenton's reagent process for the detoxification of hydrophilic chloroorganic pollutants in effluent water. The use of this combined sonoelectrochemical/Fenton treatment process achieved almost 50% oxidation of 2, 4-D solution in 60 sec using very less amount of current density at 20 kHz (Yakov et al. 2004). Ioan et al investigated the sonoelectrochemical degradation of cyanide ions (CN^-) using six types of electrodes (aluminum, titanium, nickel, copper, stainless steel and graphite) for highlighting the influence of electrode type on degradation process efficiency (Ioan et al. 2004). Gogate overviewed different ways for the intensification of cavitation phenomena using additional methods or combining cavitational effect with different oxidation processes (Gogate, 2008). The dye degradation process is the involvement of the final decomposition of the parent compounds and their intermediates. TOC reduction is a common way to monitor this degradation process. Simona et al observed the mineralization and decolouration of RB 5 dye, by ultrasonic frequencies and investigated reduction in TOC (Simona et al. 2007). Mineralization of an anthraquinone RB 19, by single sonolysis, single ozonation and sonolysis combined with ozonation (US/O_3) processes was studied (He et al. 2008). Using GC-MS and IC methods intermediate and end products were identified and probable reaction mechanism was proposed. Weschenfelder et al monitored the chemical and physicochemical treatment of textile wastewater using LC-MS and GC-MS and MS-MS for the identification of degraded products (Weschenfelder et al. 2007). Rajkumar et al studied RB 19 degradation by electrochemical process in chloride medium, and

the degradation of dye UV-visible spectra were recorded and the degraded products were identified using GC-MS (Rajkumar et al. 2007).

2.7 Thermal Pressure Hydrolysis Process

Thermal pressure hydrolysis is an important method for degrading many environmentally stable organic compounds in aquatic environment at atmospheric pressure. Numerous studies have been performed to determine the effect of atmospheric and high pressure hydrolysis on organic compounds degradation in aqua media (Robina et al. 2002). The hydrolysis of fenitrothion was studied in the dark in buffered distilled water, natural lake water and buffered lake water. Hydrolysis products are constituted of the 3-methyl- 4-nitrophenol and dimethylfenitrothion at 50 °C and up to 2.7 pH. In contrast, only two products were formed in reaction at pH 9 and above (Jiping and Scott, 2000). The hydrolysis of organophosphorous pesticide omethoate under natural conditions of temperature and pressure was studied (Robina et al. 2007). It was observed that the hydrolysis rate of omethoate enhanced by increasing temperature. The stability of omethoate in aqueous solution is markedly influenced by pH. The rate of hydrolysis in strong acidic and strong basic conditions was higher than normal or slightly acidic and basic conditions. The mechanism of hydrolysis under acidic and basic conditions was also proposed. The kinetic studies indicate that the hydrolysis rate followed 2nd order of reaction apparently. The half life studies show that the half-life of the pesticide is inversely proportional to temperature (Robina et al. 2007).

The breakdown of several organophosphorous pesticides both in aqueous solution and moist soil was studied. The hydrolysis rate of phosmate, dialifor, malathion, methyl chloropyrifos, dicapthon, chloropyrifos and parathion are measured at 20 °C and 37.5 °C (pH 4) in aqueous solutions (Mabey and Mill, 1978; Xiaomei et al. 1992). A similar study was conducted at pH 6.1 and 20 °C. The half lives at 20 °C (pH 7.4) range from 7.1 h for phosmate to 130 days for parathion; the corresponding rates at 37.5 °C are approximately five- seven times greater than those at 20 °C.

The literature showed that at temperature of 200 °C and 300 °C, the reactivity of organic compounds in water phase has been thoroughly studied using different reactants i.e., aromatic and aliphatic species that contained the functional groups of oxygen, nitrogen and sulphur (Fenghour and Wakeham, 1993). The degradation kinetics and pressure effect on environmentally stable omethoate pesticide by hydrolysis were investigated. The results showed that by increasing pressure the value of $k_{(obs)}$ was increased and activation volume decreased. Among different pH conditions i.e., 3.58, 6.01, 8.8; the best found pH was 8.5 which was stable and its half-life was lessened from 263 min to 19.37 min from 1 atm to 10 atm pressure. The obtained results described that under high pressure hydrolysis, the conversion of toxic organic phosphorus into inorganic phosphorus could take place in an effective manner (Robina et al. 2002).

The catalytic hydrolysis of organophosphorous pesticides facilitated by the suspension of manganese dioxide was investigated (Robina et al. 2005). It was found that the concentration of organophosphorous pesticides in solution apparently decayed showing the second order kinetics. Also the rate constant value was highest at strong acidic conditions and it continued to decrease as the pH of the solution was increased gradually. In basic conditions, the rate constant value decreased to minimum. Manganese dioxide under acidic conditions converted into Mn^{+2} ions, then these ions in water formed hexaaquamanganese (II) ion- $[Mn (H_2O)_6]^{+2}$. This ion then adsorbed itself on the S or O atom of the organophosphorus compound, thus increasing the efficiency of hydrolysis. It was studied that methidathion hydrolyzed more efficiently than omethoate. The rate constants of catalytic hydrolysis were improved by increasing the amount of manganese dioxide. It was found that the pesticides had undergone adsorption on catalyst in the first few minutes and there was rapid drop of total phosphorus observed. After the addition of alkaline earth metal cations (Ca^{+2} and Mg^{+2}) along with manganese, the rate of hydrolysis at near neutral conditions was successfully increased (Robina et al. 2005).

2.8 Ultrasound and Photocatalytic Process

The integrated approach of ultrasound and photochemical is an established method for the treatment of wastewater (Augugliaro et al. 2006). The ultrasound usage for treating textile wastewater is reported in literature (Hua and Hoffmann, 1997; Suslick, 1999). Vajnhandl and Marechal reviewed the fundamentals of ultrasound and its applications in industrial processes, with the detailed dyeing procedures and the decolorization/decomposition of wastewaters (Vajnhandl and Marechal, 2005). Gogate and Pandit in their review highlighted the status of the hydrodynamic cavitation reactors with bubble dynamic analysis and also the optimum design illustrating the utilities of reactors (Gogate and Pandit, 2005). The sonochemical degradation of dichlorvos was investigated using a batch reactor and observed that sparge gas and acoustic power are two main factors which affect the sonochemical degradation efficiency (Schramm and Hua, 2001).

A comparative degradation of azo dyes at ultrasonic irradiation of 520 kHz and its combinations with ultraviolet light and/or ozone was investigated using a probe dye Acid Orange 7 (Guyer and Ince, (2004). It was observed that generally the degradation process was most quick under simultaneous operation of the three (UV/US/O₃) in the presence of a continuous flow of gas mixture (oxygen and argon). The kinetic study on degradation of trihalomethanes (CHBrCl₂, CHCl₃, CHBr₂Cl, CHBr₃ and CHI₃) was conducted under 20 kHz ultrasonic frequency (Shemer and Narkis, 2005). It was found that the most important parameter affecting the sonodegradation efficiency and kinetics was the vapor pressure. Okitsu et al reported the sonochemical degradation /decolorization of azo dyes e.g., Methyl Orange and RR 22. It was concluded that azo dye molecules were chiefly decomposed by ·OH radicals formed from the water sonolysis (Okitsu et al. 2005). The effect of sodium chloride, hydrogen peroxide, ultrasonic power and external gases was studied on the degradation of oxalic acid (Dukkanci and Gunduz, 2006). An optimal concentration of sodium chloride was found to improve the degradation of oxalic acid. On the other hand, the use of hydrogen peroxide had negative effect on the degradation of oxalic acid. Mahamuni and Pandit studied a hybrid technique of ozonation coupled with cavitation for the degradation of

phenol. He concluded that this hybrid technology leads to the formation of intermediates that can further be subjected to biodegradation (Mahamuni and Pandit, 2006). Zeng and James studied the audible frequency sonolytic ozonation for pentachlorophenol (PCP) degradation in water solution. The first-order rate constant of PCP degradation by ozonation combined with sonication was found to be 15 times more than that with bubbling ozone alone, while the rate constant with mechanical stirring was only four times faster (Zeng and James, 2006). Simona et al found that the sonochemical decolorization/degradation of RB 5 using low and high ultrasonic frequencies i.e., 20 kHz and 279/817 kHz (high ultrasonic frequencies), without using any additional oxidant. It was concluded that ultrasound is capable for RB 5 color removal when used alone but the decomposition rate strongly depends on the operating parameters in use e.g., frequency, acoustic power, solution pH, transducer type, dye initial concentration. Nevertheless ultrasound alone is quite unsuccessful for the degradation of the dye (after 6 h of treatment only 50% degradation efficiency was achieved); by *V. fischeri* as test organisms negligible toxic degraded by products were detected under the conditions employed (Simona et al. 2007).

The combined ultrasound and photocatalysis process was used for the degradation of phenol solution (Wu et al. 2001; Naffrechoux et al. 2000) and found the enhancement in the degradation rate of phenol. Selli reported that sonolysis and photocatalysis showed the synergistic effects in the removal of Acid Orange 8 in aqueous solutions, when low ultrasound frequency is used (Selli, 2002). Mrowetz et al confirmed the influence of initial substrate concentration (2-Chlorophenol) and photocatalyst amount on the degradation and mineralization rates which were found to ascertain the origin of the synergistic effect (Mrowetz et al. 2003). Gogate and Pandit critically evaluated the status of the sonophotocatalytic reactors with a particular focus on wastewater treatment applications. Different hybrid techniques with their different reactor configurations have been analyzed and recommendations have been made for the optimum configuration designing (Gogate and Pandit, 2004). Hirano et al subjected the chlorinated organic compounds to sonication followed by photocatalytic treatment. The

sonication results the formation of some intermediate products, which are rapidly oxidized to carbon dioxide on further photocatalysis (Hirano et al. 2005).

Velegraki et al investigated the oxidation of Acid Orange 7 using sonophotocatalytic process with different effect i.e., ultrasonic frequency, reaction temperature and time on. It was found that under same operational parameters, ultrasonic irradiations resulted in better efficiency than photocatalysis. Furthermore, by observing reaction pathways it was found that the solutions irradiated sonochemically contained always low aliphatic intermediates whereas the solution irradiated photocatalytically, mostly consisted of aromatic intermediates (Velegraki et al. 2006). Adrian et al investigated the treatment efficiency of 13 compounds containing model solution usually found in olive mill effluents, by means of sono-photocatalysis at 50 mgL⁻¹ concentration of each, over 0.75 gL⁻¹ Degussa TiO₂ suspensions. It was found that, photocatalytic efficiency improved with increasing UVA power, whereas ultrasonic process when used as only method showed negligible degradation. In addition the process coupling as well as addition of extra oxidant resulted in considerable high level of degradation (Adrian et al 2007). Antonia and Martínez studied the sono-photocatalytic degradation of basic blue 9 dye using ultrasound with 20 kHz ultrasonic frequency, over a TiO₂ slurry employing an UV lamp (15 W, 352 nm). It was concluded from the results that the first order rate constants obtained with sonophotocatalysis were twofold and tenfold than those attained under sonolysis and photocatalysis, respectively (Antonia and Martínez, 2008). Shuo et al prepared the carbon nanotubes (TiO₂/CNTs composite and investigated the sonophotocatalytic activity of TiO₂/CNTs nanoparticles. Their results showed a remarkable increase in the photocatalytic efficiency of TiO₂/CNTs when combined with ultrasonic technique, and the sono-photocatalysis process was found to follow first order kinetics (Shuo et al. (2009). Zielinska et al conducted the photocatalytic removal of organic dyes by TiO₂ under UV/Vis light. The photo removal of these dyes was monitored by FTIR spectroscopy on the surface of the photocatalyst (Zielinska et al. 2003). Several researchers have used various analytical techniques to study the mechanism and degradation path ways of pollutants. Prevot et al observed the photocatalytic removal of Acid Blue 80 in a solution containing TiO₂ catalysts. The mechanism of dye removal was studied by HPLC and its end products

by GC and TOC (Prevot et al. 2001). Also low aliphatic compounds and aromatic intermediates of acid orange 7 in water solution by ultrasound and photocatalysis were investigated by GC-MS analysis (Velegaki et al. 2005).

Based on literature review it is concluded that different individual and combined treatment methods have been employed and studied for the destruction of reactive dyes containing wastewater. However further research is required to justify the decolorization/degradation efficiency for wide range of dye compounds and industrial effluents. In physicochemical methods, adsorption is an effective treatment technique applied for the purification of wastewaters but their use is limited because the process requires regenerating the adsorbent materials. Ozonation provides fast decolorization and degradation of dyes but the process is not completely accepted due to its expensive nature and operational problems and the disadvantage of photocatalysis is the extra expenditure of UV artificial light. Hydrolysis process alone is not sufficient a combination of other techniques is required to enhance the degradation efficiency of process. Application of combined techniques for the decolorization and degradation of reactive dyes containing wastewaters have also been reviewed and the further application of these techniques can be expected in near future. The combined ultrasound and electrochemistry process may possibly make up the remarkable technique for treating wastewater because of its different beneficial effects i.e., changed adsorption phenomena, increased mass transport, and surface effects, management of reaction mechanism, reducing the electrode fouling, generation of altered product, increased current and yields efficiencies, enhanced limiting current in analytical applications and decrease cell power requirements. It can be argued that the sonoelectrochemistry is applicable for the degradation of reactive compounds specifically and for wastewater treatment generally. It seems effective for the wastewaters which can be degraded by applying electrochemical process. Ultrasound would certainly increase the effects induced by electrochemistry. However, further studies are need of the time for the real application of these techniques for wastewater treatment systems to obtained promising results.

Chapter 3

Material and Methods

The present study was conducted in order to decompose the reactive dyes in model solutions. The same set of pH, temperature, concentrations and retention time was used for different techniques i.e. sono-electrochemical degradation, atmospheric, high pressure and sono-photocatalytic degradation.

3.1 Materials

3.1.1 Chemicals and Reagents

The following chemicals were used for the preparation of synthetic wastewater.

- Reactive Blue 19 dye (RB 19) was provided generously by Arzoo Textile Mill, Faisalabad, Pakistan and it was used further with out purification. The specification and chemical structure of the RB 19 is presented in (Figure 3.1 & Table 3.1) (Rajkumar et al. 2007).

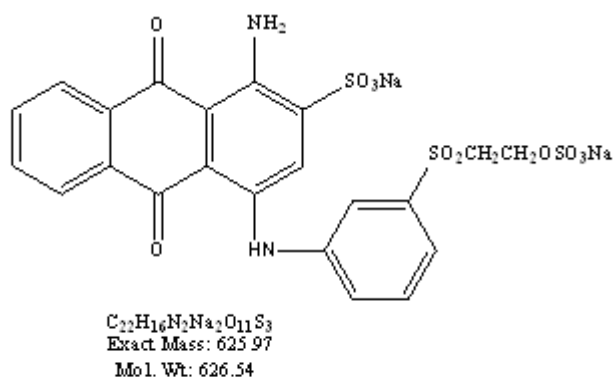


Figure 3.1: Molecular Structure of RB 19

Table 3.1: Chemical information of RB 19

Commercial name	Rifazol Brill Blue R
Synonym	Reactive Blue 19
Molecular Formula	$C_{22}H_{16}N_2Na_2O_{11}S_3$
Molecular Weight	626.54 g/mol
Classification	Anthraquinone, Vinyl Sulfone
λ max	594nm
CAS Number	2580-78-1
Color Index Number	61200

- Hydrochloric acid and Sodium hydroxide (Merck, Germany) were used for adjusting pH.
- Hydrogen peroxide (37% pure) (Merck, Germany) was used for dye degradation experiments
- Titanium dioxide catalyst was purchased from Acros Organics, Scientific Fisher Company, Belgium and was used as received. It consists of 70% anatase.
- The reagents used for analysis of TOC were NaHCO_3 , Na_2CO_3 , Potassium hydrogen phthalate, HgSO_4 (Merck, Germany).

3.2 Equipments and Instruments

There were different kinds of equipments, which were used to apply different experimental conditions to study the degradation processes.

3.2.1 pH meter

The pH meter (Jenway 3505 UK) used in the present study was calibrated for accurate measurements according to the procedure given in manual.

3.2.2 Ultrasonic Bath

The ultrasonic effect was investigated by immersing the different reactor assemblies in to Digital Ultrasonic Bath, Cleaner Model UTECH PRODUCTS, INC (300W, 35 kHz).

3.2.3 Electrodes

In this study lead oxide (14 x 15 x 0.1 cm) was used as an anode and a stain less mesh steel plate was used as a cathode (14 x 15 x 0.2 cm).

3.2.4 Autoclave

WisecraveTM Digital Fuzzy Control System (DAIHAN Scientific) was used to study the atmospheric and high pressure hydrolysis of dye solutions.

3.2.5 Ultraviolet Lamp

Irradiation was provided by 9-Watt UV source (Philips, with maximum emission at 254 nm) placed vertically in the center of the photo reactor.

3.2.6 Filtration

Samples were taken at different time intervals during photocatalysis and were filtered by Milli pore filter (0.45 μm).

3.2.7 UV-Visible Spectrophotometer

In model solutions the dye concentration and color were determined by UV-Visible Spectrophotometer (Model U2020 - IRMECO) at scanning spectrum of 200-800 nm. Cuvette with path length of 10 mm was used.

3.2.8 TOC Analyzer

TOC analyzer (Shimadzu, model TOC-V CSH) was used to determined the total organic carbon contents of the samples.

3.2.9 GC-MS Analyzer

GC-MS analyzer (Perkin Elmer Clarus 600) was used to identify the degraded products of the samples.

3.3 Experimental Methods

In order to degrade the reactive dye (RB 19), three different kinds of degradation methods were used; sono-electrochemical, thermal pressure hydrolysis and sono-photocatalytic degradation. The detail of each set of experiments conducted is given below.

3.3.1 Sonoelectrochemical

Sonoelectrochemical degradation experiments were carried out in an undivided electrolytic cell made up of perspex sheet (Figure 3.2) at ambient conditions.

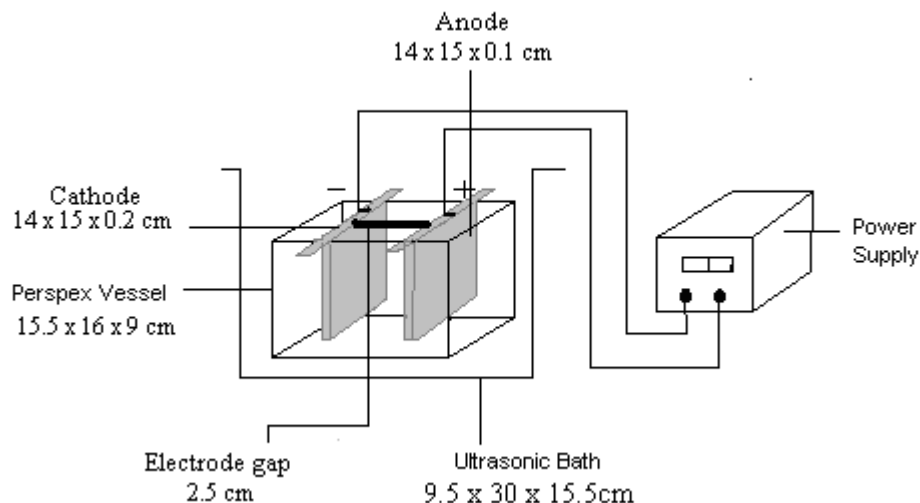


Figure 3.2: Experimental setup of sonoelectrochemical reactor

The working electrode and counter electrode were placed vertically and parallel to each other with an inter electrode gap of 2.5 cm in the electrolytic cell (14.5 x 16 x 9 cm). Lead oxide was used as working electrode (anode) (14 x 15 x 0.1 cm) and stainless mesh steel plate was used as counter electrode (cathode) (14 x 15 x 0.2 cm). Voltage was adjusted at 10 V and was provided by means of DC power supply (DAZHENG PS-305D). To study the effect of ultrasound the designed electrolytic cell immersed in the Digital Ultrasonic Bath (9.5 x 30 x 15.5 cm) (Cleaner Model UTECH PRODUCTS, INC).

The stock RB 19 dye solution of 1000 mg was dissolved in distilled water and diluted to 1000 mL. The standard dye solutions of 20, 40, 60, 80 and 100 mgL⁻¹ were prepared from stock solution. As dyes are found in textile effluents in the hydrolyzed form, two sets of experiments were performed to test the efficiency of the proposed technique by unhydrolyzed (sulphatoethyl-sulphone) and hydrolyzed (hydroxyethyl-sulphone) form of the dye. The unhydrolyzed dye solution was prepared from stock solution directly as per requirements. The hydrolyzed dye solution was prepared by heating the dye solution to 60 °C and maintained for 6 hours at alkaline pH to allow complete hydrolysis (Vajnhandl and Marechal, 2007). The hydrolyzed and unhydrolyzed dyes were confirmed by GC-MS analysis.

The experiments were conducted at various pH values in the range of 3-9 and various ultrasonic irradiation power (120-240 W) using 50 mgL⁻¹ dye concentration for 120 min. The initial pH of the sample was set using 1M NaOH or 1M HCl. In order to study the effect of initial dye concentration, the experiments were conducted at 20, 40, 60, 80 and 100 mgL⁻¹ of RB 19 dye solutions in distilled water. The total solution volume for each experiment was used 1 L. Samples were drawn periodically at 0, 30, 60, 90, 120 min, respectively and were immediately analyzed by spectrophotometer at $\lambda_{\text{max}} = 256$ and 594 nm. Each experiment was performed in duplicates.

3.3.2 Hydrolysis

Hydrolysis process consisted of

- a. Atmospheric Pressure Hydrolysis
- b. High Pressure Hydrolysis

The atmospheric pressure and high pressure hydrolysis were carried out in autoclave. The pressure was adjusted and measured by inbuilt pressure gauge which was attached on autoclave. The stock solution of RB 19 dye was prepared at lab scale by dissolving 1000 mg in 1L of distilled water. For the hydrolysis studies the stock solution was further diluted as per requirements of the experiment. Dye solution was distributed into different flasks (1 L capacity) and then pH was adjusted as per requirements of the experiment with the help of pH meter. The initial pH of the sample was set using dilute sodium hydroxide (1M) or hydrochloric acid (1M). The initial dye concentration in each sample was 100 mgL⁻¹ after dilution contained in 200 mL of the sample. The atmospheric pressure and high pressure hydrolysis experiments were conducted in autoclave under different conditions of temperatures (40, 60, 80, 100, 120 °C) and pressures (1 and at 2 atm pressure). The pressure was adjusted and measured by inbuilt pressure gauge which was attached on autoclave. The hydrogen peroxide effect was investigated on dye degradation by adding different concentrations of hydrogen peroxide in the solution. A range of pH conditions used was 2, 4, 6, 8 and 10. The samples were airtight to prevent any contamination. The duration of each experiment was about 120 min and samples were taken at regular time intervals of 0, 30, 60, 90

and 120 min respectively and were analyzed immediately using spectrophotometer at $\lambda_{\text{max}} = 256$ and 594 nm for measuring the dye decolorization and degradation. Experiments were performed in duplicates (Siddique et al. 2009).

3.3.3 Sonophotocatalysis

The sonophotocatalytic experiments were carried out in photo-reactor at ambient conditions. The designed reactor was consisted of well equipped- a pyrex glass water circulating jacket (28 x 7.5 x 6.5 cm) for maintaining reaction temperature (Figure 3.3). Irradiation was provided by 9-Watt UV source (Philips, with maximum emission at 254 nm) placed vertically in the middle of the reactor. The whole photo-reactor was immersed in the reaction vessel (capacity 1 L) and suspension containing dye and catalyst (TiO_2) in the reaction vessel was positioned on magnetic stirrer and stirred magnetically with the continuous exposure to UV irradiations. To study the effect of ultrasound the whole photo reactor was immersed in an ultrasonic bath (9.5 x 30 x 15.5 cm). Samples were with drawn at different irradiation times for the analysis of decolorization and degradation.

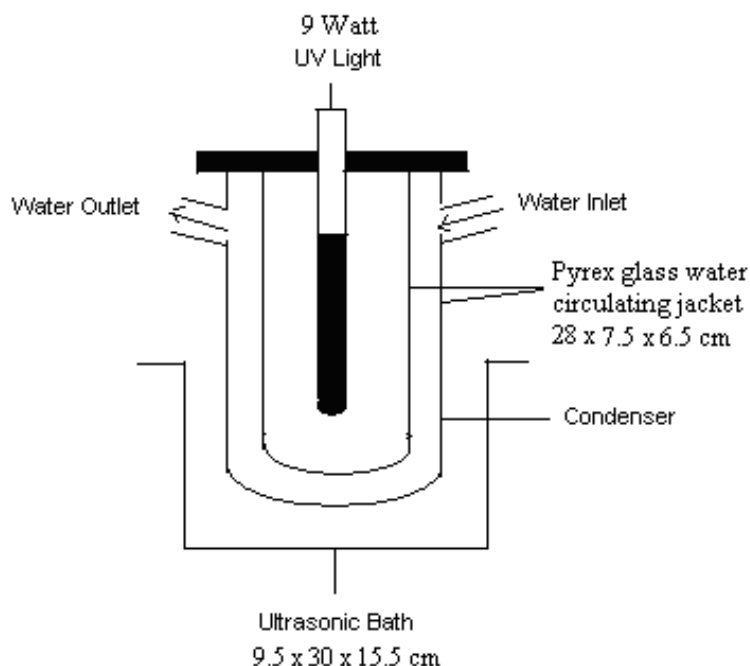


Figure 3.3: Experimental set up of sonophotocatalytic reactor

In distilled water stock solution of hydrolyzed dye was prepared. The 500 ml of dye solution having concentration of 100 mgL^{-1} with different concentrations of TiO_2 (20, 50, 100, 200, 300, 400 and 500 mgL^{-1}) was used. Using dilute hydrochloric acid (1M) and sodium hydroxide (1M) the initial pH of the samples was maintained. The solution containing dye and TiO_2 in the reaction vessel was stirred magnetically at constant temperature of 25°C with the continuous exposure to UV irradiations. The 10 ml of dye sample was taken over regular intervals of time i.e., 30, 60, 90 and 120 min, filtered and analyzed for the determination degradation of dye at maximum $\lambda_{\text{max}} = 256 \text{ nm}$ and 594 nm using UV-Visible spectrophotometer. Experiments were performed in duplication.

3.4 Analytical Method

3.4.1 UV-Visible Spectrophotometer

The dye concentration and color in the model solutions were determined using UV-Visible Spectrophotometer at scanning spectrum of 200-800 nm. The system was switched on and warm up. Quartz Cuvettes were used. To get the relation between concentration and absorbance of the dye compound, a calibration curve was made. Calibration solutions were made from standard solutions of known concentration. The absorbance is plotted against known concentration of the calibration samples at 594 nm . The calibration curves were stored in the system itself and the concentration of unknown sample was calculated directly from the absorbance. Further the calibration curve was prepared from RB 19 dye standard concentrations. Absorbencies vs. dye concentrations were plotted to give a straight line shown in figure 3.4.

The percentage (%) decolorization was determined using following formula.

$$\text{Dye \% decolorization} = (1 - C_t/C_0) \times 100 \quad (3.1)$$

where C_t and C_0 are the concentrations (mgL^{-1}) of dye at reaction time t and 0 , respectively (Enes, 2008).

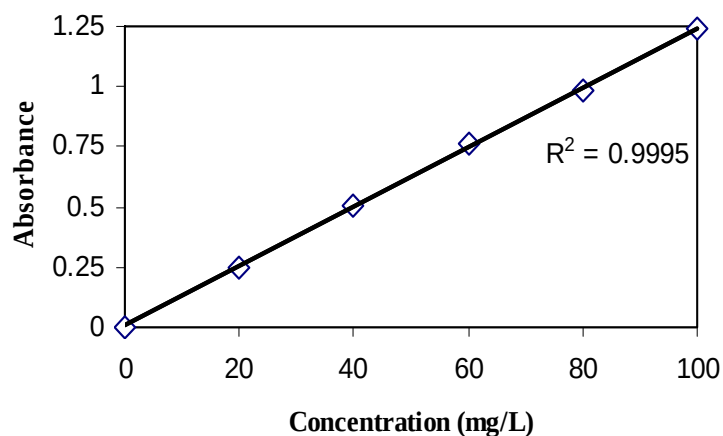


Figure 3.4: Calibration curve of dye for concentration vs. absorbance

The change in solution concentrations were calculated by Beer-Lambert law while the residual dye concentrations were determined using the value of absorbance at the characteristic wavelength ($\lambda_{\text{max}} = 256$) from the spectrum. (Lucas et al. 2007).

$$A = \epsilon l C \quad (3.2)$$

Where A = absorbance, l = path length (cm), ϵ = molar coefficient extinction ($\text{mol}^{-1}\text{cm}^{-1}$) and C = dye concentration at time t (mol L^{-1}) (Lucas et al. 2007).

3.4.2 TOC Analysis

The TOC instrument was heated up to 680 °C (furnace temperature) and 20 ml sample injection. Reduction in percentage total organic carbon content was measured using following equation (Carneiro et al. 2004).

$$\text{TOC (\%)} = (\text{TOC}_{\text{initial}} - \text{TOC}_{\text{final}} / \text{TOC}_{\text{initial}}) \times 100 \quad (3.3)$$

The reagents used for TOC analysis are mentioned in section 3.1.1. The preparation of reagent solutions is as follows.

Inorganic Carbon (IC) determination by adopting following procedure

3.5 g of NaHCO_3 was measured that was previously dried for 2 hours in silica gel desiccator, and 4.41 g of Na_2CO_3 previously dried for 1 hour at 280-290 °C and cooled in desiccator. The weighed material was transferred to 1L volumetric flask and deionized water was added.

Total Carbon (TC determination by adopting following procedure

2.125 g of reagent grade potassium hydrogen phthalate was weighed that was previously dried at 105-120 °C for about 1 hour and cooled in desiccator. The weighed material was transferred to 1L volumetric flask and deionized water was added.

3.4.3 GC-MS Analysis

The samples were withdrawn at various time intervals and were extracted according to the procedure reported in the literature (Rajkumar et al. 2007). The GC was equipped with an Elite- xlb column (30 m x 0.25 mm) and 0.25 µm film thickness and connected directly to MS. The GC column was operated at 40 °C for 1.50 min which was then increased to 300 °C at the rate of 20 °C /min. The other experimental conditions were: helium as a carrier gas with the flow rate of 1 ml, sample volume 1 µl, injection temperature 200 °C, injection mode split, and split ratio is 50 (Siddique et al. 2009).

3.5 Calculations of Energy Consumption

Energy consumption was calculated for the simple electrochemical process and ultrasound assisted electrochemical process. The total energy consumption implied the power used to generate electro-chemical reactions and to operate ultrasonic bath. The energy calculations for electrochemical reactions based on input voltage and flow of current through the solution while in case of ultrasonic process total power consumption (300 W) by ultrasonic bath was included. In order to heat the system in simple electrolysis process the electric power of (200 W) was used.

Electrical energy consumption was calculated using the following equation.

$$EC \text{ (kW h L}^{-1}\text{)} = (P \times t) / V \times 60 \times \log (C_0/C_t) \quad (3.4)$$

where P (kW) = power, V =volume (L) of water treated, t = oxidation time (min), C_0 and C_t = concentrations of dye in (mgL^{-1}) at reaction time t and 0 (Azbar et al. 2004).

3.6 Statistical Analysis and Graphical Work

All experiments were carried out in duplicate and mean values are presented in the results. Statistical comparisons of the mean values were performed by analysis of variance (ANOVA), followed by Duncan's multiple range test ($p < 0.05$), using SAS 8.3 software (SAS Ins. Inc., Cary, USA). Graphical work was carried out using computer program Sigma PlotTM v.10 (Siddique et al. 2009)

Chapter 4
Results and Discussion
Sonoelectrochemical Degradation of RB 19

Sonolysis involves the use of ultrasonic waves and is generally based on the generation of short-lived radical species produced in violent cavitation events. These radical species can diffuse out of the bubble into the bulk fluid medium where they are able to react with solute molecules. A steady state concentration of reactive radical species in the liquid phase is then maintained by continuous irradiation with ultrasound. Non-volatile organic compounds present in the liquid phase, can undergo degradation mainly by reaction with the powerful oxidizing agents ($\cdot\text{OH}$ radicals) produced (Mamdouh et al. 2002). Ultrasound combined with electrochemical process is another promising method for the treatment of wastewater and degradation of some compounds (Iordache et al. 2004). The electrochemical process also involves the oxidation of water molecules that led to the formation of hydroxyl radical through the following reaction.



The $\cdot\text{OH}$ radical generated from water discharge according to reaction (4.1) is then used in organics oxidation process (Martinez-Huitle and Brillas, 2009). The application of ultrasound enhances the process of the generation of electrochemical species which in turn can significantly improve the efficiency of oxidation process. The sono-electrochemistry has been effectively applied for the removal of organic pollutants (Mamdouh et al. 2002). In present research the effect of different parameters (pH, dye concentration, reaction time and electrode material) was studied to investigate the sono-electrochemical degradation of RB 19 dye varying ultrasonic power. Sonoelectrochemical degradation of dye solution is carried out in a reactor by setting with the purpose of determining the optimum conditions. Under optimized conditions the chemical kinetics, degradation mechanism and intermediates and end products of RB 19 is also investigated.

4.1 Sonochemical Degradation

Sonochemical degradation experiments are conducted by ultrasound alone for the degradation and decolorization of 50 mg L^{-1} RB 19 dye concentration at various initial pH values (3-9) and ultrasonic power ranged (120-240 W) for the reaction time of 120 min. The working volume was 1 L. The dimensions of reaction vessel and ultrasonic bath are described in section 3.3.1. From results it is found that basic pH is more

suitable than acidic pH. Maximum 13.33% dye decolorization and negligible dye degradation is observed at maximum ultrasonic power of 240 W at pH 8 after the reaction time of 120 min (Table 4.1). The effect of decolorization can be interrelated with the dye's chemical structure but not with the TOC content. Therefore, reduction in TOC is also investigated and the results shown in Table 4.6 demonstrates that only 7.2% TOC was reduced in sonochemical process alone. Further experiments are conducted by electrochemical process alone and ultrasound assisted electrochemical processes to compare the degradation efficiency of the dye.

Table 4.1: Percentage decolorization of RB 19 dye at different ultrasonic power

Dye	Ultrasonic power (W)	Decolorization (% age)			
		30 min	60 min	90 min	120 min
RB 19	120	1.17	3.32	5.21	7.10
	180	2.51	5.11	6.89	9.62
	240	4.41	7.62	10.1	13.3

Reaction conditions: Dye concentration = 50 mg L⁻¹, pH= 8

The obtained results showed the similar trend as reported in the literature (Ince and Tezcanli, 2001) that the decolorization of reactive dyes is insignificant by individual ultrasonic process. For treating acid and basic dyes using ultrasound, it was found that basic dyes were only decolorized by ultrasound (Lorimer et al. 2001). While a number of studies stated the valuable use of ultrasonic irradiation for the decolorization of different industrial dyes but the total decomposition of these complex compounds were found difficult using ultrasonic process alone. Therefore, the combined use ultrasound with other advanced oxidation methods i.e., the electrolysis is a more suitable approach for the treating organic contaminants (Rivera et al. 2009).

4.2 Sonoelectrochemical Degradation

A combined electrochemical and ultrasound process for the degradation and decolorization of RB 19 dye is studied and a comparison study of the alone

electrochemical and sono-electrochemical process is performed with different operational parameters i.e., pH, ultrasonic Power, dye concentration and reaction time.

4.2.1 Effect of pH

The pH value is an important factor in determining the performance of combined ultrasound and electrochemical process (Chen et al. 2002; Kobya et al. 2006; Sengil and Ozacar, 2006). The effect of initial pH on the percentage RB 19 degradation is investigated at various initial pH values (3-9). The dye degradation is markedly influenced by solution pH. The results show that rate of degradation enhanced with the increase of pH from acidic to basic conditions (He et al. 2008) (Figure 4.1). The maximum degradation efficiency of 67.68% is observed at pH 8. In sonoelectrolysis of dye aqueous solutions more hydroxyl radicals are expected to generate in alkaline pH conditions. Under alkaline conditions the main anions is OH^- which changes into $\cdot\text{OH}$ by losing electrons on the anode surface. The transfer of OH^- ions towards anode is enhanced by ultrasonic waves. The increased production of these $\cdot\text{OH}$ enhances the oxidation process of dye (De et al. 2008).

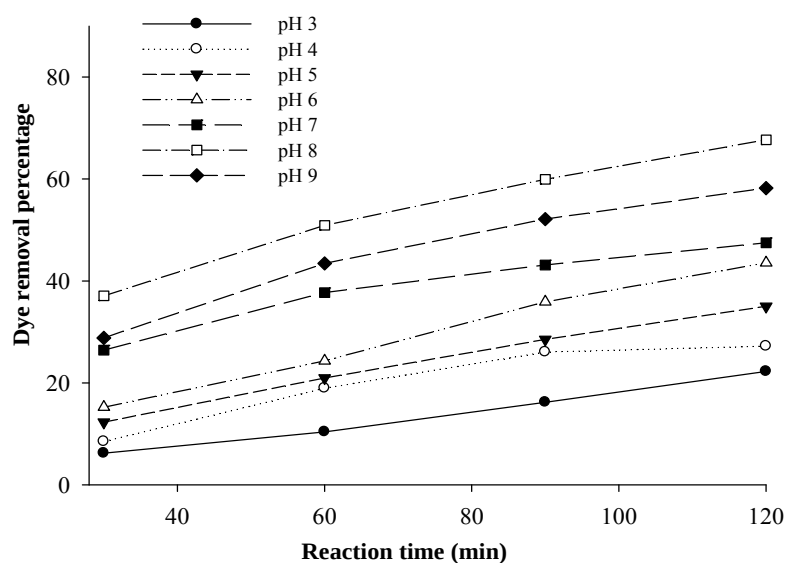


Figure 4.1: Effect of initial pH on the percentage removal of dye concentration by sonoelectrochemical process

Reaction conditions: Dye concentration= 50 mgL^{-1} , US power = 240 W, voltage= 10 volts

At pH above 8, more free radicals scavengers such as CO_3^{-2} , SO_4^{-2} may exist and lead to a decrease in the amount of $\cdot\text{OH}$ radicals which ultimately results the decrease in the rate of decomposition at pH 9 (He et al. 2008).

4.2.2 Effect of Ultrasonic Power

By increasing ultrasonic power the mixing intensity would enhanced due to turbulence produced by collapse of cavitation bubble in addition to micro jetting which results in the increase of rate of reaction (Price, 1992; Simona et al. 2007). Sonoelectrochemical experiments are conducted at pH 8 with different ultrasonic power ranged from 120-240 W (Figure 4.2). The results show that the increase in ultrasonic power caused a decrease in the residual dye concentration. The maximum 71% decrease in dye concentration is observed at ultrasonic power of 240 W after 120 min of reaction time. However, at optimum frequency by increasing ultrasonic power from 240 to 300 W, no significant effect on the decrease of residual dye concentrations is observed. This was due to the reasons that a maximum rate of reaction can be obtained in any chemical reaction when an optimum acoustic power exists therefore a great number of cavitation bubbles are generated at higher ultrasonic power. For further transfer of acoustic energy they induce some hurdles through the whole liquid. (Price, 1992; Petrier and Francony, 1997; Simona et al. 2007).

4.2.3 Dye Decolorization

The comparison of different techniques on the percentage dye decolorization shown in Figure 4.3. It is observed that 13.33% dye decolorization in heterogeneous ultrasonic process is obtained at the maximum ultrasonic power of 240 W during the experiment of 120 min. In simple electrochemical process, 52% decolorization is observed in 120 min. These results are in agreement with the studies conducted by Rivera et al. They reported the use of ultrasonic irradiations for the decolorization and COD reduction of many industrial dyes. The removal of these complex compounds was not easy to attain by alone ultrasound. Therefore combination of ultrasound with electrochemical was found a convenient approach for pollutant remediation (Rivera et al. 2009).

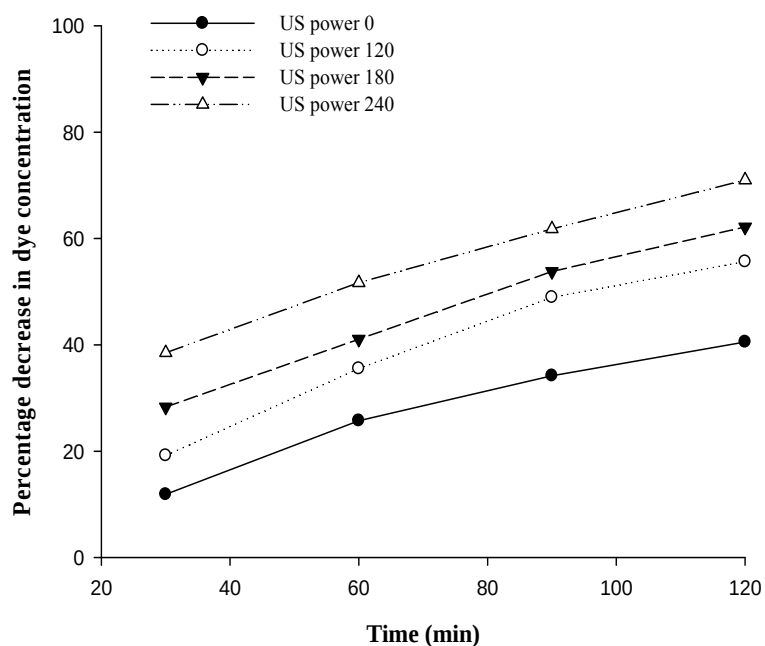


Figure 4.2: Effect of ultrasonic power on percentage decrease in dye concentration by sonoelectrochemical process
 Reaction conditions: Dye concentration= 50 mgL⁻¹, pH= 8, voltage= 10 volts

Table 4.6 shows profiles of the dye decolorization by different techniques and results indicated the superiority of ultrasound assisted electrochemical process over ultrasound and electrochemical methods. By ultrasound assisted electrochemical process, at US power of 240 W for 120 min, decolorization was reached to 90%. The additive effect of ultrasonic and electrochemical methods can be explained in terms of: (1) the presence of high energy micro jets ($\cdot\text{OH}$ produced by violent collapse of ultrasonic cavitations) (Pelegrini et al. 1999), (2) and water molecules oxidation during electrochemical procedure leading to the generation of $\cdot\text{OH}$ radical thus enhancing the dye decomposition.

During the ultrasound assisted electrochemical process, strong agitation of the aqueous solutions and constant degassing on the surface of electrodes was reported (Lorimer et al. 2001). The agitation by means of cavitations at the surface of electrode assists ion movements across the electrode double layer throughout the electrochemical process and decrease ion depletion in the diffusion layer and ultrasonic degassing at an

electrode surface avoid gas bubble accumulation interfering with the passage of current. The continuous activation and cleaning of the electrode was achieved by bubbles at and near the electrode surface. The increase in decolorization rates observed was may be the combine effect as discussed above (Rivera et al. 2009; Lorimer et al. 2001).

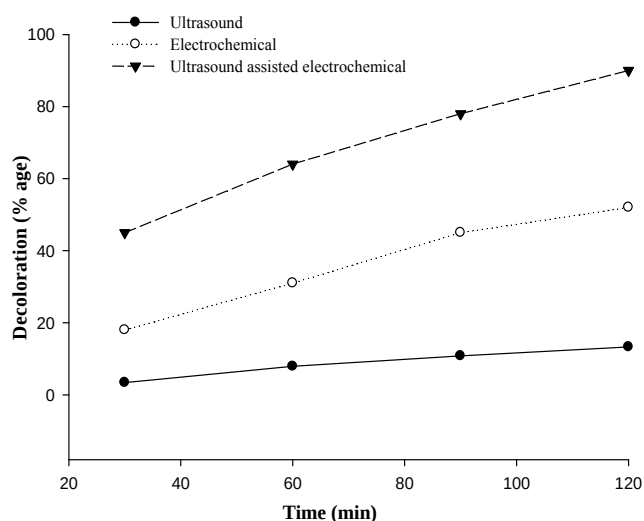


Figure 4.3: Comparison of ultrasound, electrochemical and ultrasound assisted electrochemical processes for decolorization of dye
 Reaction conditions: initial pH = 8, US power = 240 W, dye concentration = 50 mgL⁻¹

4.2.4 UV-Visible Absorption Spectral Changes

The changes in the absorption spectra (both at UV and visible regions with respective wavelengths of 256 nm and 594 nm) at various time intervals during combined treatment of RB 19 through ultrasonic and electrochemical techniques are presented in Figure 4.4. The peak observed in the visible region is because of blue color of chromophore, while peak observed in the ultraviolet region was as a result of anthraquinone structure of the dye (Rajkumar et al. 2007). The disappearance of the visible band in a short period might be caused by the fragmentation of the quinone links by $\cdot\text{OH}$ radical attack during the oxidation process. All together, the reduction in the absorbance at 256 nm is considered as the evidence of chromophore degradation in the dye molecule and its intermediates. It is found that both the color removal and

decomposition in the dye structure are attained after 120 min of ultrasound assisted electrolysis for 50 mgL^{-1} of dye concentration.

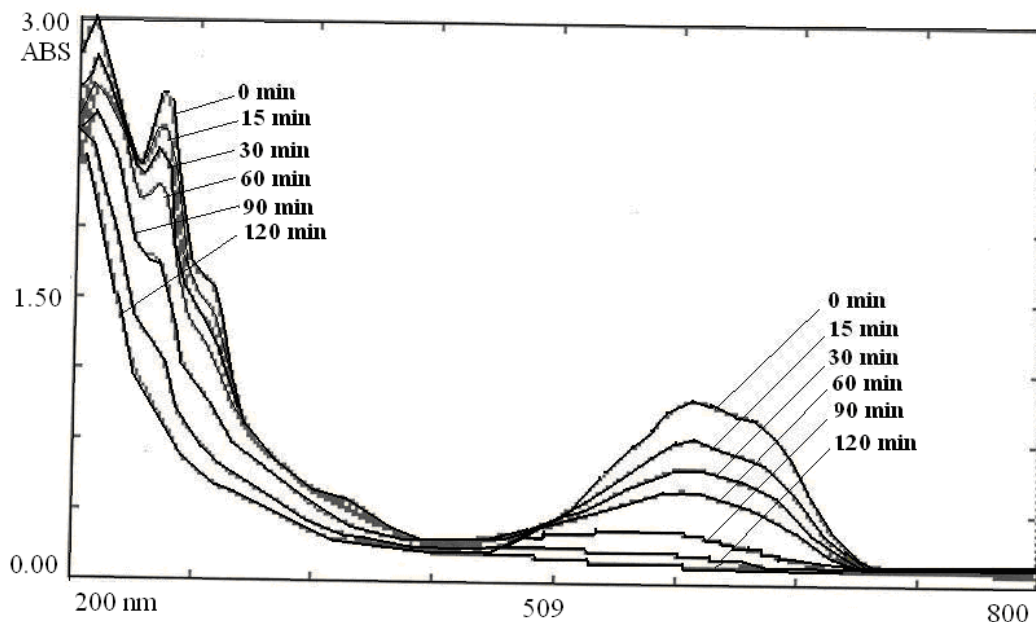
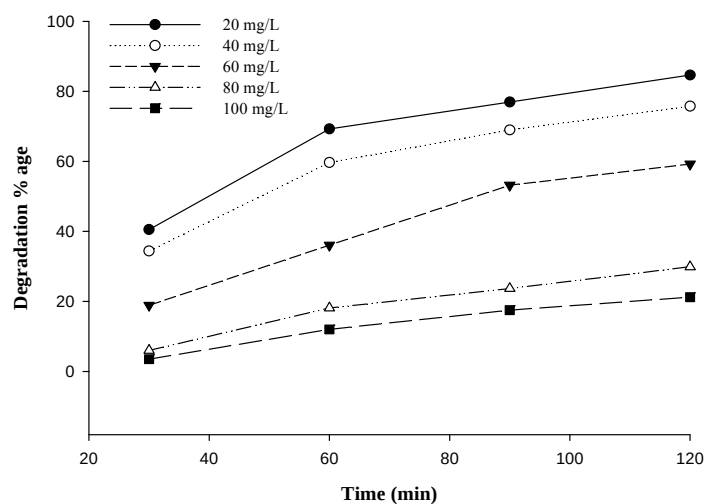


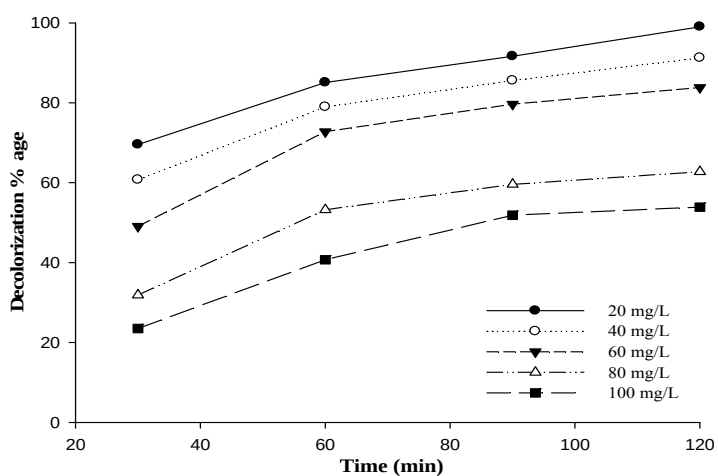
Figure 4.4: UV-Vis spectra during the sonoelectrochemical degradation of RB 19, Reaction conditions: initial pH = 8, US power = 240 W, dye concentration = 50 mgL^{-1}

4.2.5 Effect of Initial Dye Concentration

The effect of initial dye concentrations ($20\text{-}100 \text{ mgL}^{-1}$) on sonoelectrochemical process is also investigated under the conditions pH 8, ultrasonic power of 240 W for 120 min. It is observed that the extent of degradation decreased with the increase of initial dye concentration. The dye decolorization and degradation are inversely proportional to the dye concentration used in the experiment. The increase of RB 19 concentration from 20 to 100 mgL^{-1} decreased the degradation from 84.64% to 21.23% (Figure 4.5a) and decolorization from 99% to 53% (Figure 4.5b). The obtained results fits best with the results reported in literature (Mrowetz et al. 2003). Higher concentration of dye enhances the number of dye molecules, but not the $\cdot\text{OH}$ radical concentration so; the removal rate becomes slow (Mrowetz et al. 2003). However, with the increase in reaction time from 120 to 150 min, better degradation and decolorization is achieved for increasing dye concentration. In this experiment, for the degradation of 50 mgL^{-1} of RB 19 a reaction time of 120 min is sufficient.



(a)



(b)

Figure 4.5(a): Percentage degradation of RB 19 (b) Percentage decolorization of RB 19 by sonoelectrochemical process
 Reaction conditions: pH = 8, US power = 240 W, voltage = 10 volts

4.2.6 Effect of Reaction Time

The degradation and decolorization of dye using simple ultrasound and combined electrochemical/ultrasound process at the reaction time of 120 min was investigated. From the results it was found that, 54% of color removal and 39% of dye degradation was obtained by simple electrochemical process and 90% of color removal and 65% of

dye degradation was obtained using combined ultrasound and electrochemical process at the reaction time of 120 min. So the use of combined techniques enhances the removal efficiency as compared to individual technique at same reaction time of 120 min.

4.2.7 Kinetic Studies

Kinetic study for sonoelectrochemical degradation is undertaken by residual concentrations of RB 19 with the passage of time and measuring the rate constant (k) for first, second and third order reactions (Table 4.2). Kinetic measurements are performed as a function of RB 19 concentrations. Values of rate constant (k) for first, second and third order shows that the order of reaction within the current experimental conditions is of first order.

Table 4.2: Determination of rate constant (k) for various order of reaction

Concentrations (mgL ⁻¹)	Reaction time (min)	Ist order kinetics	2 nd order kinetics	3 rd order kinetics
20	30	0.02	0.1x 10 ⁻²	0.1 x 10 ⁻³
	60	0.02	0.2 x 10 ⁻²	0.3 x 10 ⁻³
	90	0.02	0.2 x 10 ⁻²	0.3 x 10 ⁻³
	120	0.02	0.3 x 10 ⁻²	0.6 x 10 ⁻³
40	30	0.02	0.6 x 10 ⁻³	4.1 x 10 ⁻⁸
	60	0.02	0.9 x 10 ⁻³	4.5 x 10 ⁻⁸
	90	0.02	0.9 x 10 ⁻³	4.5 x 10 ⁻⁸
	120	0.02	0.9 x 10 ⁻³	4.6 x 10 ⁻⁸

Reaction conditions: US power = 240 W, pH = 8

The order of reaction is confirmed by plotting the graph between $\ln (C_t/C_0)$ and time (Figure 4.6) at different initial concentrations, using first order rate equation.

$$\ln (C_t/C_0) = -kt \quad (4.2)$$

Where C = dye concentration at time t and 0 (mgL^{-1}), k = first order rate constant (min^{-1}) and T = reaction time in min (Fung et al. 2000).

The relationship between $\ln (C_t/C_0)$ and irradiation time is linear (straight line). This is a typical first order reaction plot (Figure 4.6). The slopes of the lines gives the clear rate constant (k). The regression coefficient R^2 obtained (Figure 4.6) for first order reaction at different concentrations of RB 19 is shown in (Table 4.3). The R^2 values ranged from 0.99 to 0.97, confirming that ultrasound assisted electrochemical degradation of RB 19 followed the first order reaction.

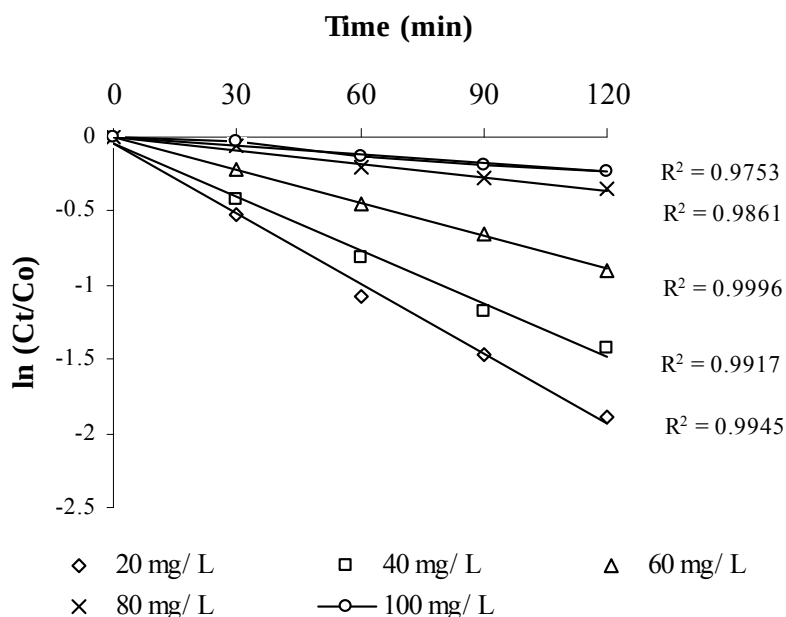


Figure. 4.6: First order kinetic plot of RB 19 degradation by sono-electrochemical process at different dye concentrations
 Reaction conditions: pH = 8, US power = 240 W, voltage = 10 volts, temperature = 25 °C, reactor volume = 1 L.

Carneiro et al. (2004) evaluated the dependence of initial degradation rate on the RB 4 dye concentration from slopes of the curves $\ln (A - A_\infty)$ as a function of time. The results obtained from his study showed that the curves of $\ln (A - A_\infty)$ vs. time are linear and the degradation followed a first order kinetic with a rate constant. The results

described in Figure 4.6 are in good agreement with those reported in literature (Kaur and Singh, 2007).

Table 4.3: Integrated rate law and Regression coefficient for first order reaction at different concentrations of RB 19

Conc. (mgL ⁻¹)	First order lnC = -k ₁ t + C'	R ²
20	lnC = - 0.47t + 0.42	0.994
40	lnC = -0.35t + 0.31	0.991
60	lnC = -0.22t + 0.23	0.999
80	lnC = -0.09t + 0.09	0.986
100	lnC = -0.06t + 0.06	0.975

Reaction conditions: US power = 240 W, pH = 8, Time = 120 min

4.2.8 Reduction of Half Life

In kinetic study half life for RB 19 of concentration 50 mgL⁻¹ is determine at different ultrasonic power settings. Table 4.4 shows the values of rate constant and half life at different ultrasonic power. It is seen from the table 4.4, that by increasing ultrasonic power from 0 to 240 W, half life is decreased 1/3 at power of 240 W as compared to 0 W power. The half life of RB 19 in natural environment is 46 years at pH 7 and at temperature of 25 °C which is equal to 23.8 x 10⁶ min but by applying ultrasonic power it decreases to 51.3 min. So by applying ultrasonic power the half life becomes reduced up to 21.5 million times.

As order for the RB 19 is first order, therefore following equation is used to determine the half life:

$$t_{1/2} = \ln 2/k \quad (4.3)$$

Table 4.4: The effect of Ultrasonic power on half life

Chemical kinetics	Ultrasonic power (W)			
	0	120	180	240
k (min⁻¹)	4.6 x 10 ⁻³	6.9 x 10 ⁻³	10 x 10 ⁻³	13.5 x 10 ⁻³
t_{1/2} (min)	149.4	99.3	68.1	51.3

Reaction conditions: Dye concentration = 50 mgL⁻¹, Time = 80 minutes, pH = 8

4.2.9 RB 19 Degradation Analysis

The results of degradation analysis of unhydrolyzed dye obtained by TOC analysis are presented in Table 4.5. It was observed that the heterogeneous nature of treatment (ultrasonic and electrochemical oxidation processes) permitted an overall TOC reduction of about 56% in 120 min. Individually, ultrasonic and electrochemical techniques caused 7.2% and 11.0% respective reduction of TOC after 120 min.

Table 4.5: Comparison of ultrasound, electrochemical and ultrasound assisted electrochemical processes for decolorization and reduction of the total organic carbon content of RB 19 dye

Process	Decolorization (%)	TOC reduction (%)	
		(Unhydrolyzed dye)	(hydrolyzed dye)
Ultrasound	13%	7.2%	-----
Electrochemical	52%	11.0%	-----
Ultrasound assisted electrochemical	90%	56.47%	81%

Reaction conditions: Dye concentration = 50 mgL⁻¹, US power = 240 W

In case of hydrolyzed dye solution containing 50 mgL⁻¹ of RB 19, the application of ultrasonic assisted electrochemical method results in 81% reduction in TOC in 120 min at pH 8. The enhancement in the mineralization of RB 19 by the effect of ultrasound can be explained by the increased mass transport of chemical species between the solution and electrodes surface and additional production of ·OH radicals by cavitation phenomenon (Bahena et al. 2008). Thus, it is again confirmed that a combination of ultrasonic and electrochemical processes is effective to decompose the RB 19. The

results obtained from TOC reductions of RB 19 from individual and heterogeneous treatments are in good agreement with the observations reported (Bahena et al. 2008). The overall comparison of TOC/TOC₀ ratio of hydrolyzed and unhydrolyzed RB 19 is presented in Figure 4.7.

However, further studies are required to determine the precise mechanism for the degradation of hydrolyzed and unhydrolyzed RB 19 dye by ultrasound assisted electrochemical process.

The products which are formed after the treatments of hydrolyzed and un-hydrolyzed dye are identified using GC-MS. Samples at different intervals (10, 15, 30, 45, 60, 90 and 120 min) are collected during the sonoelectrolysis of 400 mgL⁻¹ RB 19 at pH 8.0. The sample is extracted under alkaline conditions followed by acidic conditions using ethyl acetate (HPLC grade) in a separatory funnel. Each extraction is done several times and extract is dehydrated using anhydrous sodium sulfate. The solvent is removed under reduced pressure and the residual mass was analyzed by GC-MS.

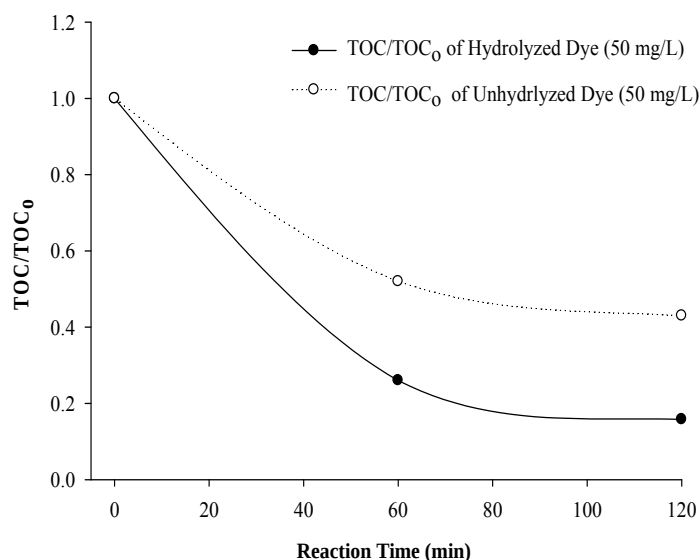


Figure 4.7: The relative changes in TOC removal of RB 19 at 120 min
Reaction conditions: dye concentration = 50 mgL⁻¹, pH = 8, voltage = 10 volts,
operating power = 240 W, temperature = 25 °C, reactor volume = 1 L

The degradation pathway is illustrated in Figure 4.8. In this process of oxidation the C(5)-C(6), C(13)-C(14), C(6)-C(7), C(12)-C(13), C(8)-N, C(9)-S, C(11)-N, C(17)-S, C(15)-N bonds are prone to cleave. In case of un-hydrolyzed dye the degradation took longer time. The only decomposed product observed after the treatment of 10 min is anthraquinone, formed after the cleavage of C(8)-N, C(9)-S, C(11)-N, along with the residuals of the dye. Treatment of 15 min results in the formation of isoindoline-1,3-dione, isobenzofuran-1,3-dione and 2,3-dihydronaphthalene-1,4-dione along with small dye fragments. The formation of these compounds is due to the cleavage of C(6)-C(7), C(12)-C(13) bonds. However, a treatment for 30 min results in the formation of products e.g. acetic acid, benzoic acid etc (Figure 4.8) with the complete removal of dye. Further treatment only results in the increased peak areas of acetic acid with the disappearance of the other compounds. Whereas, in case of hydrolyzed dye, the 10 min treatment proves to be enough and the results are comparable with the 30 min treatment of un-hydrolyzed dye.

Reactive Blue 19

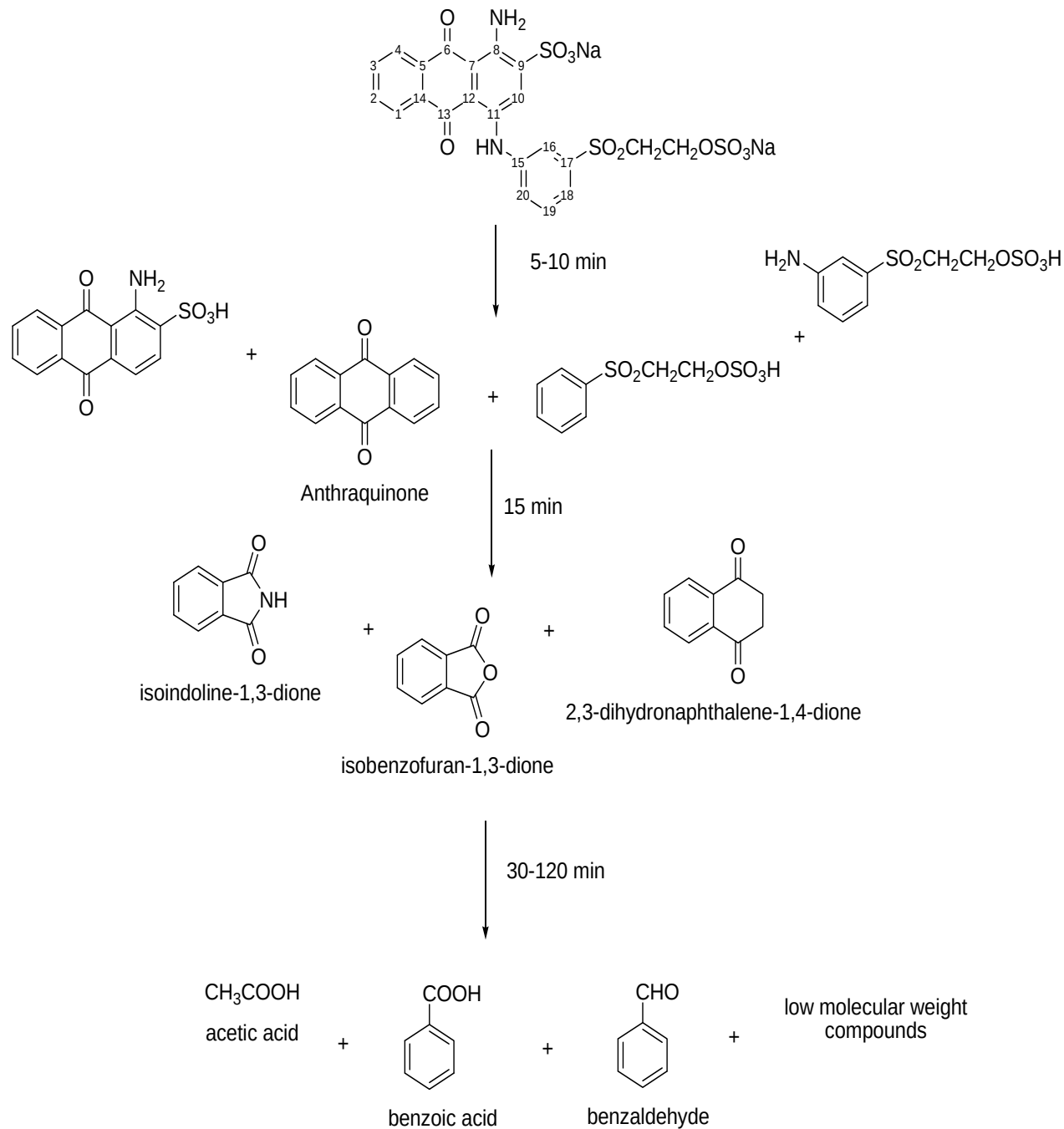


Figure 4.8: Proposed pathways of ultrasound assisted electrochemical degradation of RB 19 identified by GC-MS

Reaction conditions: initial pH = 8, US power = 240 W, dye concentration = 400 mgL⁻¹, voltage = 10 volts, temperature = 25 °C, reactor volume = 1 L

4.2.10 Energy Consumption of the Process

Electrical energy consumption was calculated according to the formula mentioned in section 3.5 (Azbar et al. 2004; Mahamuni et al. 2010). The relative energy consumptions for the degradation and decolorization of I L dye solution in the absence of ultrasonic technique or in combination of ultrasound and electrochemical methods are presented in Table 4.6. It is evident that the energy consumption is lower when combination of ultrasonic and electrochemical methods is used to treat RB 19. Moreover, the efficiency of the method in terms of percentage degradation/decolorization is also very high (almost double) as compared with the situation when alone electrochemical method is used. It is clear from Table 4.6 that energy consumption for degradation decreases from 1.20 to 0.75 kW h L⁻¹; moreover, percentage dye removal is increases from 39 to 65% with the increase of ultrasonic power (120 to 240 W) at reaction time of 120 min. In case of dye decolorization, energy consumption also decreases from 0.86 to 0.44 (kW h L⁻¹) and percentage color removal increases from 54 to 90% for same US power and reaction time. However dye degradation required more time and energy than the color removal.

Table 4.6: Comparison of electrical energy consumption with no ultrasonication and at different ultrasonic power setting during electrochemical process

Ultrasonic power (W)	Degradation		Decolorization	
	Energy Consumption (kW h L ⁻¹)	Removal %	Energy Consumption (kW h L ⁻¹)	Removal %
No ultrasonication	1.20	39	0.86	54
120	1.14	49	0.86	65
180	0.96	58	0.63	76
240	0.75	65	0.44	90

Reaction conditions: pH= 8, Time= 120 min

Chapter 5

Hydrolysis of RB 19

The percentage degradation, energy consumption, TOC removal, half life determination, kinetics and mechanism etc, for RB 19 dye is investigated by hydrolysis process in the present study. At high temperature and pressure, pure liquid water becomes surprisingly effective medium for the degradation of organic compounds. By increasing pressure the rate of chemical reaction increases due to increase in dissociation constant of water. Rapid conversions are observed for the majority of organic compounds (Robina et al. 2004). Also hydrolysis by-products are normally less toxic to the environment than parent compound (Mabey and Mill, 1978). Water at high temperature and pressure simultaneously acts as a solvent, catalyst and reagent for reactions that are typically catalyzed by acids or bases. By this process very selective transformations are accessible by reactions in pure, hot water without using toxic and environmentally destructive materials (Siddique et al. 2009). The aim of this study is to explore the hydrolysis of RB 19 at different conditions of temperatures and pressures. The hydrolytic study is divided in to two categories i.e. atmospheric pressure and high pressure hydrolysis. The hydrolytic process is carried out setting different parameters (pH, dye concentration, temperatures and pressures. Under optimum conditions of temperature and pressures degradation kinetics and reaction mechanism is investigated. The intermediates and end products are identified and a possible degradation pathway is proposed.

5.1 Effect of pH

The effect of pH under atmospheric pressure and high pressure hydrolysis were investigated and detail of experiments conducted is given below.

5.1.1 Under Atmospheric Pressure

The degradation and decolorization of 50 mgL⁻¹ of RB 19 at different pH conditions (2, 4, 6, 8 and 10) and temperatures (40 °C, 60 °C, 80 °C and 100 °C) during atmospheric pressure hydrolysis are investigated. To study the degradation and decolorization rate, the procedure given in section 3.3.2 is adopted.

Table 5.1: Residual concentration and percentage degradation of RB 19 at different conditions of temperature during atmospheric pressure hydrolysis

Time (min)	pH									
	2		4		6		8		10	
	RC	%D	RC	%D	RC	%D	RC	%D	RC	%D
T = 40 °C										
30	49.93	0.13	48.44	3.12	49.61	0.79	49.82	0.35	49.87	0.25
60	49.84	0.31	48.35	3.29	49.52	0.96	49.69	0.60	49.74	0.51
90	49.76	0.48	48.26	3.46	49.43	1.14	49.56	0.87	49.62	0.76
120	49.67	0.69	48.18	3.63	49.34	1.31	49.43	1.13	49.49	1.01
T = 60 °C										
30	48.98	2.03	48.85	2.30	49.20	1.59	49.75	0.49	49.15	1.70
60	48.62	2.76	48.43	3.13	49.11	1.77	49.58	0.82	48.06	3.88
90	48.42	3.15	47.76	4.47	49.05	1.90	49.34	1.31	47.94	4.12
120	47.75	4.49	47.51	4.99	48.96	2.08	49.14	1.73	47.94	4.11
T = 80 °C										
30	46.84	6.32	46.42	7.15	49.12	1.75	49.31	1.38	49.11	1.77
60	46.79	6.40	45.78	8.44	48.97	2.04	49.06	1.88	48.02	3.96
90	46.38	7.23	45.31	9.36	48.72	2.56	48.81	2.38	47.79	4.41
120	46.12	7.74	45.01	9.96	48.36	3.28	48.45	3.09	47.75	4.49
T = 100 °C										
30	46.08	7.84	45.82	8.34	48.50	2.99	48.57	2.84	48.02	3.94
60	45.64	8.71	45.20	9.59	47.83	4.34	48.01	3.97	47.84	4.31
90	45.44	9.10	44.75	10.49	47.36	5.27	47.67	4.64	47.16	5.68
120	44.96	10.06	44.24	11.52	47.04	5.91	47.55	4.89	46.89	6.20

Reaction conditions: Initial Concentration of dye = 50 mgL⁻¹

Note: **RC = Residual Concentration and %D = Percentage Degradation**

Table 5.2: Percentage decolorization of RB 19 at different conditions of temperature during atmospheric pressure hydrolysis

Time (min)	2	4	pH 6	8	10
T = 40 °C					
30	1.53	4.08	0.87	0.63	0.80
60	2.35	6.60	0.76	1.26	1.49
90	3.30	7.86	3.38	2.10	2.42
120	4.00	9.11	3.81	2.95	3.11
T = 60 °C					
30	5.34	5.67	1.47	0.69	1.75
60	6.48	9.62	3.79	1.66	3.25
90	7.63	14.07	4.77	2.77	4.38
120	8.78	17.03	5.75	3.60	5.75
T = 80 °C					
30	7.18	12.02	2.37	3.70	5.11
60	14.36	18.03	4.71	7.67	7.93
90	17.95	33.88	5.76	11.11	9.85
120	25.13	36.61	9.69	13.22	11.76
T = 100 °C					
30	26.24	28.93	5.35	3.63	7.21
60	39.59	44.91	8.82	7.01	9.45
90	43.43	48.61	16.31	9.35	14.68
120	46.15	53.24	17.38	12.72	16.41

Reaction conditions: Initial Concentration of dye = 50 mgL⁻¹

The percentage residual concentration, degradation and decolorization at different temperatures, 1 atm pressure and pH values (table 5.1 and 5.2) are studied.

5.1.2 Under High Pressure

To determine the degradation and decolorization of 50 mgL⁻¹ of RB 19, experiments for high pressure hydrolysis (2 atm) are also conducted at different pH conditions (2, 4, 6, 8 and 10) and at 120 °C temperature. The table 5.3, 5.4 and 5.5 shows the percentage residual concentration, percentage degradation and percentage decolorization at 120 °C temperatures, 2 atm pressure and different pH values.

Table 5.3: Residual concentration of RB 19 at 120 °C during high pressure hydrolysis

Time (min)	2	4	pH 6	8	10
T = 120 °C, P = 2 atm					
30	45.96	45.79	47.75	47.95	47.05
60	43.91	43.69	45.87	46.91	45.95
90	41.97	41.21	44.78	45.01	44.85
120	39.92	39.12	43.98	44.06	43.22

Reaction conditions: Initial Concentration of dye = 50 mgL⁻¹

Table 5.4: Percentage degradation of RB 19 at 120 °C during high pressure hydrolysis

Time (min)	2	4	pH 6	8	10
T = 120 °C, P = 2 atm					
30	8.06	8.41	4.49	4.08	5.89
60	12.17	12.60	8.26	6.18	8.09
90	16.04	17.58	10.42	9.98	10.29
120	20.14	23.76	12.03	11.88	13.54

Reaction conditions: Initial Concentration of dye = 50 mgL⁻¹

Table 5.5: Percentage decolorization of RB 19 at 120 °C during high pressure hydrolysis

Time (min)	2	4	pH 6	8	10
T = 120 °C, P = 2 atm					
30	28.87	31.05	5.41	4.73	5.93
60	47.37	48.28	13.65	8.92	10.68
90	59.30	61.47	23.00	27.84	20.17
120	73.15	74.39	30.26	38.38	30.86

Reaction conditions: Initial Concentration of dye = 50 mgL⁻¹

From the tables 5.3, 5.4 and 5.5, it is found that the degradation and decolorization rate of the dye under investigation at atmospheric and high pressure is highly influenced by the reaction pH (Figure 5.1). A significant increase ($p < 0.05$) in the percentage degradation and decolorization of dye is observed with the increasing pH and the highest value is obtained up to pH 4. A further increase in pH above 4 caused a decrease in the degradation rate. It seems that the hydrolytic reaction might be catalyzed by hydronium ions in acidic medium. Since hydrogen ions (H^+) are not consumed during hydrolysis and just act as a catalyst, so they act as a better catalyst as compared to OH^- for the conversion of RB 19 into inorganic compounds (Robina et al. 2008, Siddique et al. 2009). Moreover, the H^+ ions not only act as catalysts but also enhance the electro negativity of the leaving group in acidic conditions, which helps in breaking of the bonds in the RB 19. Thus, the rate of hydrolysis continues to increase with increasing H^+ ion concentrations (Robina et al. 2004). The present experiment has an interesting observation that hydrolytic rate does not increase further when pH is lowered below 4. Insignificant difference for dye degradation is observed for pH 2 and 4, but the pH 4 is considered as optimum experiment. These results are in good agreement with Rajkumar et al. (2007).

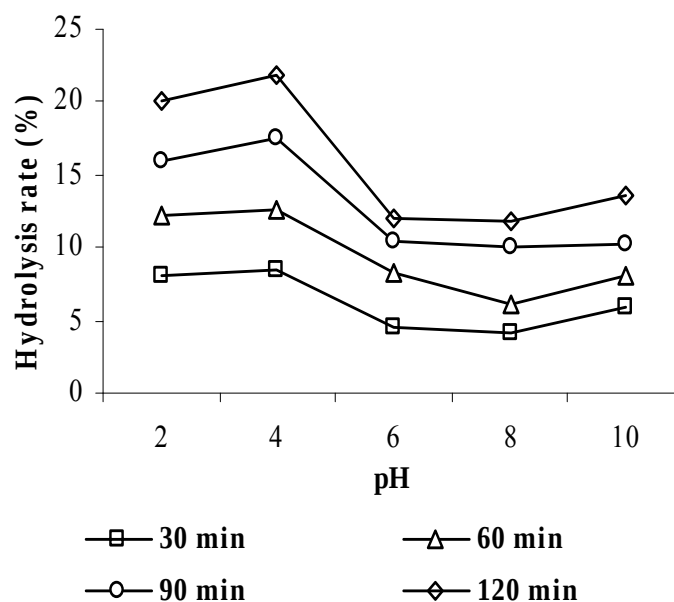


Figure 5.1: Effect of pH on the hydrolysis of RB 19 under high pressure

5.2 Effect of Temperature and Pressure

As the temperature and pressure are increased from 40 °C to 120 °C and from 1 to 2 atmospheric pressure, the rates of degradation are also significantly ($p < 0.05$) increased at different pH conditions (Figure 5.2 a-e). Water provides more suitable and favorable reaction medium for organics by increasing pressure and temperature. With the increase in temperature from 40 to 120 °C, the ionic product (dissociation constant) of water increases and the dielectric constant of water falls rapidly. These changes in the physical properties alter the solvent properties of water (Robina et al. 2004).

At high temperature and pressure, water acts simultaneously as a convenient solvent, catalyst and reagent for reactions that are typically catalyzed by the acid or base. The chances of pollution are also less thus it is an environmental friendly process of treating the organic compounds.

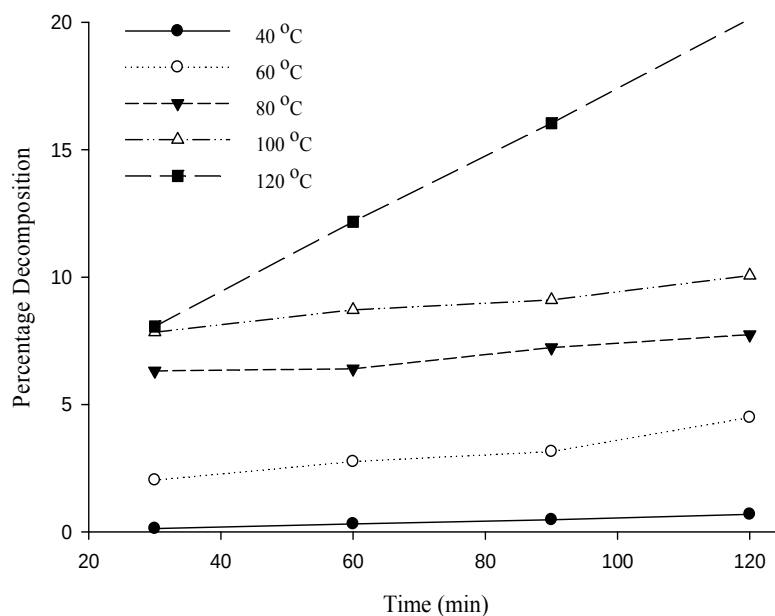


Figure 5.2 (a): Effect of temperature on the percentage degradation of RB 19 at pH 2

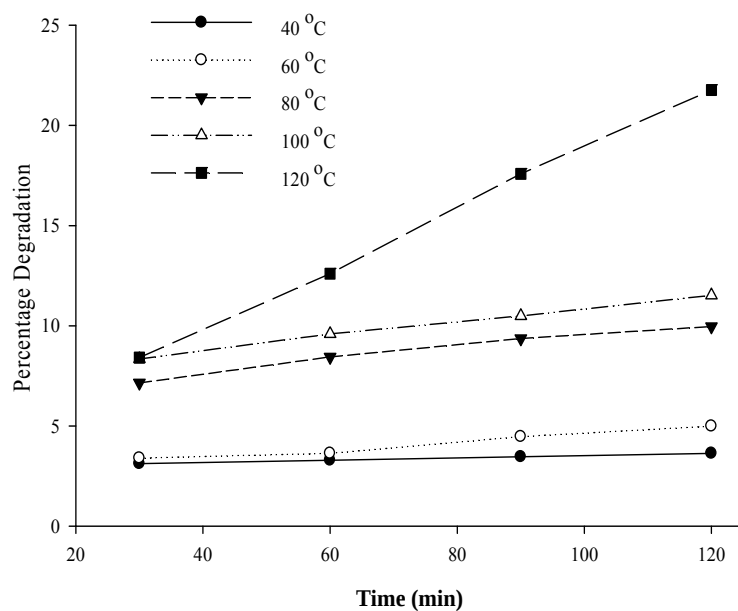


Figure 5.2 (b): Effect of temperature on the percentage degradation of RB 19 at pH 4

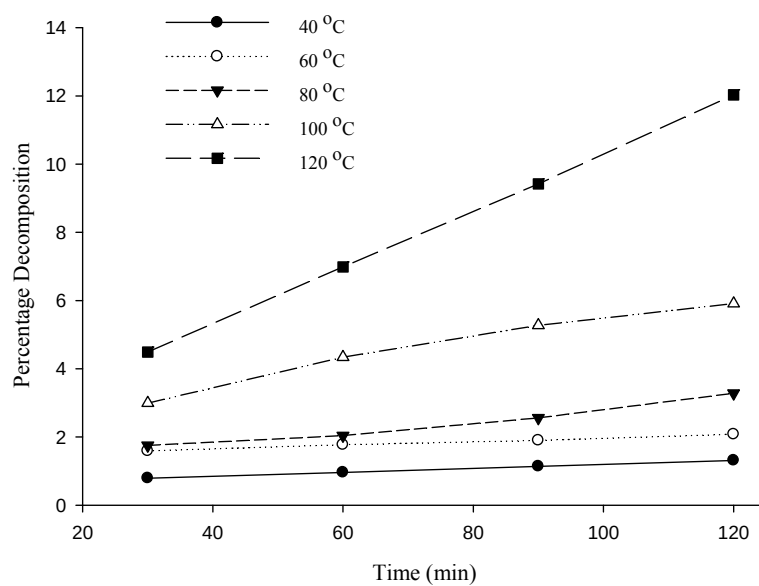


Figure 5.2 (c): Effect of temperature on the percentage degradation of RB 19 at pH 6

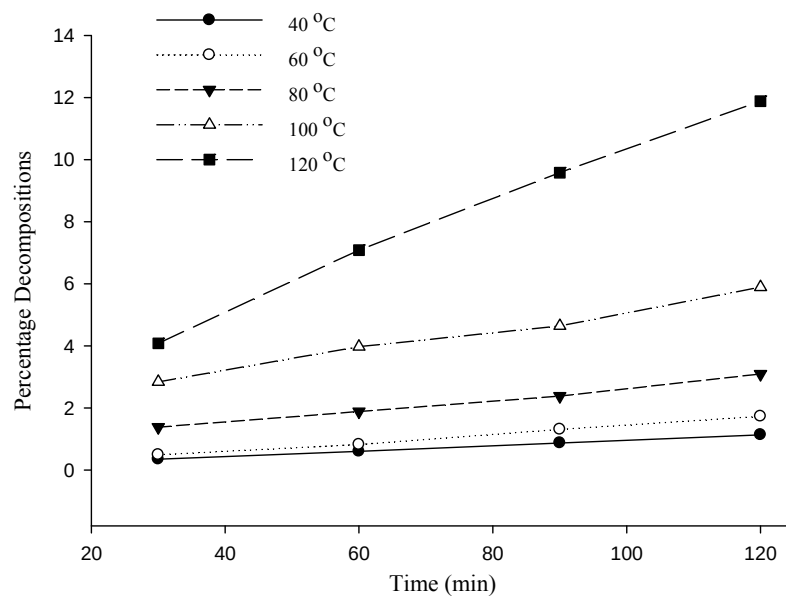


Figure 5.2 (d): Effect of temperature on the percentage degradation of RB 19 at pH 8

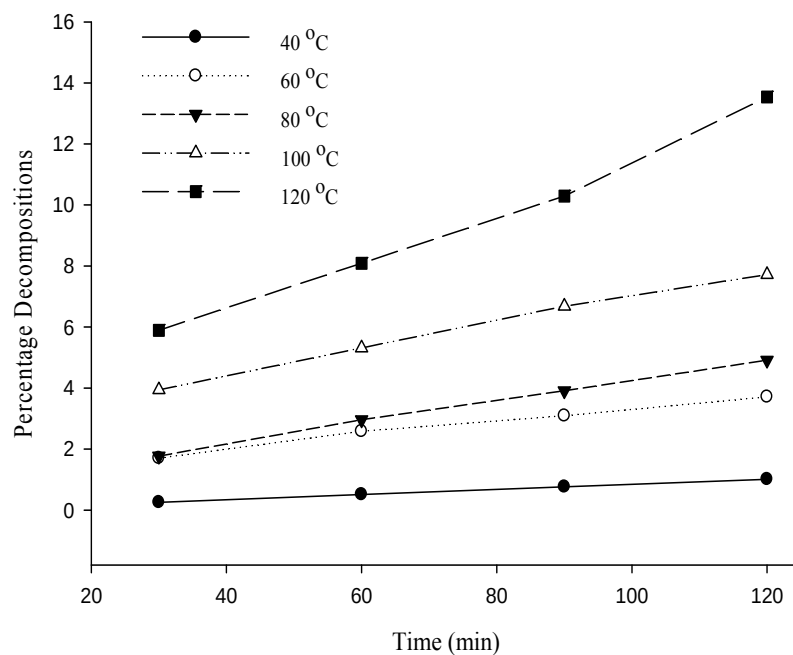


Figure 5.2 (e): Effect of temperature on the percentage degradation of RB 19 at pH 10

5.3 Degradation Kinetics of RB 19 at Atmospheric and High Pressure

Under different conditions of temperatures (40, 60, 80, 100 and 120 °C) and 1 to 2 atmospheric pressures the order of reaction is determined. A graph between the reciprocal of remaining dye concentrations against time at pH values 2-10 are plotted. The dye degradation apparently follows 1st order of kinetics (Fung et al. 2000) (Figure 5.3 and 5.4).

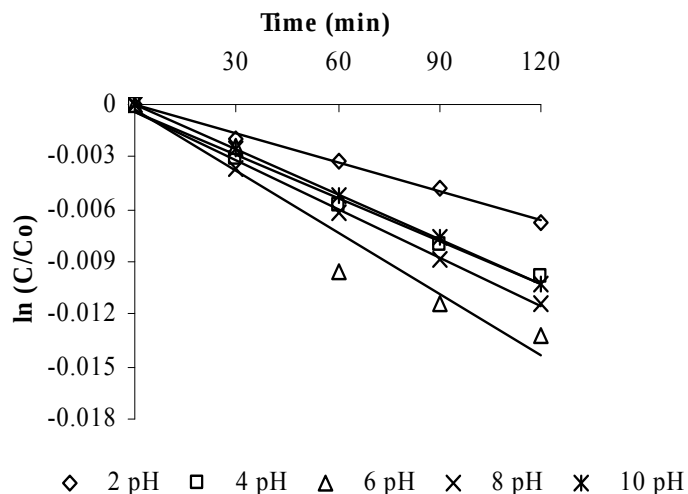


Figure 5.3: Determination of order of reaction at 40 °C

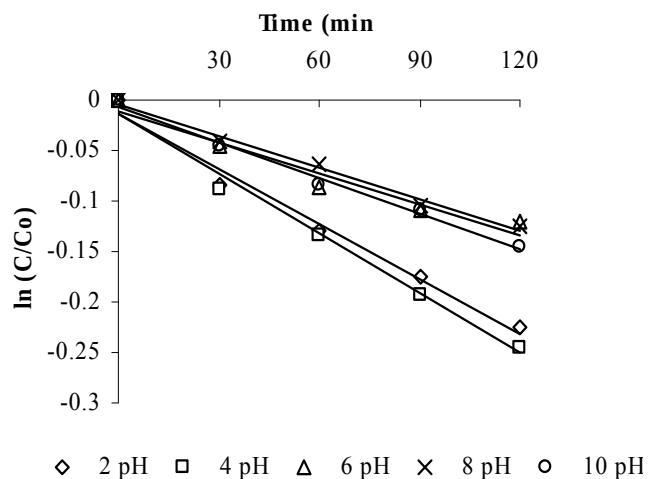


Figure 5.4: Determination of order of reaction at 120 °C

The degradation kinetics is determined for different RB 19 concentrations for various time intervals, temperatures and pressures (Table 5.6). Values of rate constant (k) for first, second and third order showed that the reaction follows first order for various experimental conditions under investigation.

Table 5.6: Determination of rate constant (k) for various order of reaction

Concentrations (mgL ⁻¹)	Reaction time (min)	1 st order kinetics	2 nd order kinetics	3 rd order kinetics
50	30	0.04	0.1×10^{-3}	0.3×10^{-5}
	60	0.04	0.1×10^{-3}	0.2×10^{-5}
	90	0.04	0.1×10^{-3}	0.2×10^{-7}
	120	0.04	0.1×10^{-3}	0.2×10^{-5}
100	30	0.04	0.7×10^{-4}	0.5×10^{-3}
	60	0.039	0.6×10^{-4}	0.5×10^{-6}
	90	0.04	0.5×10^{-4}	0.5×10^{-6}
	120	0.04	0.6×10^{-4}	0.3×10^{-4}

Reaction conditions: Temperature: 120 °C, Pressure: 2 atm, pH : 4

The order of reaction is confirmed by plotting the graph between the $\ln (C_t/C_0)$ against time (Figure 5.5) at different initial concentrations, by employing first order rate equation.

$$\ln (C_t/C_0) = -kt \quad (5.1)$$

Where, C = the dye concentration (mgL⁻¹) at time t and 0, k = first order rate constant (min⁻¹) and T = reaction time in minutes (Kaur and Singh, 2007).

The correlation between $\ln (C_t/C_0)$ and treatment time is linear (straight line). This is a typical first order reaction plot (Figure 5.5). The slopes of the lines show the apparent rate constant (k). The regression coefficient R² obtains (Figure 5.5) for first order reaction at different concentrations of RB 19 is shown in (Table 5.7). The R² values ranges from 0.999 to 0.995, confirming that hydrolysis of RB 19 follows the first order reaction.

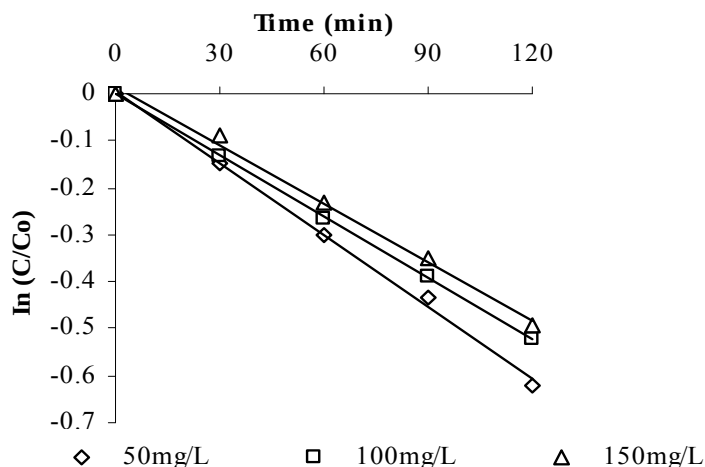


Figure 5.5: First order kinetic plot of RB 19 degradation by hydrolysis process at different concentrations at 120 °C

The reaction kinetics describes the reaction rates while the reaction order defines the dependence of the reaction rate on the concentrations of reacting species. The reaction order is determined experimentally and not necessarily related to the stoichiometry of the reaction. However, it is governed by the mechanism of the reaction, that is, by the number of chemical species that must collide for the reaction to occur (Zainal et al. 2006). The reaction rate for first order kinetics depends on one specie i.e. RB 19 alone. Thus the mechanism involved in the Thermal-pressure hydrolysis of RB 19 is the first order reaction.

Table 5.7: Integrated rate law and Regression coefficient for first order reaction at different concentrations of RB 19

Concentration mgL ⁻¹	First order lnC = -k ₁ t + C'	R ²
50	lnC = - 0.15t + 0.16	0.99
100	lnC = -0.13t + 0.13	0.99
150	lnC = -0.12t + 0.14	0.99

Reaction conditions:: Temperature: 120 °C, Pressure: 2 atm

5.4 Half Life Reduction

Increasing temperature from 40-120 °C results in the significant ($p < 0.05$) decrease of half life. At pH 4, half life is 2247.5 min at 40 °C which reduces to 339.4 min when the temperature is increased to 120 °C. The values of rate constant and half life at different temperatures and pH 4 are shown in (Table 5.8). Because the reaction order for the RB 19 degradation is first order, therefore following equation is used to determine the half life.

$$t_{1/2} = \ln 2/k \quad (5.2)$$

Half life has been calculated for the degradation of organophosphorous pesticides, under natural conditions and under high temperatures and pressures. It was found that half-life decreased with increasing temperatures and pressures (Robina et al. 2004 and 2008). It is apparent from above discussion that thermal-pressure mediated hydrolysis is very effective in degradation of RB 19 in synthetic dye solution.

Table 5.8: Effect of different conditions of Temperature on half life reduction

Chemical kinetics	Temperature °C				
	40	60	80	100	120
k (min⁻¹)	0.31 x 10 ⁻³	0.42 x 10 ⁻³	0.87 x 10 ⁻³	1.02 x 10 ⁻³	2.04 x 10 ⁻³
t_{1/2} (min)	2247.5	1630.5	792	681.6	339.4

Reaction conditions:: Dye concentration = 50 mgL⁻¹, Time = 120 min, pH = 4

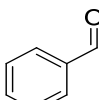
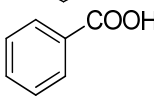
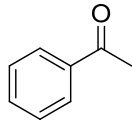
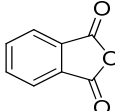
5.5 Total Organic Carbon Reduction

The most common way of estimating the dye degradation is to monitor the reduction of TOC. In this experiment, almost 32.8% TOC reduction is attained from the treated samples under following optimized conditions: dye concentration 50 mgL⁻¹, initial pH 4, temperature 120 °C, pressure 2 atm and reaction time 120 min. The reduction in TOC indicated the loss of reactive group during the reduction process. Although considerable reduction of TOC (32%) is obtained which is comparable to previous studies (Ronaldo et al. 1999; Rajkumar et al. 2007; Shuang et al. 2008) however, it is also noted that dye hydrolysis takes longer time compared with previous studies.

5.6 Identification of Degraded Products

The products which are formed during the degradation of RB 19 were identified by GC-MS as shown in Table 5.9. Samples at different intervals are collected during the high pressure hydrolysis of 500 mgL⁻¹ RB 19 at pH 4.0. The sample is extracted under alkaline conditions followed by acidic conditions using ethyl acetate (HPLC grade) in a separatory funnel. Each extraction is done several times and extract was dehydrated using anhydrous sodium sulfate. The solvent is removed under reduced pressure and the residual mass is analyzed by GC-MS. The degradation pathway is proposed and illustrated in Figure 5.6. In this process of oxidation the C(5)-C(6), C(13)-C(14), C(6)-C(7), C(12)-C(13), C(8)-N, C(9)-S, C(11)-N, C(17)-S, C(15)-N bonds are prone to cleave. The treatment of dye after 10 min showed the formation of benzaldehyde, acetophenone, benzoic acid and isoindoline-1,3-dione. Benzaldehyde is formed through the cleavage of C(6)-C(7) and C(13)-C(14), whereas benzoic acid is formed after the oxidation of benzaldehyde. The isobenzofuran-1,3-dione may be formed after the cleavage of C(6)-C(7) and C(12)-C(13) bonds. The compounds identified after 20 min treatment are similar except the appearance of acetic acid peak and disappearance of isoindoline-1,3-dione. The samples at 30 min show the presence of benzaldehyde, acetic acid, and newly appeared oxalic acid peak. The formation of oxalic acid and acetic acid results from the ring cleavage and its further oxidation is also evident by the products determined after the final treatment for 120 min.

Table 5.9: Intermediates identified by GC-MS analysis

Table S.3: Intermediates identified by GC-MS analysis							
Compounds	Structure	Time (min)					
		10	20	30	45	60	120
Benzaldehyde		P	P	P	A	A	A
Benzoic acid		P	A	A	P	P	A
Acetophenone		P	A	A	A	A	A
Isobenzofuran-1,3-dione		P	A	A	A	A	A
Acetic acid	CH ₃ COOH	A	P	P	P	P	P
Oxalic acid		A	A	P	P	P	P

*P = present, A = absent

Reaction conditions: Dye concentration = 500 mgL⁻¹, Temperature = 120 °C, Pressure = 2 atm, pH= 4

RB 19

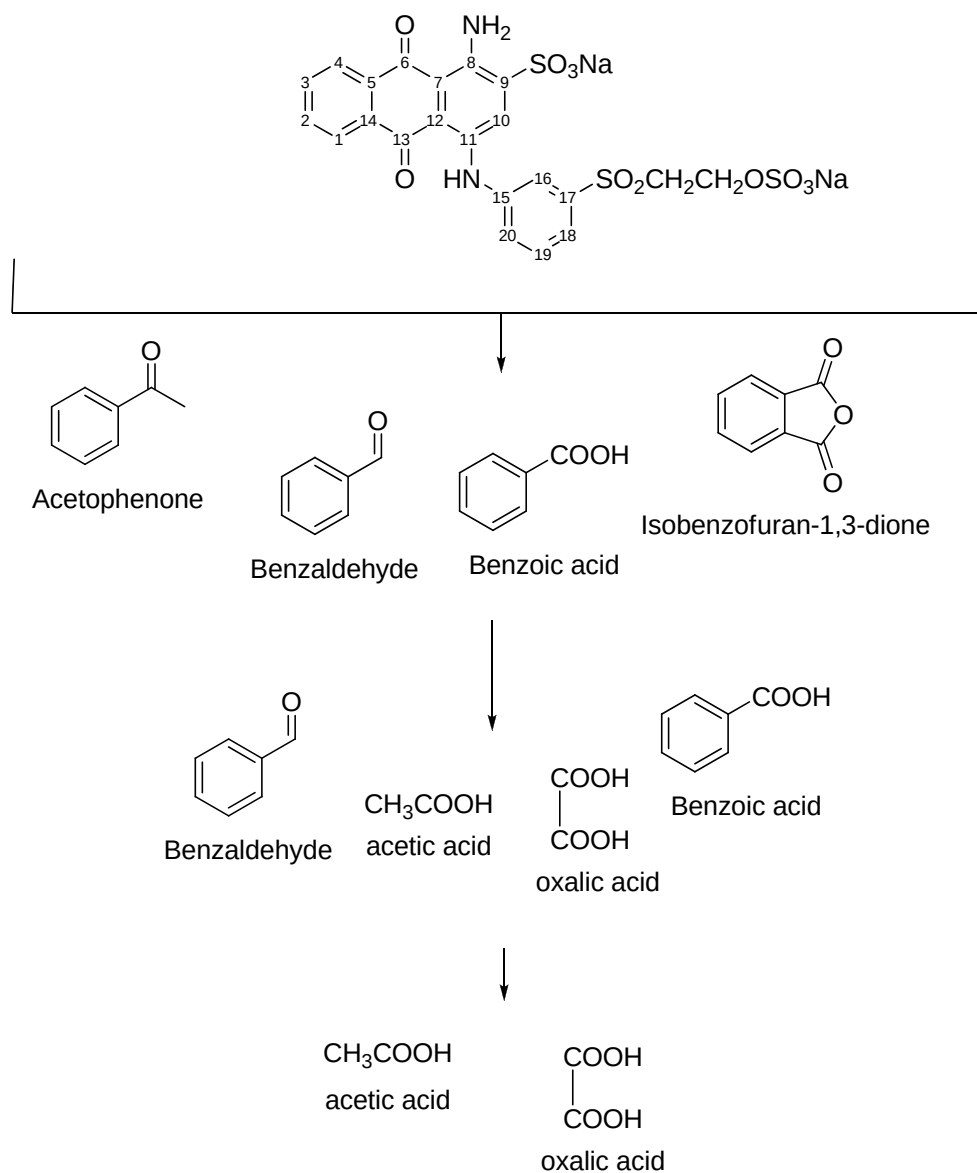


Figure 5.6: Proposed degradation path way of RB 19 by thermal pressure mediated hydrolysis, Reaction conditions: pH = 4, conc. = 500 mgL⁻¹, temp = 120 °C, pressure = 2 atm

5.7 Decolorization of RB 19

It is observed that a maximum of 31% decolorization take place with first 30 min of treatment (Table 5.10). GC-MS results show that RB 19 break into benzaldehyde, benzoic acid, acetophenone, isobenzofuron-1, 3-dione by the cleavage of its chromophores within first 30 min which might have caused decolorization within this time period. Moreover, the benzoic acid, acetophenone and isobenzofuron-1, 3-dione is decomposed into either acetic acid or oxalic acid that might have resulted in decolorization. However, ultimate decolorization occurred is 74 % due to RB 19 degradation after 120 min.

Table 5.10: Percentage decolorization (%) of RB 19 at pH 4

Time (min)	Percentage Decolorization
30	31.05
60	48.28
90	61.47
120	74.39

Reaction conditions: Dye concentration = 50 mgL⁻¹, Temperature = 120 °C and Pressure =2 atm

5.8 Effect of Hydrogen Peroxide

An important parameter which effects the degradation of RB 19 is hydrogen peroxide addition. Therefore it is very important to study the effect of hydrogen peroxide concentration to determine the optimum doze of hydrogen peroxide for the effective decolorization. Experiments are conducted by changing the concentration of hydrogen peroxide from 0.5 to 3.0 mL⁻¹ (Figure 5.7). From the results it is found that the best oxidant dosage is 2ml L⁻¹. So, further experiments are conducted by using the optimum dose of hydrogen peroxide.

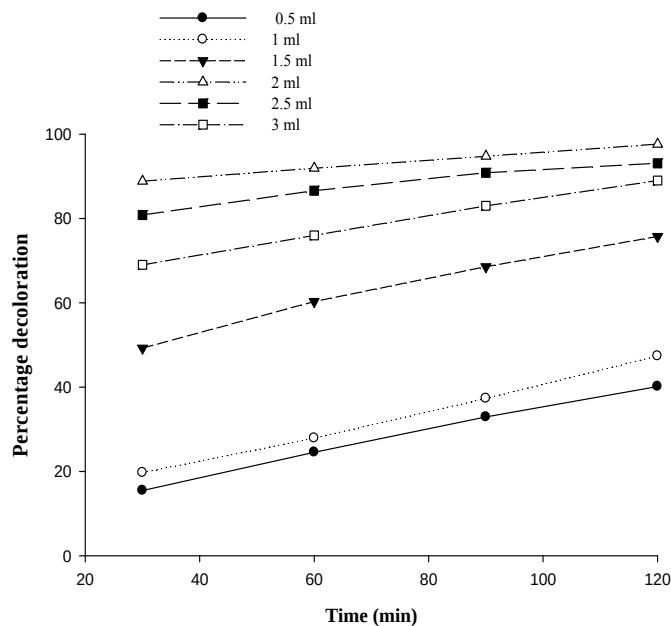


Figure 5.7: Effect of H₂O₂ addition on the decolorization of RB 19

The addition of hydrogen peroxide to the solution increases the concentration of $\cdot\text{OH}$ radicals, thus enhancing the decolorization of organic dyes. From the figure 5.7, it is concluded that the addition of hydrogen peroxide is effective for the degradation of RB 19, upon further addition from 2.0 to 3.0 ml L⁻¹; the rate of decolorization is reduced. Possibly it is due to the saturation of $\cdot\text{OH}$ radicals in the solution. Therefore further addition of hydrogen peroxide failed to enhance the reaction. Moreover at high concentration of hydrogen peroxide it also acts as a scavengers as shown in Eq. 5.3 and 5.4 (Kaur, 2007).



5.8.1 Effect of Oxidant (H₂O₂) at High Pressure

The degradation of 50 mgL⁻¹ of RB 19 at different pH conditions (2, 4, 6, 8 and 10), at temperature 120 °C, pressure 2 atm and reaction time 120 min and with optimum concentrations (Figure 5.7) of hydrogen peroxide is investigated. The tables 5.11, 5.12

and 5.13 show the residual concentration, percentage degradation and percentage decolorization at different pH values and 120 °C temperature.

Table 5.11: Residual concentration of RB 19 at 120 °C during degradation with hydrogen peroxide

Time (min)	2	4	pH 6	8	10
T = 120 °C, P = 2atm					
30	39.75	40.76	42.79	43.32	42.06
60	35.61	37.71	38.99	39.77	37.96
90	31.43	33.53	34.89	35.52	33.12
120	27.82	29.92	31.59	33.61	30.58

Reaction conditions: Initial Concentration of dye = 50 mgL⁻¹

Table 5.12: Percentage degradation of RB 19 at 120 °C during degradation with hydrogen peroxide

Time (min)	2	4	pH 6	8	10
T = 120 °C, P = 2atm					
30	18.49	19.73	14.42	13.37	15.87
60	24.57	27.90	22.01	20.45	24.07
90	32.93	35.34	30.21	28.96	33.77
120	40.15	47.38	36.82	32.78	27.28

Reaction conditions: Initial Concentration of dye =50 mgL⁻¹

Table 5.13: Percentage decolorization of RB 19 at 120 °C during degradation with hydrogen peroxide

Time (min)	2	4	pH 6	8	10
T = 120 °C, P = 2atm					
30	87.83	88.83	33.25	16.88	17.16
60	92.59	91.94	60.30	25.25	18.95
90	93.85	94.77	72.57	31.13	27.26
120	95.11	96.61	75.73	39.12	34.84

Reaction conditions: Initial Concentration of dye =50 mgL⁻¹

From the tables 5.11, 5.12 and 5.13, it is found that rate of dye degradation and decolorization under investigation by high pressure hydrolysis is highly influenced by hydrogen peroxide. The addition of hydrogen peroxide enhanced the chemical reaction and the rates of degradation and decolorization increased with the addition of optimum

dose of hydrogen peroxide concentration. The degradation rate is highest at pH 4 and the dye is 96.61% decolorized. This is due to the presence of hydroxyl radicals in the sample which are very stable and when activated reduce the decolorization and enhance the degradation. The hydroxyl radicals from hydrogen peroxide and water at high temperature and pressure provided an excellent medium for the reaction. Hydrogen peroxide is a strong oxidizing agent and also used as a bleaching source in the textile industries. As hydrogen peroxide radicals work as a strong bleaching agent and are being used in the industries so extra chemical is not added in this process but hydrogen peroxide already added in the process of dyeing is used to decompose and decolorize the dye effluent.

5.9 UV-Visible Absorption Spectral Changes

The changes in the absorption spectra (both at UV and visible regions with respective wavelengths of 256 nm and 594 nm) at various time intervals during high pressure hydrolysis of RB 19 are found and present in Figure 5.8. It is obvious that both the dye decolorization and degradation of is achieved at 120 min of high pressure hydrolysis for 50 mgL^{-1} of dye concentration.

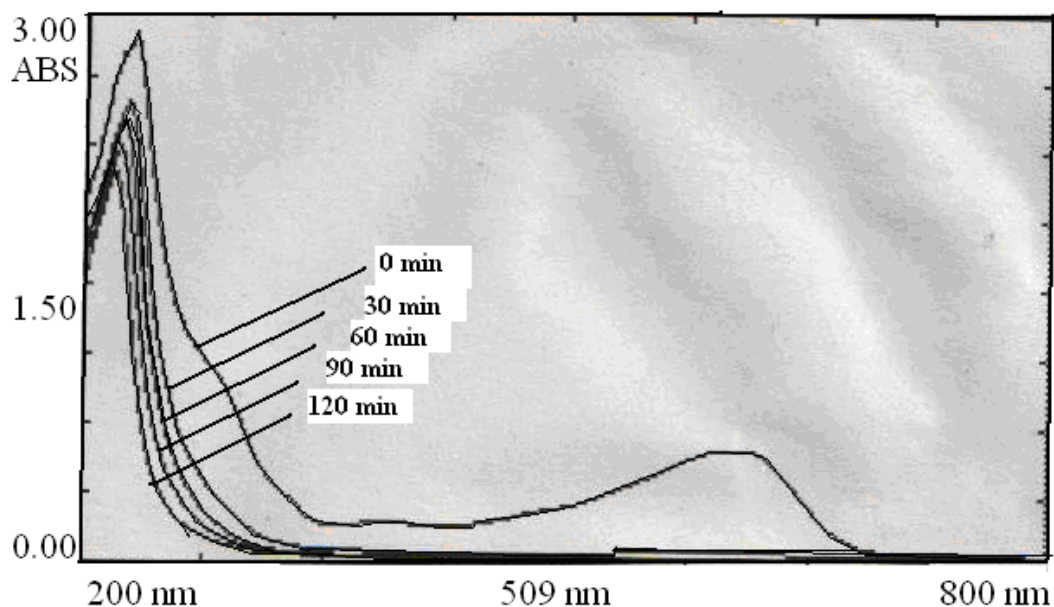


Figure 5.8: UV-Visible spectra during the high pressure hydrolysis of RB 19
 Reaction conditions: initial pH = 4, temperature = 120°C , pressure = 2 atm,
 conc. = 50 mgL^{-1} , H_2O_2 conc. = 2 ml L^{-1}

5.10 Electrical Energy Consumption

The energy consumption for the degradation of RB 19 at different conditions of temperatures and pressures and with the addition of optimized H₂O₂ dosage is presented in Table 5.14. It is clear from the results that the energy consumption is lowered when hydrogen peroxide is used at 120 °C temperatures and at 2 atm pressure. Also it is clear that energy consumption is gradually decrease from 285.7 to 20.6 kW h L⁻¹. Moreover, percentage dye removal is increase from 3.63 to 47.38% with the increase of temperatures from 40 to 120 °C and with addition of hydrogen peroxide at reaction time of 120 min.

Table 5.14: Comparison of electrical energy consumption at different conditions of temperature and pressure during hydrolysis of RB 19

Temperature (°C)	Degradation	
	EC (kW h L ⁻¹)	% Removal
40	285.71	3.63
60	209.0	4.99
80	102.2	9.96
100	86.8	11.52
120	43.4	21.76
120/H ₂ O ₂	20.6	47.38

Reaction conditions:: dye concentration = 50 mgL⁻¹, Pressure = 2 atm, Time =120 min, pH= 4, H₂O₂ conc. = 2ml L⁻¹

Chapter 6

Sonophotocatalytic Degradation of RB 19

The sonochemical effect is based upon the ultrasonic propagation of a pressure wave in aqueous solution, which leads to the formation of cavitation bubble phenomenon, i.e. nucleation, growth and collision of micro bubbles in the liquid. These bubbles collisions bring about localized supercritical conditions of high pressure and temperature. The extreme conditions further resulted in the cleavage of water molecules to produce hydrogen and hydroxyl radicals as a consequence (Kotronarou et al. 1991; Suslick, 1998). Heterogeneous photocatalysis process consists of utilizing the near UV radiation to photo-excite a semiconductor catalyst. Under these conditions $\cdot\text{OH}$ or free holes are generated. It is found that heterogeneous photocatalysis and ultrasonic irradiation can cause degradation of organic pollutants in water by the same species i.e. $\cdot\text{OH}$ radicals (Serpone et al. 1994). This chapter deals with the photocatalytic and sono-photocatalytic degradation of RB 19 in the presence of catalyst, UV light and ultrasonic power in a photo reactor. Effect of different operational parameters like pH, catalyst dosage and initial dye concentrations is studied to determine the optimized conditions for degradation. Under optimized conditions the degradation of dye by sono-photocatalysis is also carried out. Further the chemical kinetics and order of reaction was investigated.

6.1 Photocatalytic Degradation

6.1.1 Photodegradation of RB 19

A number of controlled experiments are conducted on RB 19 (100 mgL^{-1}) under only UV irradiations, presence of TiO_2 without and with UV irradiations over a reaction time of 120 min according to procedure given in section 3.3.3. Negligible decrease in the concentration of dye is observed by irradiating UV light and in the presence of TiO_2 very little (not significant) dye degradation is observed due to dye adsorption on TiO_2 surface (Vinu and Madras, 2009). However in the presence of TiO_2 with light source, it is seen that 35% of the dye is decomposed within 120 min of irradiation as shown in Figure 6.1.

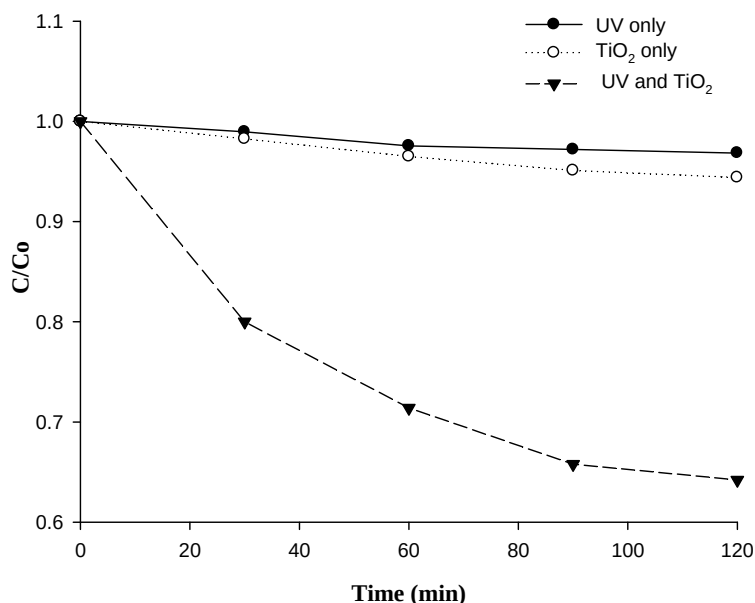


Figure 6.1: Degradation of RB 19 in the presence of different conditions

Reaction conditions: initial pH = 4, dye concentration = 100 mgL^{-1} , TiO_2 Conc. = 300 mgL^{-1}

6.1.2 Effect of TiO_2 Concentration

The concentration of catalysts is very important parameter for the decomposition of organic compounds. The optimum dose of catalyst is very necessary in order to avoid the excessive use of catalyst, for the degradation of dye. The effect of catalyst on the degradation of RB- 19 is investigated using different concentrations (20, 50, 100, 200, 300, 400 and 500 mgL^{-1}) of TiO_2 under UV light. It is found that rate of degradation is increased with the increase in catalyst concentration and reached to maximum and beyond a certain level it remained almost constant. The optimum catalyst concentration was found to be 300 mgL^{-1} (kaur and Singh, 2007).

The number of photons absorbed and the number of dye molecules adsorbed increase with the increase in catalyst concentration, therefore improved the rate of degradation. Over a certain level the number of substrate molecules is not sufficient to fill the surface active sites of TiO_2 . Therefore, addition of further catalyst does not lead in the increment of degradation rate. The decrease in rate of degradation is may be due to the reduced light penetration in the presence of excess amount of titanium dioxide

catalysts. Due to the excess addition of the catalyst, the solution becomes more opaque resulted in reduced light penetration with in the sample. These results are according to those reported in previous literature (Toor et al. 2006; Subramani et al. 2007).

6.1.3 Effect of Initial Dye Concentration

The effect of initial concentration of dye solution on the degradation of RB 19 is also investigated varying the dye concentrations from 50 to 250 mgL⁻¹ in the presence of optimum concentration of TiO₂ catalyst and UV light. The obtained results showed that the rate of degradation is increased at low concentrations and decreased by increasing initial dye concentrations. Similar results were documented for the photocatalytic treatment of other dyes (Davis et al. 1994; Poullos and Aetopoulou, 1999; San et al. 2001).

The low degradation of dye at high concentration can be due to the increased concentration of unabsorbed dye in the solution. The high initial concentration of the dye leads to less penetration of light through the solution. Subsequently there is less effect of light on TiO₂. Thus the production of ·OH radicals on the surface is also decreased. Therefore, this resulted in a decreased degradation rate. However, there is a reverse effect at lower dye concentration, where the light intensity and time of irradiation is same but the interception of photons to the catalyst surface is decreased leading to the formation of more number of ·OH radicals. This increased the rate of degradation (Neppolian et al. 2002; Subramani et al. 2007).

6.1.4 Effect of pH

The solution pH is an important parameter and the effect of different pH conditions between (3 to 10) on the degradation of RB 19 is investigated. The degradation of dye is higher in acidic conditions and decreased with the increased in pH of the solution up to alkaline conditions (Figure 6.2). Therefore the photodegradation experiments are conducted in the acidic pH conditions.

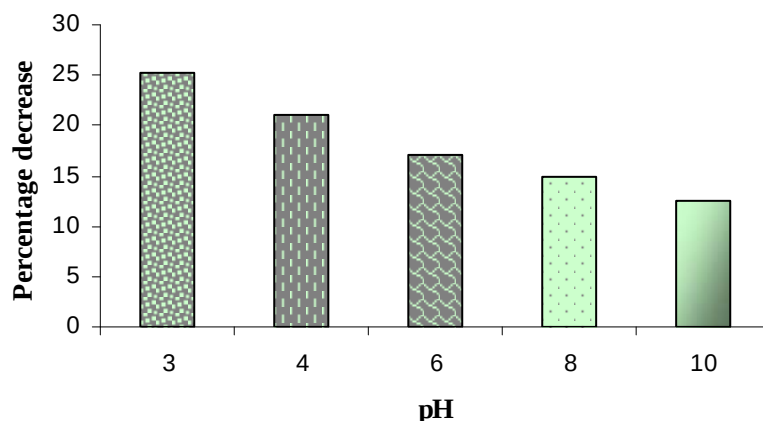


Figure 6.2: Effect of pH on photodegradation of dye

The RB 19 used in this study contained sulfonic group in the structure that is negatively charged, hence in acidic conditions the contact between the dye and surface of catalyst promote the adsorption. In contrast, the catalysts (titanium dioxide) surface is negatively charged in basic pH conditions, and dyes adsorption does not favor (Kiriakidou et al. 1999). In the acidic pH, the surface of TiO_2 attains a positive charge so attracting the RB 19, leading to the greater adsorption and increasing the degradation rate in acidic media. The reverse effect is observed in the basic medium where the TiO_2 surface is negatively charged which repels the dye and decrease the degradation rate as shown in Eq 6.1 and 6.2.



6.1.5 Decolorization of RB 19

To study the effect of decolorization on dye, photocatalytic degradation of 100 mgL^{-1} is carried out in the presence of UV light and optimized dosage of catalyst. It is found that color of dye solution is decreased with the passage of time, and after 120 min of treatment considerable color is removed. The fading of color during photocatalysis is shown in Figure 6.3.

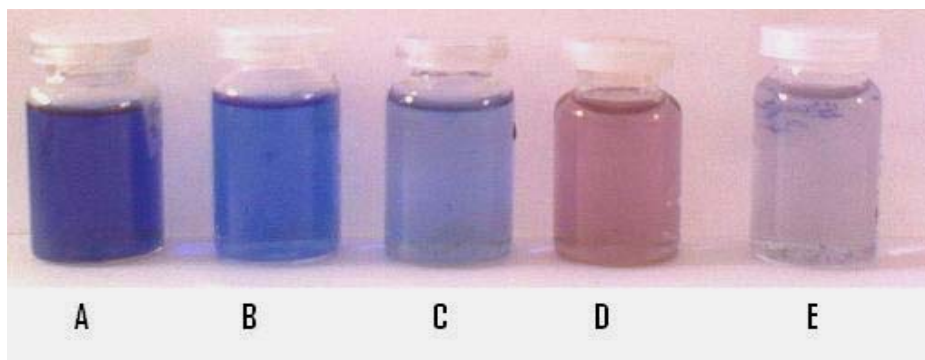


Figure 6.3: Decolorization of RB 19 dye during photocatalysis

6.1.6 Mineralization of RB 19

Reduction in total organic carbon contents reflects the mineralization of organic compound. The reduction in total organic carbon is studied for the dye sample having initial concentration of 100 mgL^{-1} , pH 4, and catalysts loading of 300 mgL^{-1} under Ultraviolet light. The TOC is reduced only 10.18% after 120 min of irradiation which indicate the mineralization of dye compound is to some extent.

6.2 Sonophotocatalytic Degradation

Under optimized conditions of dye concentration (100 mgL^{-1}), catalysts concentrations (300 mgL^{-1}) (Kaur and Singh, 2007) and 4 pH, further experiments are conducted under different experimental conditions of sonolysis (US), photocatalysis (UV+ TiO_2) and sonophotocatalysis (US+UV+ TiO_2) to study the effect of ultrasound on degradation rate. It is found from the results (Figure 6.4) that 73%, 35% and 12% dye degradation takes place under sonophotocatalysis, photocatalysis and sonolysis processes after 120 min.

The dye degradation under photocatalysis is increase by ultrasound. Both in photocatalysis and sonophotocatalysis the dye is decomposed mainly through the generation of $\cdot\text{OH}$ radicals. In sonophotocatalysis process, $\cdot\text{OH}$ radicals are generated from splitting of water molecules under high temperature and pressure conditions created by collusion of cavitation bubbles. In photocatalysis process the $\cdot\text{OH}$ radicals are generated via photosensitization which involve the excitation of dye molecules

rather than TiO_2 particles. Charge is then injected from singlet or triplet excited states of dye in to the conduction band of semiconductor particle and the dye is converted in to cationic radicals. The injected electron can reduce surface chemisorbed oxidants, usually O_2 to yield oxidizing species like $\cdot\text{OH}$ radicals. The combine effect thus increases the amount of reactive radical species inducing oxidation of dye molecules (Kaur, 2007).

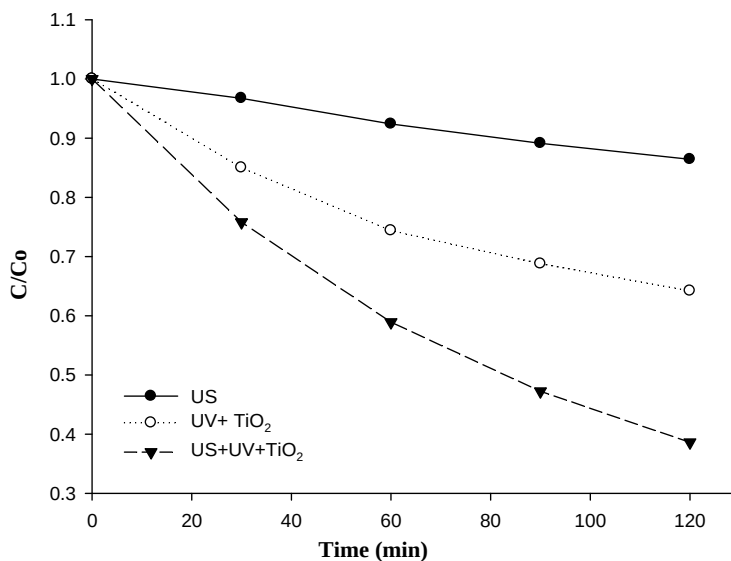


Figure 6.4: Comparison of ultrasound, photocatalysis and sonophotocatalysis processes for degradation of RB 19, Reaction conditions: initial pH = 4, dye conc. = 100 mgL^{-1} , TiO_2 conc. = 300 mgL^{-1} , US power = 240 W

6.2.1 Effect of Ultrasonic Power

To investigate the effect of ultrasonic power sonophotocatalytic experiments are conducted with optimized conditions i.e. dye concentrations of 100 mgL^{-1} , TiO_2 concentration of 300 mgL^{-1} and pH 4 with different ultrasonic power settings ranged from 120-300 W (Figure 6.5). The results show that the increase in ultrasonic power causes a decrease in the residual dye concentration. The maximum 73% dye degradation is observed at power 240 W after 120 min of reaction time. Ultrasound produces its sonochemical effects through the formation of cavitation bubbles. The increase in ultrasonic power has a significant effect on the collapse of cavitation bubbles. At higher power, the life time of bubbles is shorter and collapse occurs very

quickly with the production of $\cdot\text{H}$ and $\cdot\text{OH}$ radicals, thus enhancing the possibility of radical's attack on dye molecule. In general, an increase in ultrasonic power results in an increase in the rate of reaction (Price, 1992; Simona et al. 2007). But by increasing ultrasonic power from 240 to 300 W, no significant increase in dye degradation is observed. This was due to the reasons that a maximum rate of reaction can be obtained in any chemical reaction when an optimum acoustic power exists therefore a great number of cavitation bubbles are generated at higher ultrasonic power. For further transfer of acoustic energy they induce some hurdles through the whole liquid (Price, 1992; Petrier and Francony, 1997; Simona et al. 2007).

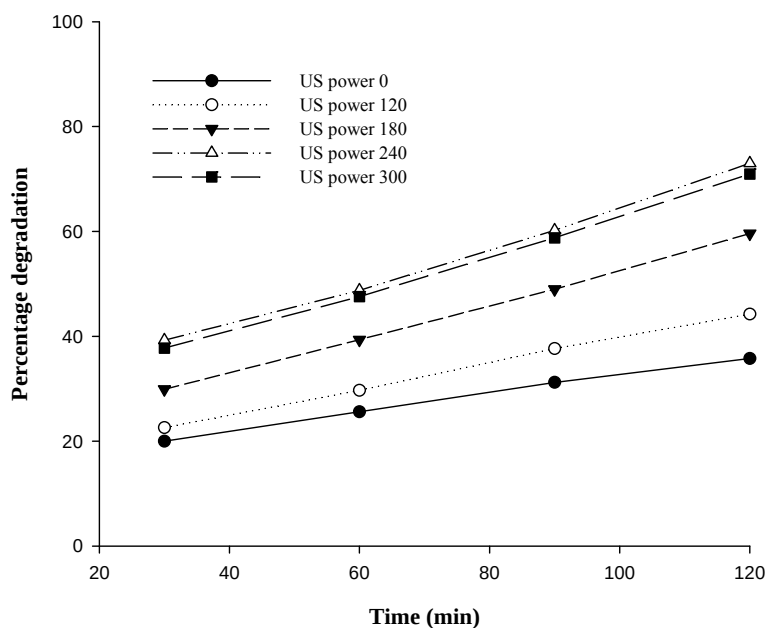


Figure 6.5: Effect of ultrasonic power settings on percentage degradation of RB- 19 by sono-photocatalysis process, Reaction conditions: initial pH = 4, dye conc. = 100 mgL^{-1} , TiO_2 conc. = 300 mgL^{-1}

6.3 Kinetics Studies

Under different experimental conditions of sonolysis (US), photocatalysis (UV+ TiO_2) and sonophotocatalysis (US+UV+ TiO_2), order of reaction is determined. A graph between the reciprocal of remaining dye concentrations against time is plotted. The dye degradation apparently follows 1st order of kinetics (Fung et al. 2000) (Figure 6.6).

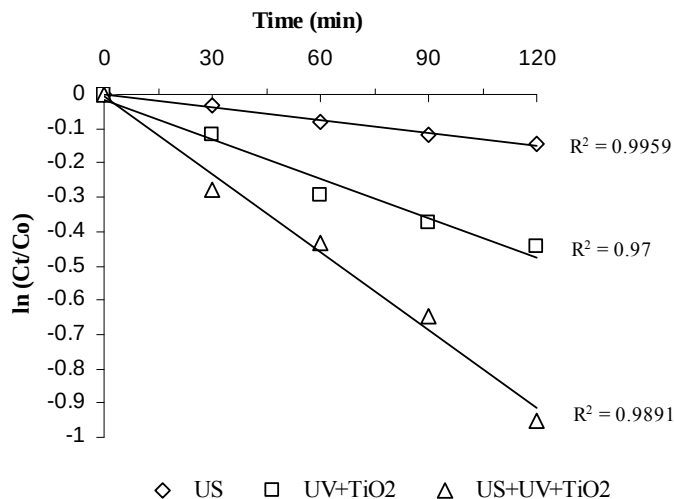


Figure 6.6: First order kinetics plot of RB 19 degradation under sonolysis (US), photocatalysis (UV+TiO₂) and sonophotocatalysis (US+UV+ TiO₂)
 Reaction conditions: initial pH = 4, dye conc. = 100 mgL⁻¹, TiO₂ conc. = 300 mgL⁻¹, US power = 240 W

The correlation between $\ln(C_t/C_0)$ and treatment time is linear (straight line). This is a typical first order reaction plot (Figure 6.6). The slopes of the lines show the apparent rate constant (k). The regression coefficient R^2 obtains (Figure 6.6) for first order reaction at different experimental conditions is shown in (Table 6.1). The R^2 values ranges from 0.97 to 0.99, confirming that degradation of RB 19 under different experimental conditions i.e. sonolysis (US), photocatalysis (UV+TiO₂) and sonophotocatalysis (US+UV+ TiO₂), follows the first order reaction.

Table 6.1: Integrated rate law and Regression coefficient for first order reaction at different experimental conditions

Experimental conditions	First order $\ln C = -k_1 t + C'$	R^2
US	$\ln C = -0.04 + 0.038t$	0.99
US +TiO ₂	$\ln C = -0.11t + 0.096$	0.97
US+UV+ TiO ₂	$\ln C = -0.23 + 0.22t$	0.98

Reaction conditions: initial pH = 4, dye conc. = 100 mgL⁻¹, TiO₂ concentration = 300 mgL⁻¹, US power = 240 W

6.4 TOC Analysis

Reduction in TOC contents reflects the mineralization of organic compound. The reduction in total organic carbon is studied for sonophotocatalysis process under optimum conditions; initial concentration of 100 mgL^{-1} , pH 4, catalysts loading of 300 mgL^{-1} and ultrasonic power 240 W under Ultraviolet light.

The results of degradation analysis of RB 19 obtained through total TOC analysis are presented in Table 6.2. It was observed that the heterogeneous nature of treatment (ultrasonic and photocatalysis processes) permitted an overall TOC reduction of about 54.7% in 120 min. Individually, ultrasonic and electrochemical techniques caused 7.2% and 10.18% respective reduction of TOC after 120 min.

Table 6.2: Reduction of the total organic carbon content

Process	TOC reduction (%)
Ultrasound	7.2 %
Photocatalysis	10.2 %
Sonophotocatalysis	54.7 %

Reaction conditions: initial pH = 4, dye conc. = 100 mgL^{-1} , TiO_2 conc. = 300 mgL^{-1} ,
US power = 240 W

Chapter 7

Conclusions

7.1 Sonoelectrochemical Degradation of RB 19

The results obtained from ultrasound assisted electrochemical study indicated that the combined processes efficiently degrade RB 19 and the efficiency of electrochemical process was enhanced three times by applying ultrasonic cavitations. The dye degradation resulted in the formation of small molecular weight products e.g. acetic acid and benzoic acid with the complete removal of dye.

7.2 Hydrolysis of RB 19

A linear relationship was observed between hydrolysis rate of RB 19 and increasing temperature and pressure. In acidic conditions half life was reduced by 6.6 times at 120 °C as compare to 40 °C. The major intermediate and end products formed during the degradation were identified are benzaldehyde, acetophenone, benzoic acid and isoindoline-1,3-dione, acetic acid and oxalic acid.

7.3 Sonophotocatalytic Degradation of RB 19

The efficiency of combined ultrasound with photocatalysis technique was increased to about two folds in acidic conditions as compare to individual processes at same experimental conditions (100 mgL⁻¹ of dye concentration, 300 mgL⁻¹ of TiO₂ concentration, 240 W ultrasonic power and at pH 4). It is concluded that the technique is environmental friendly in the sense that catalysts can be recovered during the treatment of wastewater.

It is concluded that the degradation of RB 19 followed first order reaction by applying sonoelectrochemical, thermal pressure hydrolysis and sonophotocatalysis techniques and sonoelectrochemical degradation technique was found to be the most efficient as compare to other used treatment techniques in the current study.

Recommendations for Future Work

- The degradation and decolorization of RB 19 by sonoelectrochemical process can further be investigated using different kinds of electrode materials.
- Further research is required to find out the precise mechanism of the degradation of RB 19 and other dyes through thermal-pressure mediated hydrolysis.
- The results obtained from this study can be used to design wastewater treatment plant for dyeing manufacturing industry.

References

- Adewuyi, Y.G. (2001). Sonochemistry: environmental science and engineering applications. *Ind. Eng. Chem. Res.* 40 (22), 4681-4715
- Adrian, M.T.S., Nouli, E., Apolinario, A. C. C., Xekoukoulotakis, N. P. & Mantzavinos, D. (2007). Sonophotocatalytic/H₂O₂ degradation of phenolic compounds in agro-industrial effluents. *Catalysis Today*. 124, 232-239.
- Aksu, Z. (2003). Reactive dye bioaccumulation by *Saccharomyces cerevisiae*. *Process Biochem.* 38, 1437-1444.
- Aksu, Z. & Donmez, G. (2003). A comparative study on the biosorption characteristics of some yeasts for Remazol Blue reactive dye. *Chemospher.* 50, 1075-1083.
- Alinsafi, A., Evenou, E., Abdulkarim, M., Pons, M.N., Zahraa, O., Benhammou, A., Yaacoubi, A. & Nejmeddine A. (2007). Treatment of textile industry wastewater by supported photocatalysis. *Dyes Pigm.* 74, 439-445.
- Andrade, L.S., Ruotolo, L.M.M., Rocha-Filho, R.C., Bocchi, N., Biaggio, S.R., Iniesta, J., Garcia-Garcia, V. & Montiel, V. (2007). On the performance of Fe and Fe, F doped Ti-Pt/PbO₂ electrodes in the electrooxidation of the Blue Reactive 19 dye in simulated textile wastewater. *Chemosphere.* 66, 2035- 2043.
- Andrzejewska, A., Krysztafkiewicz, A. & Jesionowski, T. (2004). Adsorption of organic dyes on the aminosilane modified TiO₂ surface. *Dyes Pigm.* 62, 121-130.
- Andrzejewska, A., Krysztafkiewicz, A. & Jesionowski, T. (2007). Treatment of textile dye wastewater using modified silica. *Dyes Pigm.* 75, 116-124.
- Anjaneyulu, Y., Chary, S. & Raj, N.D.S.S. (2005). Decolorization of industrial effluents -available methods and emerging technologies - review. *Rev. Environ. Sci. Bio/Technol.* 4, 245- 273.
- Antonia, S. G & Martínez, S. S. (2008). Study of the sonophotocatalytic degradation of basic blue 9 industrial textile dye over slurry titanium dioxide and influencing factors. *Ultrason Sonochem.* 15, 1038-1042.
- Augugliaro, V., Litter, M., Palmisano, L. & Soria, J. (2006). The combination of heterogeneous photocatalysis with chemical and physical operations: A tool

for improving the photoprocess performance. *J. Photochem. Photobiol. C: Photochem. Rev.* 7, 127-144.

- Awad, H.S. & Galwa, N. A. (2005). Electrochemical degradation of Acid Blue and Basic Brown dyes on Pb/PbO₂ electrode in the presence of different conductive electrolyte and effect of various operating factors. *Chemospher.* 61, 1327-1335.
- Azbar, N., Yonar, T. & Kestioglu, K. (2004). Comparison of various advanced oxidation processes and chemical treatment methods for COD and color removal from a polyester and acetate fiber dyeing effluent. *Chemospher.* 55, 35-43.
- Babuna, F. G., Orhon, D., Cokgor, E. U., Insel G. & Yaprakli, B. (1998). Modeling of activated sludge for textile wastewaters. *Wat. Sci. Technol.* 38 (4/5), 9-17.
- Bahena, C. L., Martinez, S. S., Guzman, D. M. & Hernandez, M. R. T. (2008). Sonophotocatalytic degradation of alazine and gesaprimcommercial herbicides in TiO₂ slurry. *Chemospher.* 71, 982-989.
- Bard, A.J. (1979). Photo electrochemistry and heterogeneous photo-catalysis at semiconductors. *J. Photochem.* 10 (1), 59-75.
- Baughman, G.L. & Weber, E. J. (1994). Transformation of dyes and related compounds in anoxic sediment: kinetics and products. *Environ. Sci. Technol.* 28, 267-276.
- Carneiro, A.P., Boralle, N., Stradiotto, N. R., Furlan, M. & Zanoni, M.V.B. (2004). Decolorization of Anthraquinone Reactive Dye by Electrochemical Reduction on Reticulated Glassy Carbon Electrode. *J. Braz. Chem. Soc.* 15(4), 587-594.
- Champagne, P.P. & Ramsay, J.A. (2007). Reactive blue 19 decolorization by laccase immobilized on silica beads. *Appl Microbiol Biotechnol.* 77, 819-823.
- Chatzisyneon, E., N. Xekoukoulotakis, P., Coz, A., Kalogerakis, N. & Mantzavinos, D. (2006). Electrochemical treatment of textile dyes and dye house effluents. *J. Hazard. Mater.* 137 (2), 998-1007.

- Chen, G. (2004). Electrochemical technologies in wastewater treatment. *Sep. Purif. Technol.* 38 (1), 11-41.
- Chen, X.M., Chen, G.H. & Yue, P.L. (2002). Investigation on the electrolysis voltage of electrocoagulation. *Chem. Eng. Sci.* 57, 2449-2455.
- Chiang, L.C., Chang, J. E. & Tseng, S. D. (1997). Electrochemical oxidation pretreatment of refractory organic pollutants. *Water Sci. Technol.* 36 (2-3), 123-130.
- Christie, R. (2001). *Color Chemistry. The Royal Society of Chemistry*, Cambridge, UK.
- Comninellis, C. (1994). Electrocatalysis in the electrochemical conversion/combustion of organic pollutants for wastewater treatment. *Electrochim. Acta.* 39, 1857-1862.
- Davis, R.J., Gainer, J.L., Neal, G.O. & Wen, W.I. (1994). Photocatalytic decolorization of wastewater dyes. *Water Environ Res.* 66, 3-50.
- De, W.J., Ye, Z.R., Xia, C. & Meng, C.J. (2008). Mechanism and kinetics of 2-chlorophenol decomposition using coupled ultrasound and electrocatalysis. *Sci. China Ser. B-Chem.* 51, 577-585.
- Donmez, G. (2002). Bioaccumulation of the reactive textile dyes by *Candida tropicalis* growing in molasses medium. *Enzym. Microb. Technol.* 30 (3), 363-366.
- Dukkanci, M. & Gunduz, G. (2006). Ultrasonic degradation of oxalic acid in aqueous solutions. *Ultrason. Sonochem.* 13 (6), 517-522.
- Enes, S. (2006). Optimization and modeling of decolorization and COD reduction of reactive dye solutions by ultrasound-assisted adsorption. *Chem. Eng. J.* 119, 175-181.
- Enes, S. & Edecan, M. E. (2008). An optimization study using response surface methods on the decolorization of Reactive Blue 19 from aqueous solution by ultrasound, *Ultrason. Sonochem.* 15 (4), 530-538.
- Epolito, W.J., Lee, Y.H., Bottomley, L.A. & Pavlostathis, S.G. (2005). Characterization of the textile anthraquinone dye Reactive Blue 4, *Dyes Pigm.* 67 (1), 35-46.

- Fanchiang, J.M. & Tseng, D.H. (2009). Decolorization and transformation of anthraquinone dye Reactive Blue 19 by ozonation. *Environ. Technol.* 30 (2), 161-172.
- Feng, W., Nansheng, D. & Helin, H. (2000). Degradation mechanism of azo dye C. I. Reactive red 2 by iron powder reduction and photo-oxidation in aqueous solutions. *Chemospher.* 41 (8), 1233-1238.
- Fenghour, A. & Wakeham, W.A. (1993). Automated isochoric apparatus for the measurements of density of fluid mixtures at temperature from 298.15K to 773.15K and pressures up to 40 MPa results for helium and for nitrogen. *J. Chem. Thermodynam.* 25 (7), 831-845.
- Fernandes, A., Morao, A., Magrinho, M., Lopes A. & Goncalves, I. (2004). Electrochemical degradation of C.I. Acid Orange 7. *Dyes Pigm.* 61(3), 287-296.
- Foord, J. S., Katherine, B., Richard, H., Compton, G., Frank, M. & Kim, D. H. (2001). Mechanistic aspects of the sonoelectrochemical degradation of the reactive dye Procion Blue at boron-doped diamond electrodes. *Diamond Related Mater.* 10 (3-7), 662-666.
- Fryda, M., Herrmann, D., Schafer, L., Klages, C.P., Perret, A., Haenni, W., Comninellis, C. & Gandini, D. (1999). Properties of diamond electrodes for wastewater treatment. *New Diamond Front. Carbon Technol.* 9, 229-240.
- Fung, P. C., Sin, K. M. & Tsui, S. M. (2000). Decolorization and degradation kinetics of reactive dye wastewater by a UV/ultrasonic/ peroxide system, *J.S.D.C.* 116, 1170-1173.
- Gahr, F., Hermanutz, F. & Oppermann, W. (1994). Ozonation- an important technique to comply with new German laws for textile wastewater treatment. *Wat. Sci. Technol.* 30(3), 255-263.
- Galindo, C., Jacques, P. & Kalt, A. (2001). Photo-oxidation of the phenylazonaphthol AO20 on TiO₂: kinetic and mechanistic investigations. *Chemospher.* 45 (6-7), 997-1005.
- Ganesh, R., Boardman, G. D. & Michelsen, D. (1994). Fate of azo dyes in sludges. *Wat. Res.* 28(6), 1367-1376.

- Georgiou, D., Aivasidis, A., Hatiras, J. & Gimouhopoulos, K. (2003). Treatment of cotton textile wastewater using lime and ferrous sulfate. *Wat. Res.* 37 (9), 2248-2250.
- Gibson, R. E. & Leofeler, O. H. (1939). Pressure volume temperature relations in solutions III. Some thermodynamic properties of mixtures of aniline and nitrobenzene. *J. Biol. Chem. Oct.* 2877-2887.
- Gogate, P. R. (2008). Treatment of wastewater streams containing phenolic compounds using hybrid techniques based on cavitation. A review of the current status and the way forward. *Ultrason. Sonochem.* 15(1), 1-15.
- Gogate, P. R. & Pandit, A.B. (2005). A review and assessment of hydrodynamic as a technology for the future. *Ultrason. Sonochem.* 12 (1-2), 21-27.
- Gogate, P.R. & Pandit, A.B. (2004). Sonophotocatalytic reactors for wastewater treatment: A critical review. *A.I.C.H.E.* 50 (5), 1051-1079.
- Gonzalez, A. & Cid, A. P. (2002). Electrochemical treatment of textile dyes and their analysis by high-performance liquid chromatography with diode array detection. *J. Chromatogr. A.* 889 (1-2), 253-259.
- Gottschalk, C., Libra, J.A. & Saupe, A. (2000). *Ozonation of Water and Waste Water- A Practical Guide to Understanding Ozone and its Application*. pp. 11-15. Wiley-VCH, Weinheim, Germany.
- Gutiérrez, M.C. & Crespi, M. (1999). A review of electrochemical treatments for Color elimination. *J.S.D.C.* 115, 342-345.
- Guyer, G. T. & Ince, N. H. (2004). Structure related degradability of textile dyestuffs by acoustic cavitation: A study with dyebath effluents. *Advan. Color. Sci. Technol.* 7(2), 36-42.
- Guyer, G. T. & Ince, N.H. (2004). Individual and combined effects of ultrasound, ozone and UV irradiation: a case study with textile dyes. *Ultrasonics.* 42 (1-9), 603-609.
- Hao, O.J., Kim, H. & Chiang, P.C. (2000). Decolorization of wastewater, *Crit. Rev. Environ. Sci. Technol.* 30, 449-505.

- Hasan, M., Ahmad, A.L. & Hameed, B.H. (2008). Adsorption of reactive dye onto cross-linked chitosan/oil palm ash composite beads. *Chem. Eng J.* 136 (2-3), 164-172.
- He, Z., Lin, L., Song, S., Xia, M., Xu, L., Ying, H. & Chen, J. (2008). Mineralization of C.I. Reactive Blue 19 by ozonation combined with sonolysis: Performance optimization and degradation mechanism. *Sep. Purif. Technol.* 62 (2), 376-381.
- Heller, A. (1981). Conversion of sunlight into electrical power and photo assisted electrolysis of water in photo electrochemical cells. *Acc. Chem. Res.* 14 (5), 154-162.
- Hidaka, H., Nagaoka, H., Nohara, K., Shimura, T., Horikoshi, S., Zhao, J. & Serpone, N. (1996). A mechanistic study of the photo-electrochemical oxidation of organic compounds on a TiO₂/TCO particulate film electrode assembly. *J. Photochem. Photobiol. A: Chem.* 98 (1-2), 73-78.
- Hirano, K., Nitta, H. & Sawada, K. (2005). Effect of sonication on the photocatalytic mineralization of some chlorinated organic compounds. *Ultrason. Sonochem.* 12 (4), 271-276.
- Holcapek, M., Jandera, P. & Zderadicka, P. (2001). High performance liquid chromatography–mass spectrometric analysis of sulphonated dyes and intermediates. *J. Chromatogr. A.* 926 (1), 175-186.
- Hsu, Y. C., Chen, Y. F. & Chen, J. H. (2004). Decolorization of dye RB 19 solution in a continuous ozone process. *J. Environ. Sci. Health. A. Tox. Hazard. Subst. Environ. Eng.* 39(1), 127-44.
- Hua, M.R. & Hoffmann. (1997). Optimization of ultrasonic irradiation as an advanced oxidation technology. *Environ. Sci. Technol.* 31, 2237-2243.
- Ioan, I., Nechita, M. T., Rosca, I. & Aelene, N. (2004). Ultrasound Assisted Electrochemical Degradation of Cyanides: Influence of Electrode Type. *Tur. J. Eng. Env. Sci.* 28, 377-380.
- Jesionowski, T., Binkowski, S. & Krysztafkiewicz, A. (2005). Adsorption of the selected organic dyes on the functionalized surface of precipitated silica via emulsion route. *Dyes Pigm.* 65 (3), 267-279.

- Jiping, H. & Scott, A. (2000). Hydrolysis kinetics of fenthion and its metabolites in buffered aqueous media. *J. Agric. Food. Chem.* 48, 2582-2588.
- Kaneko, M. & Okura, I. (2003). Photocatalysis Science and Technology. pp. 1-365. Springer Press.
- Kaur, S. & Singh, V. (2007). Visible light induced sonophotocatalytic degradation of Reactive Red dye 198 using dye sensitized TiO₂. *Ultrason. Sonochem.* 14 (5), 531-537.
- Kaur, S. & Singh, V. (2007). TiO₂ mediated photocatalytic degradation studies of Reactive Red 198 by UV irradiation. *J. Hazard. Mater.* 141, 230-236.
- Kaur, S. (2007). Light induced oxidative degradation studied of organic dyes and their intermediates. Thesis, School of Chemistry and Biochemistry, Thapar University, Patiala, India.
- Kesselman, J.M., Lewis, N.S. & Hoffmann, M.R. (1997). Photo electrochemical degradation of 4 chlorophenol at TiO₂ electrodes: comparison between sorption and photoreactivity. *Environ. Sci. Technol.* 31, 2298-2302.
- Khalaf, M.A. (2008). Biosorption of reactive dye from textile wastewater by non-viable biomass of *Aspergillus niger* and *Spirogyra* sp. *Biores. Technol.* 99 (14), 6631-6634.
- Khare, U.K., Bose, P. & Vankar, P.S. (2007). Impact of ozonation on subsequent treatment of azo dye solutions. *J. Chem. Technol. Biotechnol.* 82, 1012-1022.
- Kiriakidou, F., Kondarides, D.I. & Verykios, K.E. (1999). The effect of operational parameters and TiO₂-doping on the photocatalytic degradation of azo-dyes. *Catal. Today.* 54 (1), 119-130.
- Kobya, M., Can, O.T. & Bayramoglu, M. (2006). Treatment of textile wastewaters by electrocoagulation using iron and aluminum electrodes. *J. Hazard. Mater. B*: 100 (1-3), 163-178.
- Kongsricharoern, N. (1994). Application of Electrochemical Precipitation for Treatment of Cr Wastewater; Ph.D. Thesis, Asian Institute of Technology: Bangkok, Thailand.

- Kotronarou, A., Mills, G. & Hoffmann, M.R. (1991) *J. Phys. Chem.* 95, 3630-3638.
- Kurbus, T., Slokar, Y. M. & Marechal, A. M. L. (2002). The study of the effects of the variables on H₂O₂/UV decolorization of vinylsulphone dye: part II. *Dyes Pigm.* 54 (1), 67-78.
- Kusvuran, E., Irmak, S., Yavuz, H. I., Samil, A. & Erbatur, O. (2005). Comparison of the treatment methods efficiency for the decolorization and mineralization of Reactive Black 5 azo dye. *J. Hazard. Mater.* 119 (1-3), 109-116.
- Lall, R., Raj, M., Shah, Y. T. & Prasad, D. (2003). Decolorization of the dye, Reactive Blue 19, using ozonation, ultrasound, and ultrasound enhanced ozonation. *Watr. Envirn. Res.* 75(2), 171-179.
- Legrand, J. & Coeret, F. (1993). *Chemical industry and environment*. 2, Ed. J Arnaldos and P Muntjé (Girona: UPC/UG/SCT).
- Lewis, D. M. (1999). Coloration for the next century. *Rev. Prog. Color. Related Topic.* 29, 23-28.
- Liakou, S., Pavlou, S. & Lyberatos, G. (1997). Ozonation of azo dyes. *Water Sci. Technol.* 35 (4), 278-286.
- Ligrini, O., Oliveros, E. & Braun, A. (1993). Photochemical processes for water treatment. *Chem. Rev.* 93, 671-98.
- Lin, S.H. & Peng, C.F. (1996). Continuous treatment of textile wastewater by combined coagulation, electrochemical oxidation and activated sludge. *Water Res.* 30 (3), 587-592.
- Liu, J.L., Luo, H.J. & Wei, C.H. (2007). Degradation of anthraquinone dyes by ozone. *Trans. Nonferrous. Met. Soc. China.* 17 (4), 880-886.
- Lizama, C., Freer, J., Baeza, J. & Mansilla, H. D. (2002). Optimized photodegradation of Reactive Blue 19 on TiO₂ and ZnO suspensions. *Catal. Today.* 76 (2-4), 235-246.
- Lizama, C., Yeber, M.C., Freer, J., Baeza, J. & Mansilla, H.D. (2001). Reactive dyes decolouration by TiO₂ photo-assisted catalysis. *Water. Sci. Technol.* 44 (5) 197-203.

- Lorimer, J. P., Mason, T. J., Plattes, M., Phull, S.S. & Walton, D. J. (2001). Degradation of dye effluent. *Pure Appl. Chem.* 73, 1957-1968.
- Lowwitz, D.A., Spencer, J. W., Webband, W. & Schiessler, R.W. (1959). Temperature pressure structure effects on the viscosity of several higher hydrocarbons. *J. Chem. Phys.* 30 (1), 73-83.
- Lucas, M. S. & Peres, J.A. (2007). Degradation of Reactive Black 5 by Fenton/UV-C and ferrioxalate/H₂O₂/solar light processes. *Dyes. Pigm.* 74 (3), 622-629.
- Mabey, W. & Mill, T. (1978). Critical review of hydrolysis of organic compounds in water under environmental conditions. *J. Phys. Chem. Ref. Data.* 7 (2), 383-415.
- Mahamuni, N.N. & Pandit, A.B. (2006). Effect of additives on ultrasonic degradation of phenol. *Ultrason. Sonochem.* 13 (2), 165-174.
- Mahamuni, N.N. & Adewuyi, Y.G. (2010). Advanced oxidation processes (AOPs) involving ultrasound for waste water treatment: A review with emphasis on cost estimation. *Ultrason. Sonochem.* 17, 990-1003.
- Mamdouh, E. A. & Peter, R. B. (2002). A study investigating the sonoelectrochemical degradation of an organic compound employing Fenton's reagent. *Phys. Chem. Chem. Phys.* 4, 5340-5345.
- Mantzavinos, D. & Psillakis, E. (2004). Enhancement of biodegradability of industrial wastewaters by chemical oxidation pre-treatment. *J. Chem. Technol. Biotechnol.* 79, 431-454.
- Martinez-Huitle, C.A. & Brillas, E. (2009). Decontamination of wastewaters containing synthetic organic dyes by electrochemical methods: A general review. *Appl. Catal. B. Environ.* 87 (3-4), 105-145.
- Mason, T.J. (1990). *Sonochemistry: The use of ultrasound in chemistry*, Royal Society of Chemistry, London.
- Mason, T.J., Newman, A.P. & Phull, S.S. (1993). *Sonochemistry in water treatment*, BHR Group Conf. Ser. Publ. 2nd International Conference on Advances in water and effluent treatment, 243.

- Mason, T.J. (2000). Large scale sonochemical processing: aspiration and actuality. *Ultrason. Sonochem.* 7 (4), 145-149.
- Matsui, M., Kobayashi, K., Shibata, K. & Takase, Y. (1981). Ozonation of dyes. II. Ozone treatment of 4- phenylazo-1- naphthol. *J. Soc. Dyers Colourists.* 97(5), 210-213.
- Meric, S., Kaptan, D. & Olmez, T. (2004). Color and COD removal from wastewater containing Reactive Black 5 using Fenton's oxidation process. *Chemospher.* 54 (3), 435-441.
- Mondal, S. (2008). Methods of dye removal from dye house effluent-an overview. *Environ. Eng. Sci.* 25, 383-396.
- Mrowetz, M., Pirola, C. & Selli, E. (2003). Degradation of organic water pollutants through sonophotocatalysis in the presence of TiO₂. *Ultrason. Sonochem.* 10 (4-5), 247-254.
- Muneer, M., Philips, R. & Das, S. (1997). Photocatalytic degradation of waste water pollutants. Titanium dioxide-mediated oxidation of a textile dye, Acid Blue. *Res. Chem. Intermediat.* 23, 233-246.
- Naffrechoux, E., Chanoux, S., Petrier, C. & Suptil, J. (2000). Sonochemical and photochemical oxidation of organic matter. *Ultrason. Sonochem.* 7(4), 255-259.
- National Environmental Quality Standards for Municipal and Liquid Industrial Effluents, Revised December 28, 1999.
- Naumczyk, J., Szpyrkowicz, L. & Zilio-Grandi, F. (1996). Electrochemical treatment of textile wastewater. *Water Sci. Technol.* 34(11), 17-24.
- Neppolian, B., Shankar, M. V. & Murugesan, V. (2002). Semiconductor assisted photodegradation of textile dye. *J. Sci. Ind. Res.* 61, 224-230.
- Neval, B. & Deniz, A. (2008). Application of Box-Wilson experimental design method for the photocatalytic degradation of Remazol Brilliant Blue R-A with solar UV/TiO₂/Fe (III) processes. *J. Adv. Oxid. Technol.* 11(1), 130-134.
- Nilratnisakorn, S., Thiravetyan, P. & Nakbanpote, W. (2007). Synthetic reactive dye wastewater treatment by narrow-leaved cattails (*Typha angustifolia* Linn.): Effects of dye, salinity and metals. *Sci. Total. Envt.*, 384 (1-3), 67-76.
- Ochoa, J. R. G. (1995). Ingeniería. Química., 4, 125.

- Okitsu, K., Iwasaki, K., Yobiko, Y., Bandow, H., Nishimura, R. & Maeda, Y. (2005). Sonochemical degradation of azo dyes in aqueous solution: a new heterogeneous kinetics model taking into account the local concentration of OH radicals and azo dyes. *Ultrason. Sonochem.* 12 (4), 255-262.
- Ollis, D. F., Pelizzetti, E. & Serpone, N. (1991). Destruction of water contaminants. *Environ. Sci. Technol.* 25, 1523-1529.
- Ozcan, A., Igdem, C., Meroglu, O., Erdogan, Y. & Ozcan, A. S. (2007). Modification of bentonite with a cationic surfactant: An adsorption study of textile dye Reactive Blue 19. *J. Hazard. Mater.* 140 (1-2), 173-179.
- Ozer, A., Akkaya, G. & Turabik, M. (2005). Biosorption of acid red 274 (AR 274) on *Enteromorpha prolifera* in a batch system. *J. Hazard. Mater.* 126 (1-3), 119-127.
- Paternaragis, H. & Fountoukidis, E. (1990). Disinfection of water by electrochemical treatment. *Water Res.* 24, 1491-1496.
- Pelegrini, R., Zamora, P. P., Andrade, A.R., Reyes, J. & Duran, N. (1999). Electrochemically assisted photocatalytic degradation of reactive dyes. *Appl. Catal. B: Environ.* 22 (2), 83-90.
- Perkowski, J. & Ledakowicz, S. (2002). Decomposition of anthraquinone dye in the aqueous solution by ozone, hydrogen peroxide or UV radiation. *Fibres Text. East. Eur.* 38, 72-77.
- Peter, W. C., Peter, D. M. & Christopher, J. P. (1998). The Use of Ultrasound in Industrial Chemical Synthesis and Crystallization. Applications to Synthetic Chemistry. *Org. Process Res. Dev.* 2, 34-48.
- Petrier, C. & Francony, A. (1997). Incidence of wave-frequency on the reaction rates during ultrasonic wastewater treatment. *Water Sci. Technol.* 35 (4), 175-180.
- Poullos, I. & Aetopoulou, I. (1999). Photocatalytic degradation of the textile dye reactive orange 16 in the presence of TiO₂ suspensions. *Environ Technol.* 20, 87-479.
- Prevot, A.B., Baiocchi, C., Brussino, M.C., Pramauro, E., Savarino, P., Augugliaro, V., Marci, G. & Palmisano, L. (2001). Photocatalytic Degradation

of Acid Blue 80 in Aqueous Solutions Containing TiO₂ Suspensions. *Environ. Sci. Technol.* 35, 971-976.

- Price, J.G. (1992). *Current trends in sonochemistry*. The Royal Society of Chemistry, Cambridge, UK.
- Puma, G., Li, B., Awang, D., Krishnaiah, J. & Collin, G. (2008). Preparation of titanium dioxide photocatalyst loaded onto activated carbon support using chemical vapor deposition: A review paper. *J. Hazard. Mater.* 157, 209-219.
- Rajkumar, D., Song, B. J. & Kim, J. G. (2007). Electrochemical degradation of Reactive Blue 19 in chloride medium for the treatment of textile dyeing wastewater with identification of intermediate compounds. *Dyes Pigm.* 72 (1), 1-7.
- Rajkumar, D. & Kim, J. G. (2006). Oxidation of various reactive dyes with in situ electro-generated active chlorine for textile dyeing industry wastewater treatment. *J. Hazard. Mater.* 136 (2), 203-212.
- Rehorek, A., Urbig, K., Meurer, R., Schafer, C., Plum, A. & Braun, G. (2002). Monitoring of azo dye degradation processes in a bioreactor by on-line high-performance liquid chromatography. *J. Chromatogr. A.* 949 (1-2), 263-268.
- Rezaee, A., Khavanil, G. A., Hashemian, S. J., Moussavi, G., Ghanizadeh, G. & Hajizadeh, E. (2008). Photochemical oxidation of Reactive Blue 19 dye (RB 19) in textile wastewater by UV/K₂S₂O₈ process. *Iran. J. Environ. Health. Sci. Eng.* 5 (2), 95-100.
- Rezaee, A., Ghaneian, M. & Hashemian, S. J. (2008a). Decolorization of Reactive Blue 19 Dye from Textile wastewater by UV/ H₂O₂ Process. *J. Applied Sci.* 8 (6), 1108-1112.
- Rezaee, A., Ghaneian, M., Hashemian, S. J., Mosavi, G. & Hajizadeh, E. (2008b). Enhanced decolorization of Reactive Blue 19 Dye from Synthetic Textile Wastewater through UV Photolysis in Alkaline Conditions. *Env. Eng. M. J.* 7 (2), 119-123.

- Rivera, M. C., Jimenez, M.M.D. & Gonzalez, M.P. E. (2004). Degradation of the textile dyes Basic Yellow 28 and Reactive Black 5 using diamond and metal alloys electrodes. *Chemospher.* 55, 1-10.
- Rivera, M., Pazos, M. & Sanroman, M. A. (2009). Improvement of dye electrochemical treatment by combination with ultrasound technique. *J. Chem. Technol. Biotechnol.* 84, 1118-1124.
- Robina, F. & Shaukat, S. F. (2005). Degradation of Organophosphorus pesticides by manganese dioxide and alkaline earth metals. *J. Watr. Env. Poll.* 2 (2) 1-7.
- Robina, F. & Shaukat, S.F. (2004). Pressure Hydrolysis for Degradation of Omethoate Pesticide in Water, *J. Shanghai. Uni.* 8 (2), 221-226.
- Robina, F., Shaukat S.F. & Farooq, U. (2008). Ultrasonic induced decomposition of methiadation pesticides, *J. Applied. Sci.* 8(1), 140-145.
- Robina, F., Lin, F., Wang, Y., Haung, J., Zhang, X. & Shaukat, S.F. (2004). Pressure Hydrolysis for degradation of omethoate pesticide in water. *J. Shanghai Uni.* 8 (2), 221-265.
- Robina, F., Shaukat, S. F. & Farooq, U. (2007). Omethoate hydrolysis process under natural conditions of pressure and temperature. *Pak. J. Sci.* 59, 1-2.
- Ronaldo, P., Zamora, P. P., Andrade, A. R., Reyes, J. & Duran, N. (1999). Electrochemically assisted photocatalytic degradation of reactive dyes, *Appl Catal. B: Envir.* 22, 83-90.
- Sakalis, A., Mpoulmpasakos, K., Nickel, U., Fytianos, K. & Voulgaropoulos, A. (2005). Evaluation of a novel electrochemical pilot plant process for azo dyes removal from textile wastewater. *Chem. Eng. J.* 111 (1), 63-70.
- San, N., Hatipoglu, A., Kocturk, G. & Cinar, Z. (2001). Prediction of primary intermediates and the photodegradation kinetics of 3-aminophenol in aqueous TiO₂ suspension. *J. Photochem. Photobiol. A. Chem.* 139 (2-3), 225-232.
- Sangave, P.C. & Pandit, A. B. (2004). Ultrasound pre-treatment for enhanced biodegradability of the distillery waste water. *Ultrasonic. Sonochem.* 11(2-3), 197-203.

- Schramm, J. D. & Hua, I. (2001). Ultrasonic irradiation of Dichlorvos decomposition mechanism. *Wat. Res.* 35(3), 665-674.
- Selli, E. (2002). Synergistic effects of sonolysis combined with photocatalysis in the degradation of an azo dye. *Phy. Chem. Chem. Phys.* 4 (24), 6123-6128.
- Sengil, I. A. & Ozacar, M. (2006). Treatment of dairy wastewaters by electrocoagulation using mild steel electrodes. *J. Hazard. Mater.* 137 (2), 1197-1205.
- Shemer, H. & Narkis, N. (2005). Sonochemical removal of trihalomethanes from aqueous solutions. *Ultrason. Sonochem.* 12 (6), 495-499.
- Shen, Z., Wang, W., Jia, J., Ye, J., Feng, X. & Peng, A. (2001). Degradation of dye solution by an activated carbon fiber electrode electrolysis system. *J. Hazard. Mater. B* 84 (1), 107-116.
- Serpone, N., Terzian, R., Hidaka, H. & Pelizzetti, E. (1994). *J. Phys. Chem.* 98, 2634-2640.
- Shigeru, K. I., Kobayashi, K. T. & Murakami, Y. (1996). Effect of pressure on subtilism catalysis hydrolysis and peptite synthesis. *Bull. Chem. Soc. Jpn.* 69, 3375-3380.
- Shu, H.Y. & Huang, C.R. (1995). Degradation of commercial azo dyes in water using ozonation and UV enhanced ozonation process. *Chemospher.* 31 (8), 3813-3825.
- Shuang, S., Yao, J., He, Z., Qiu, J. & Chen, J. (2008). Effect of operational parameters on the decolorization of C.I. Reactive Blue 19 in aqueous solution by ozone-enhanced electrocoagulation. *J. Hazard. Mater.* 152 (1), 204-210.
- Shuo, W., Gong, Q. & Liang, J. (2009). Sonophotocatalytic degradation of methyl orange by carbon nanotube/TiO₂ in aqueous solutions. *Ultrason. Sonochem.* 16 (2), 205-208.
- Siddique, M., Farooq, R., Abda, K., Athar, F., Qaisar, M., Umar, F., I. A, Raja. & Shaukat, S.F. (2009). Thermal-pressure mediated hydrolysis of Reactive Blue 19 dye. *J. Hazard. Mater.* 172, 1007-1012.

- Simona, V., Alenka. M. & Marechal, L. (2007). Case study of the sonochemical decolouration of textile azo dye Reactive Black 5. *J. Hazard. Mater.* 141 (1), 329-335.
- Simonsson, D. (1997). Electrochemistry for cleaner environment. *Chem. Soc. Rev.* 26 (3), 181-190.
- Sistiaga, M.G., Rodriguez, A. & Pierna, L. (1994). Electroquímica Metodo de tratamiento de aguas residuales industriales (Tenerife: Congreso Anque).
- Slokar, Y.M. & Marechal, A.M.L. (1998). Methods of decolorization of textile wastewaters. *Dyes Pigm.* 37 (4), 335-356.
- Song, S., Yao, J., Zhiqiao, H., Qiu, J. & Chen, J. (2008). Effect of operational parameters on the decolorization of C.I. Reactive Blue 19 in aqueous solution by ozone-enhanced electrocoagulation. *J. Hazard. Mater.* 152 (1), 204-210.
- Steenken, R. I. & Kermer, W. D. (1992). Decolorizing textile effluents. *J. Soc. Dyers Colourists.* 108(4), 182-186.
- Subramani, A. K., Byrappa, K., Ananda, S., Rai, K. M. L., Ranganathaiah, C. & Yoshimura, M. (2007). Photocatalytic degradation of indigo carmine dye using TiO₂ impregnated activated carbon. *Bull. Mater. Sci.* 30, (1), 37-41.
- Suslick, K.S. (1989). *Ultrasound; It's Chemical, Physical, and Biological Effects*, VCH Publishers, New York.
- Suslick, K.S. (1990). *Sonochemistry Science.* 247, 1439-1445.
- Suslick, K.S. (Ed.), (1998). *Ultrasound: Its Chemistry, Physical and Biological Effects*, VCH Publishers, New York.
- Suslick, K.S. (1999). Application of ultrasound to materials chemistry. *Annu. Rev. Mater. Sci.*, 29, 295-326.
- Swamy, J., & Ramsay, J.A. (1999). The evaluation of white rot fungi in the decolorization of textile dyes. *Enzym. Microb. Technol.* 24, 130-7.
- Tariq, M.A., Faisal, M., Saquib, M. & Muneer, M. (2008). Heterogeneous photocatalytic degradation of an anthraquinone and a triphenylmethane dye derivative in aqueous suspensions of semiconductor. *Dyes Pigm.* 76, 358-365.

- Tawabini, B.S.Al. (2003). Treatment of water contaminated with Di -N-Butyl phthalate by photo-fenton process, King Fahad University of Petroleum & minerals. *The Int. J.* 5 (1), 23-28.
- Toor, A.P., Verma, A., Jotshi, C.K., Bajpai, P.K. & Singh, V. (2006). Photocatalytic degradation of Direct Yellow 12 dye using UV/TiO₂ in a shallow pond slurry reactor. *Dyes Pigm.* 68, 53-60.
- Tubtimngam, V. (2001). Assessment of Electrocoagulation when Added to Conventional Sedimentation Treatment for paper mill wastewater; M.S. Thesis, Mahidol University: Bangkok, Thailand.
- Turchi, C. S., & Ollis, D.F. (1990). Photocatalytic degradation of organic water contaminants: mechanisms involving hydroxyl radical attack. *J. Catal.* 122 (1), 178-192.
- Uygur, A. (1997). An overview of oxidative and photooxidative decolorisation treatments of textile waste waters. *J. Soc. Dyers Colourists.* 113(7/8), 211-217.
- Uygur, A. & Kok, E. (1999). Decolorization treatments of azo dye waste waters including dichlorotriazinyl reactive groups by using advanced oxidation method. *J.S.D.C.* 115 (11), 350-354.
- Vajnhandl, S. & Marechal, A.M.L. (2005). Ultrasound in textile dyeing and the decolouration/mineralization of textile dyes. *Dyes Pigm.* 65 (2) 89-101.
- Vajnhandl, S. & Marechal, A.M.L. (2007). Case study of the sonochemical decolorization of textile azo dye Reactive Balck 5. *J. Hazard. Mater.* 141, 329-335.
- Velegraki, T., Poullos, I., Charalabaki, M., Kalogerakis, N., Samaras, P. & Mantzavinos, D. (2006). Photocatalytic and sonolytic oxidation of acid orange 7 in aqueous solution. *Appl. Catal. B: Envir.* 62, 159-168.
- Verma, M. & Ghaly, A.E. (2008). Treatment of Remazol Brilliant Blue Dye effluent by advanced Photo oxidation Process in TiO₂/UV and H₂O₂/UV reactors. *Amer. J. Eng. Appl. Sci.* 1 (3), 230-240.
- Vinodgopal, K., Hotchandani, S. & Kamat, P.V. (1993). Electrochemically assisted photocatalysis. TiO₂ particulate film electrodes for photocatalytic degradation of 4-chlorophenol. *J. Phys. Chem.* 97, 9040-9044.

- Vinu, R. Madras, G. (2009). Kinetics of sonophotocatalytic degradation of anionic dyes with Nato-TiO_2 . *Environ. Sci. Technol.* 43, 473-479.
- Vlyssides, A.G., Israilides, C. J., Loizidou, M., Karvouni, G. & Mourafeti, V. 1997. Electrochemical treatment of vinasse from beet molasses. *Water Sci. Technol.* 36, 2-3.
- Vlyssides, A.G., Loizidou, M., Karlis, P.K., Zorpas A.A. & Papaioannou, D. (1999). Electrochemical oxidation of a textile dye wastewater using a Pt/Ti electrode. *J. Hazard. Mater.* B70, 41-52.
- Wahl, M. A., Carroy, B., Jermann, M., Dolata, P., Kedzierzawski, C., Chatelain, A., Monnier, J., Augustynski, H. (1995). Photoelectrochemical studies pertaining to the activity of TiO_2 towards photodegradation of organic compounds. *J. Electroanal. Chem.* 396, 41-51.
- Walton, D. J. & Phull, S.S. (1996). Sonoelectrochemistry: In advances in Sonochemistry. 4, 205-284.
- Webber, E. J. & Stickney, V. C. (1993). Hydrolysis kinetics of reactive blue 19 - vinyl sulfone. *Wat. Res.* 27(1), 63-67.
- Weisburger, J.H. (2002). Comments on the history and importance of aromatic and heterocyclic amines in Public health. *Mutat. Res.* 506, 9-20.
- Weschenfelder, S. E., Jose, H. J., Gebhardt, W. & Schroder, H. F. (2007). Monitoring the Physicochemical and Chemical Treatment of Textile Wastewater using GC/MS, LC/MS and MS/MS Techniques. *Sep. Sci. Technol.* 42, 1535-1551.
- Wilcock, A. (1992). Spectrometric analysis of electrochemically treated simulated dispersed dyebath effluent. *Text. Chem. Color.* 24, 29-37.
- Wu, C., Liu, X., Wei, D., Fan, J. & Wang, L. (2001). Photosonochemical degradation of phenol in water. *Wat. Res.* 35(16), 3927-3933.
- Wu, J. & Wang, T. (2001). Ozonation of aqueous azo dye in a semi-batch reactor. *Water Res.* 35, 1093-1099.
- Xia, H., Zhuang, H., Xiao, D. & Zhang, T. (2008a). Photocatalytic activity of $\text{La}^{3+}/\text{S}/\text{TiO}_2$ photocatalyst under visible light. *J. Alloy Compd.* 465, 328-332.

- Xia, H., Huisheng, Z., Dongchang, X. & Tao, Z. (2008b). Photocatalytic activity of lanthanum and sulfur co-doped TiO₂ photocatalyst under visible light. *J. Wuhan Uni. Technol. Mater. Sci. Edit.* 23(4), 467-471.
- Xiaomei, H., Xiliu, J. & Yi, J. (1992). Hydrolysis of four new pesticides. *J. Huanjing hua xue.* 11 (3) 16-21.
- Yakov, Y., Bulatov, V., Gridin, V. V., Agur, S., Galil, N., Armon, R. & Schechter, I. (2004). A new sonoelectrochemical method for enhanced detoxification of hydrophilic chloroorganic pollutants in water. *Ultrason. Sonochem.* 11, 365-372.
- Yang, C. L. & Garrahan, J. M. (2005). Electrochemical coagulation for textile effluent decolorization. *J. Hazard. Mater.* B127, 40-47.
- Yasar, A., Nasir, A. & Aamir, A. A. K. (2006). Energy requirement of ultraviolet and AOPs for the post-treatment of treated combined industrial effluent. *Color. Technol.* 122, 201-206.
- Zainal, Z., Lee, C. Y., Hussein, M. Z., Kassim, A. & Yusof, N. A. (2007). Electrochemical-assisted photodegradation of mixed dye and textile effluents using TiO₂ thin films. *J. Hazard. Mater.* 146, 73- 80.
- Zainal, Z., Lee, C. Y., Hussein, M. Z., Kassim, A. & Yusof, N. A. (2006). Electrochemical assisted photodegradation of mixed dye and textile effluents using TiO₂ thin films. Department of Chemistry, Universiti Putra Malaysia, 43400 UPM Serdang, Malaysia.
- Zamora, P. P., Kunz, A., Moraes, S. G. D., Pelegri, R., Moleiro, P. de C., Reyes, J. & Duran, N. (1999). Degradation of reactive dyes I. A comparative study of ozonation, enzymatic and photochemical processes. *Chemospher.* (4), 835-852.
- Zeng, L. & James, W.M. (2006). Degradation of pentachlorophenol in aqueous by audible-frequency sonolytic ozonation. *J. Hazard. Mater.* 35(1-3), 218-225.
- Zhiqiao, H., Lili, L., Shuang, S., Min, X., Lejin, X., Haiping, Y. & Jianmeng, C. (2008). Mineralization of C.I. Reactive Blue 19 by ozonation combined with sonolysis: Performance optimization and degradation mechanism, *Sep. Pur. Technol.*, 62, 376-381.

- Zielinska, B., Grzechulska, J. and Morawski, A.W. (2003). Photocatalytic decomposition of textile dyes on TiO₂-Tytanpol A11 and TiO₂-Degussa P25. *J. Photochem. Photobiol. A: Chem.* 157, 65-70.
- Zielinska, B., Grzechulska, J., Kalenczuk, R. J. & Morawski, A. W. (2003). The pH influence on photocatalytic decomposition of organic dyes over A11 and P25 titanium dioxide. *Appl. Catal. B: Envir.* 45, 293-300.

List of Publications

Journal

1. **Siddique. M**, R. Farooq, A. Shaheen, 2011. Removal of Reactive Blue 19 from wastewaters by physicochemical and biological processes - A review, J.Chem.Soc.Pak. 33 (2), 284-293 (IF 0.22).
2. **Siddique. M**, R. Farooq, Z. M. Khan, Z. Khan, S.F. Shaukat, 2011. Enhanced decomposition of Reactive Blue 19 dye in ultrasound assisted electrochemical reactor, Ultrason. Sonochem., 18, 190-196 (IF 2.993).
3. **Siddique. M**, R. Farooq, F. Athar, M. Qaisar, F. Umar, Raja. I. A, S.F. Shaukat, 2009. Thermal-pressure mediated hydrolysis of Reactive Blue 19 dye, J. Hazard. Mater., 172, 1007-1012 (IF 4.144).

Conference

1. **Siddique. M**, R. Farooq, 2009. Photocatalytic degradation of reactive blue 19 dye in presence of titanium dioxide catalyst Under UV irradiations, 3rd International Conference of Environmentally Sustainable held at COMSATS Institute, Abbottabad Pakistan.
2. **Siddique. M**, R. Farooq, A. Yaqub, 2009. Enhanced decomposition of Reactive Blue 19 dye by Ultrasonic cavitations- A poster presented at 1st Science Conference BICMAPE -2009, held at COMSATS Institute, Abbottabad Pakistan.
3. Khalid. A, **Siddique. M**, R. Farooq, 2009. Catalytic hydrolysis of Reactive Blue 222, 3rd International Conference of Environmentally Sustainable held at COMSATS Institute, Abbottabad Pakistan.

Appendix I

Table 1. (Figure 4.1): Effect of initial pH on the percentage removal of dye concentration

Time (min)	pH 3	pH 4	pH 5	pH 6	pH 7	pH 8	pH 9
30	6.20	8.50	12.28	15.22	26.44	37.08	28.82
60	10.40	18.94	20.94	24.32	37.7	50.88	43.42
90	16.20	26.04	28.52	35.88	43.14	59.92	52.12
120	22.24	27.20	35.02	43.54	47.48	67.68	58.20

Table 2. (Figure 4.2): Effect of ultrasonic power on percentage decrease in dye concentration

Time (min)	0 W	120 W	180 W	240 W
30	11.85	19.19	28.28	38.50
60	25.71	35.53	41.05	51.67
90	34.17	48.92	53.77	61.79
120	40.52	55.63	62.16	70.97

Table 3. (Figure 4.3): Comparison of ultrasound, electrochemical and ultrasound assisted electrochemical processes for decolorization of dye

Time (min)	ultrasound	electrochemical	Ultrasound assisted electrochemical
30	3.40	18.00	45.00
60	7.90	31.00	64.00
90	10.80	45.00	78.00
120	13.30	52.00	90.00

Table 4 (Figure 4.5 (a): Percentage degradation of RB 19 (b) Percentage decolorization of RB 19

Time	Percentage degradation of different dye concentrations				
(min)	20 mgL ⁻¹	40 mgL ⁻¹	60 mgL ⁻¹	80 mgL ⁻¹	100 mgL ⁻¹
30	42.50	34.40	18.90	6.00	3.50
60	69.30	59.60	36.10	18.10	12.00
90	76.90	68.90	53.10	23.70	17.50
120	84.60	75.70	59.20	29.90	20.20

Time	Percentage decolorization of different dye concentrations				
(min)	20 mgL ⁻¹	40 mgL ⁻¹	60 mgL ⁻¹	80 mgL ⁻¹	100 mgL ⁻¹
30	69.50	60.70	49.10	31.80	23.50
60	85.10	78.90	72.70	53.20	40.70
90	91.60	85.50	79.60	59.50	51.80
120	99.00	91.20	83.80	62.70	53.80

Table 5 (Figure 4.6): First order kinetic plot of RB 19 degradation by ultrasound assisted electrochemical process

Time	Measurements of first order kinetics				
(min)	20 mgL ⁻¹	40 mgL ⁻¹	60 mgL ⁻¹	80 mgL ⁻¹	100 mgL ⁻¹
30	-0.52	-0.42	-0.21	-0.06	-0.04
60	-1.08	-0.81	-0.45	-0.20	-0.13
90	-1.47	-1.17	-0.66	-0.27	-0.19
120	-1.89	-1.42	-0.89	-0.36	-0.23

Table 6 (Figure 4.7): The relative changes in the removal of total organic carbon (TOC)

Time (min)	TOC/TOCo of Hydrolyzed Dye (50 mgL ⁻¹)	TOC/TOCo of Unhydrolyzed Dye (50 mgL ⁻¹)
30	0.9	0.53
60	0.26	0.52
90	0.169	0.46
120	0.158	0.43

Table 6 (Figure 4.7): The relative changes in the removal of total organic carbon (TOC)

Raw data of the Total Carbon and Inorganic Carbon

Time (min)	Hydrolyzed Dye (50 mgL ⁻¹)		Unhydrolyzed Dye (50 mgL ⁻¹)	
	TC (ppm)	IC (ppm)	TC (ppm)	IC (ppm)
0	132.4	0.71	43.34	14.00
30	144.5	1.15	23.70	8.08
60	27.14	4.34	24.01	8.09
90	27.65	6.84	24.34	13.65
120	27.78	3.49	23.17	9.39

Table 7 (Figure 5.1): Effect of pH on the hydrolysis of RB 19 at 120 °C and 2 atm pressure

Time (min)	2 pH	4 pH	6 pH	8 pH	10 pH
30 min	8.06	8.41	4.49	4.08	5.89
60 min	12.17	12.6	8.26	6.18	8.09
90 min	16.04	17.58	10.42	9.98	10.29
120 min	20.14	21.76	12.03	11.88	13.54

Table 8 (Figure 5.3): Determination of order of reaction at 40 °C

Time (min)	2 pH	4 pH	6 pH	8 pH	10 pH
30 min	-0.002	-0.003	-0.002	-0.004	-0.003
60 min	-0.003	-0.006	-0.009	-0.006	-0.005
90 min	-0.005	-0.008	-0.011	-0.009	-0.008
120 min	-0.007	-0.009	-0.013	-0.012	-0.010

Table 9 (Figure 5.4): Determination of order of reaction at 120 °C

Time (min)	2 pH	4 pH	6 pH	8 pH	10 pH
30 min	-0.08	-0.09	-0.05	-0.04	-0.05
60 min	-0.13	-0.13	-0.09	-0.06	-0.08
90 min	-0.18	-0.19	-0.11	-0.12	-0.11
120 min	-0.23	-0.25	-0.12	-0.13	-0.15

Table 10 (Figure 5.5): First order kinetic plot of RB19 dye degradation by hydrolysis process at different concentrations at 120 °C

Time (min)	50 mgL ⁻¹	100 mgL ⁻¹	150 mgL ⁻¹
30 min	-0.15	-0.13	-0.09
60 min	-0.30	-0.27	-0.23
90 min	-0.44	-0.39	-0.35
120 min	-0.62	-0.52	-0.49

Table 11(Figure 5.7): Effect of H₂O₂ addition on the decolorization of RB 19

Time(min)	0.5 ml	1 ml	1.5 ml	2 ml	2.5 ml	3 ml
30	15.49	19.73	49.25	88.83	80.83	69.00
60	24.57	27.9	60.3	91.94	86.59	76.00
90	32.93	37.34	68.57	94.77	90.85	83.00
120	40.15	47.38	75.73	97.61	93.11	89.00

Table 12 (Figure 6.1): degradation of RB 19 in the presence of different conditions

Time (min)	UV only	TiO ₂ only	UV and TiO ₂
0	1.00	1.00	1.00
30	0.98	0.98	0.80
60	0.97	0.96	0.71
90	0.97	0.95	0.65
120	0.96	0.94	0.64

Table 13 (Figure 6.4): Comparison of ultrasound, photocatalysis and sonophotocatalysis processes for degradation of RB 19

Time (min)	US only	UV+TiO ₂	US+UV +TiO ₂
0	1.00	1.00	1.00
30	0.96	0.85	0.75
60	0.92	0.74	0.60
90	0.89	0.68	0.50
120	0.86	0.64	0.38

Table 14 (Figure 6.5): Effect of ultrasonic power on percentage degradation of RB- 19 by sonophotocatalysis process

Time (min)	0 W	120 W	180 W	240 W	300 W
30	20.00	22.50	29.80	39.20	37.70
60	25.60	29.60	39.30	48.70	47.50
90	31.20	37.60	48.90	60.20	58.70
120	35.70	44.20	59.50	73.00	70.90

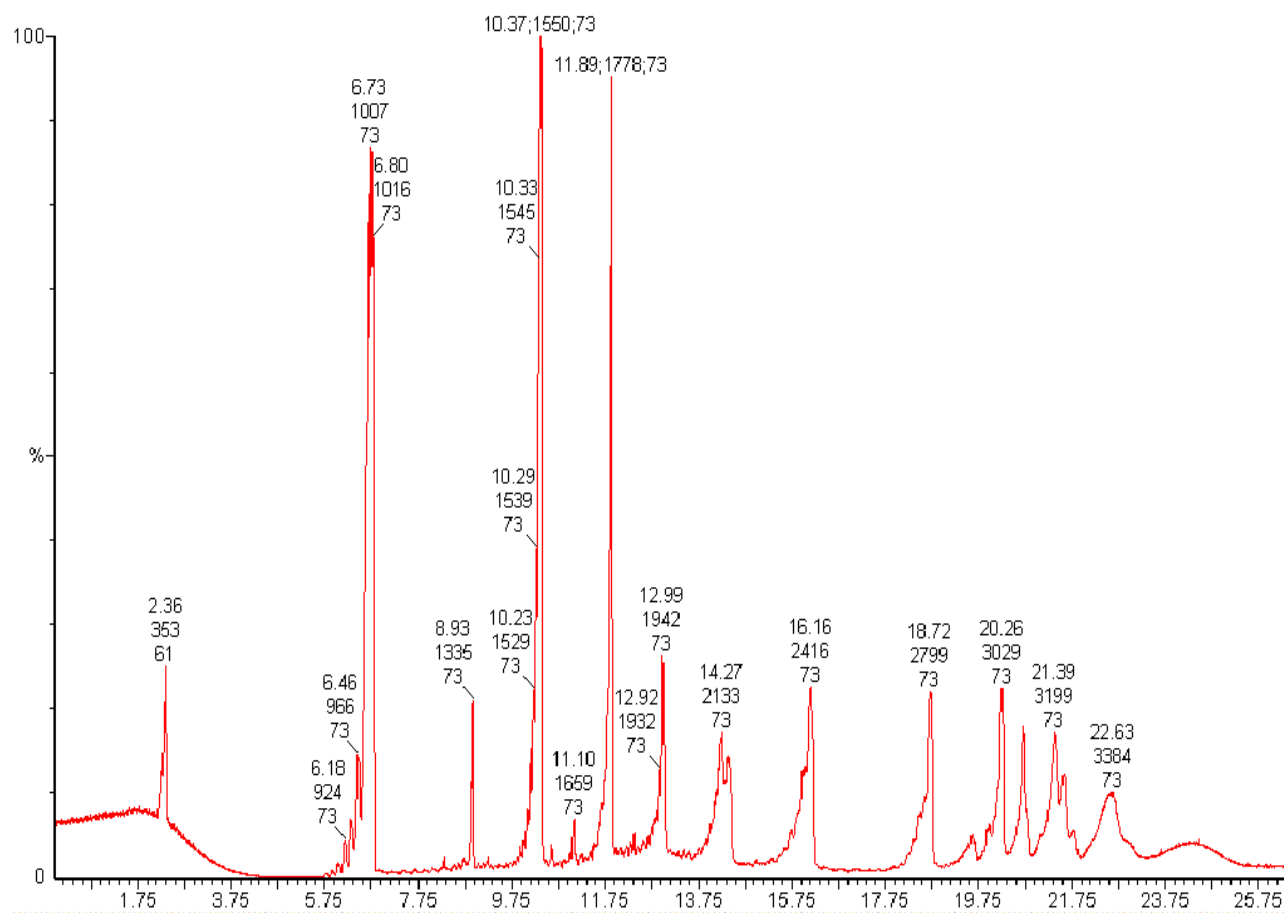
Table 15 (Figure 6.6): First order kinetics plot of RB 19 degradation under sonolysis (US), photocatalysis (UV+TiO₂) and sonophotocatalysis (US+UV+ TiO₂)

Time (min)	US	UV+TiO ₂	US+UV+TiO ₂
30 min	-0.03	-0.12	-0.28
60 min	-0.08	-0.29	-0.43
90 min	-0.12	-0.37	-0.65
120 min	-0.15	-0.44	-0.95

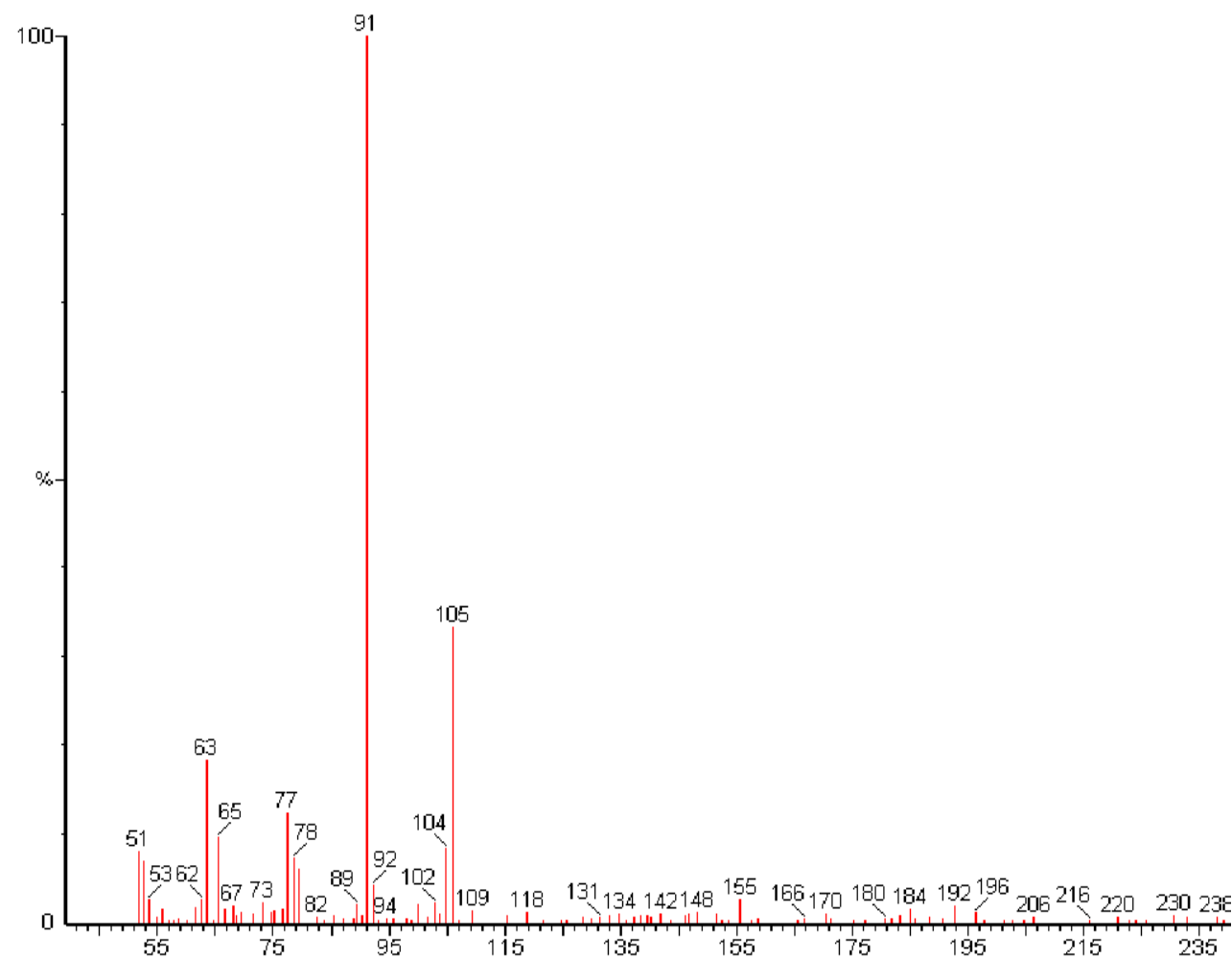
Appendix II

GC-MS Analysis of RB 19 after Hydrolysis Degradation

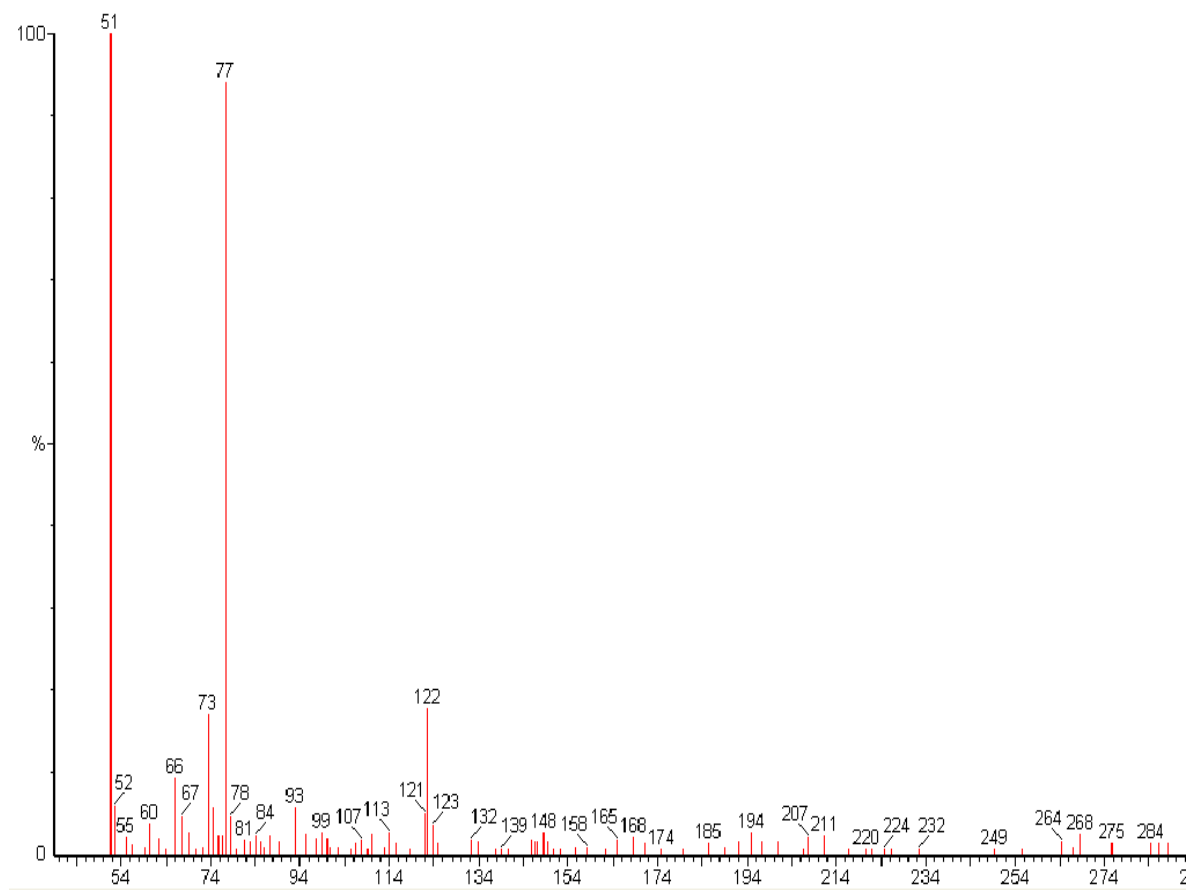
, 05-MAR-2009



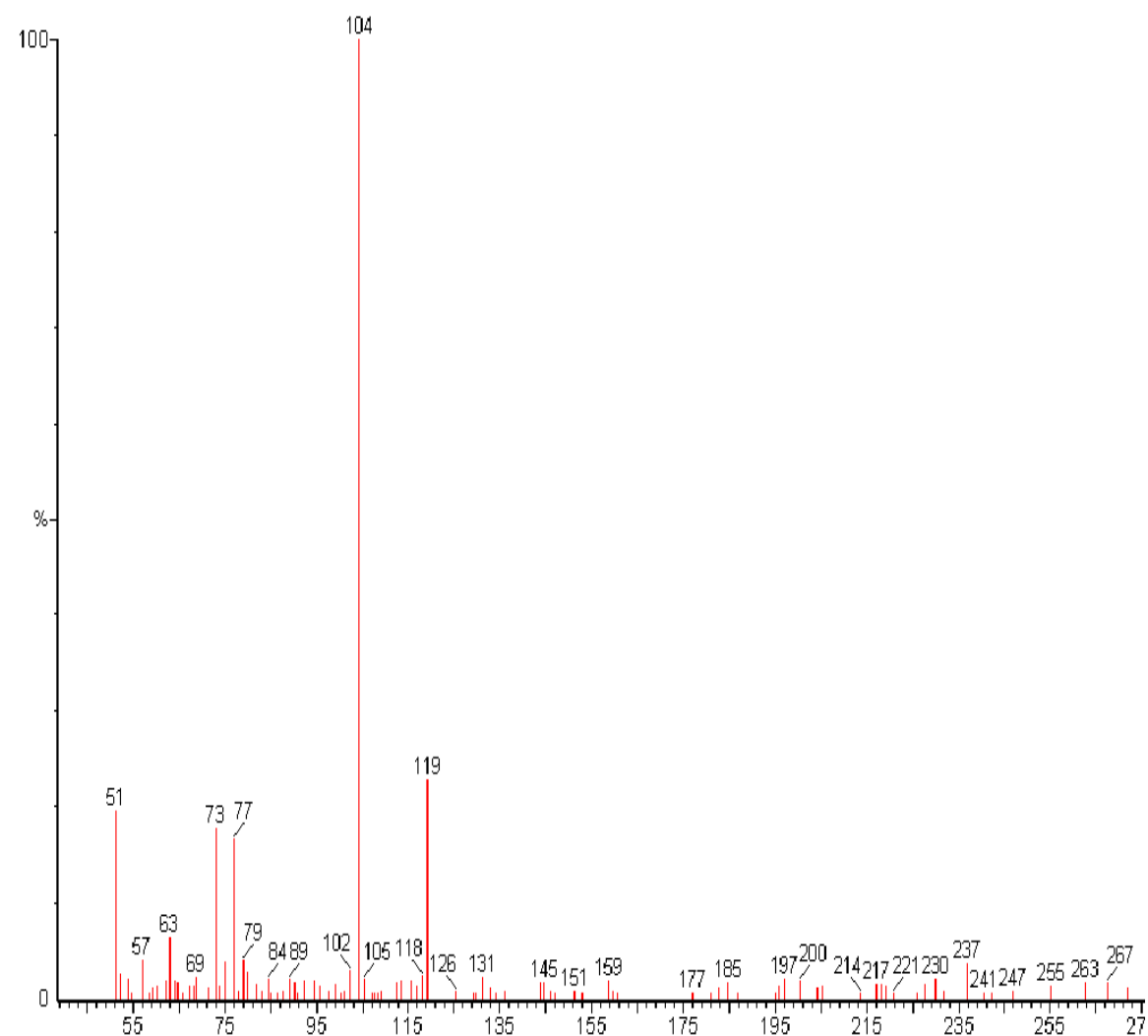
MS of Major Product (benzaldehyde) identified with fragmentation pattern



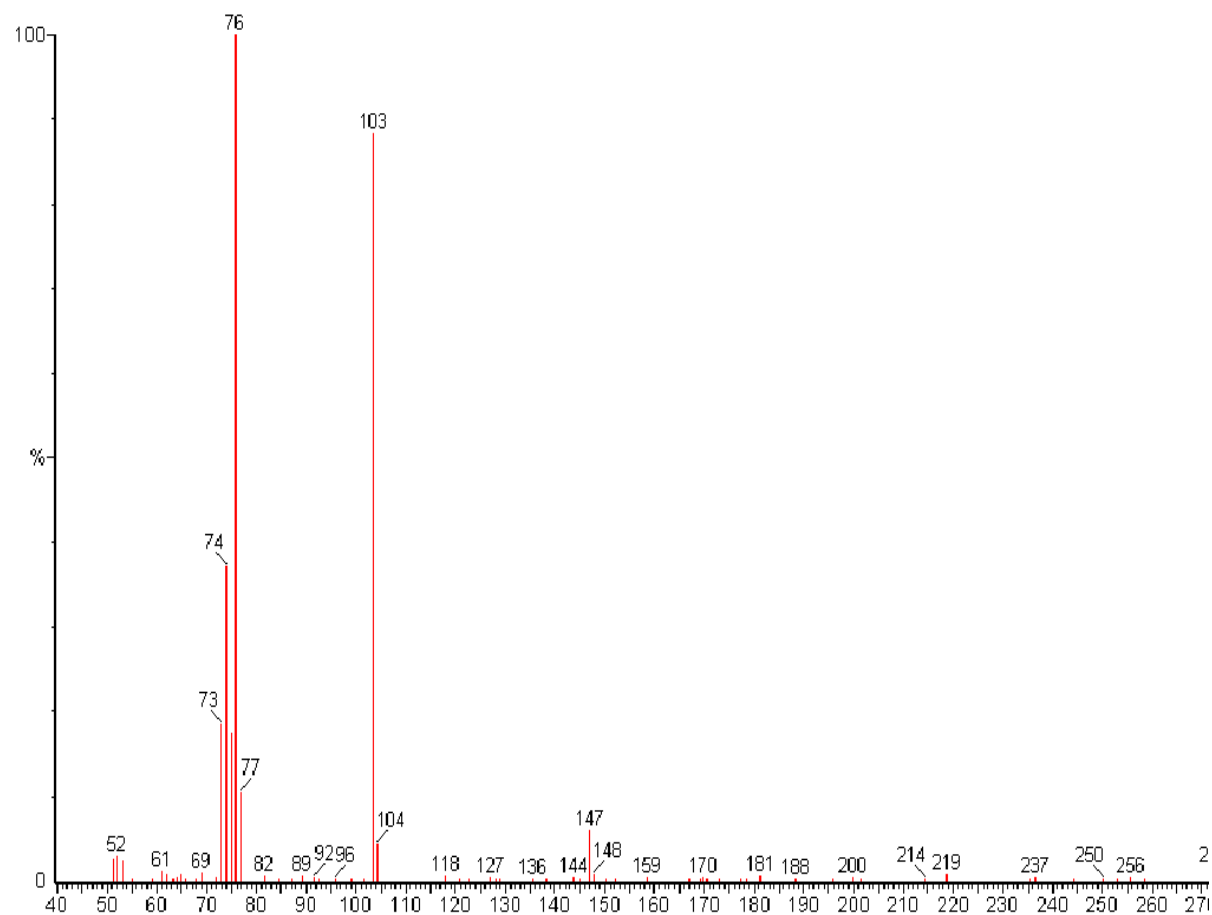
MS of Major Product (Benzoic acid) identified with fragmentation pattern



MS of Major Product (Acetophenone) identified with fragmentation pattern



MS of Major Product (Isobenzofuran-1,3-dione) identified with fragmentation pattern



Appendix III

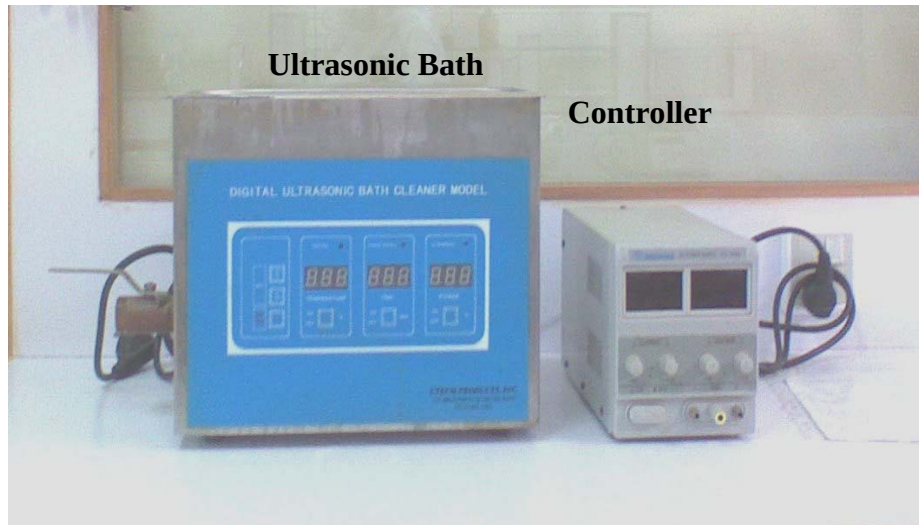


Figure 1: Ultrasonic Bath



Figure 2: Autoclave



Figure 3: UV-Visible Spectrophotometer



Figure 4: TOC Analyzer



Figure 5: GC-MS Analyzer

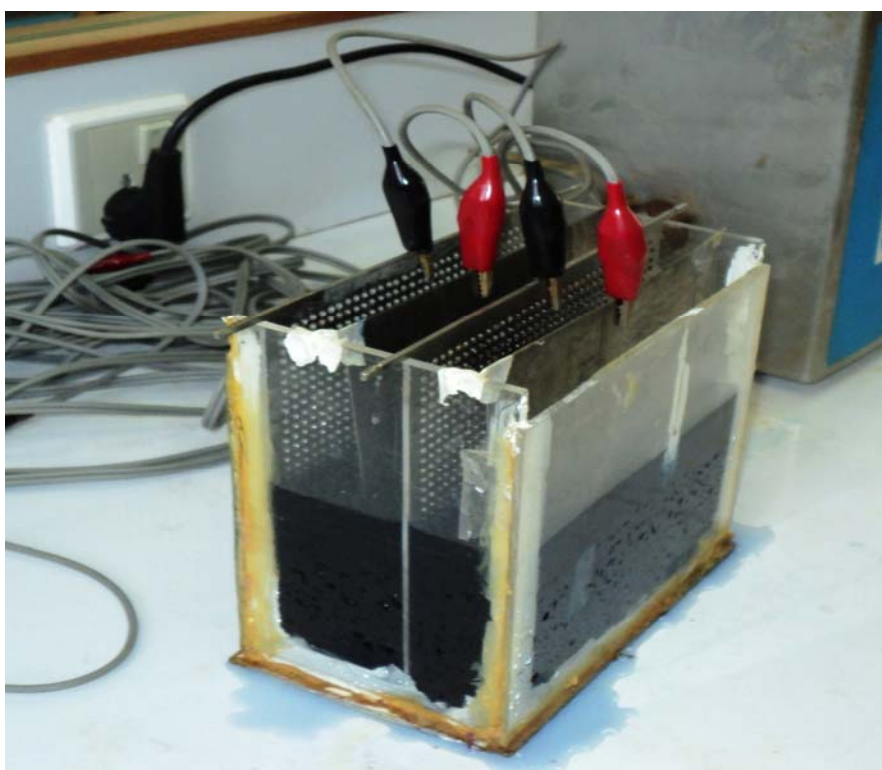


Figure 6: Electrolytic cell

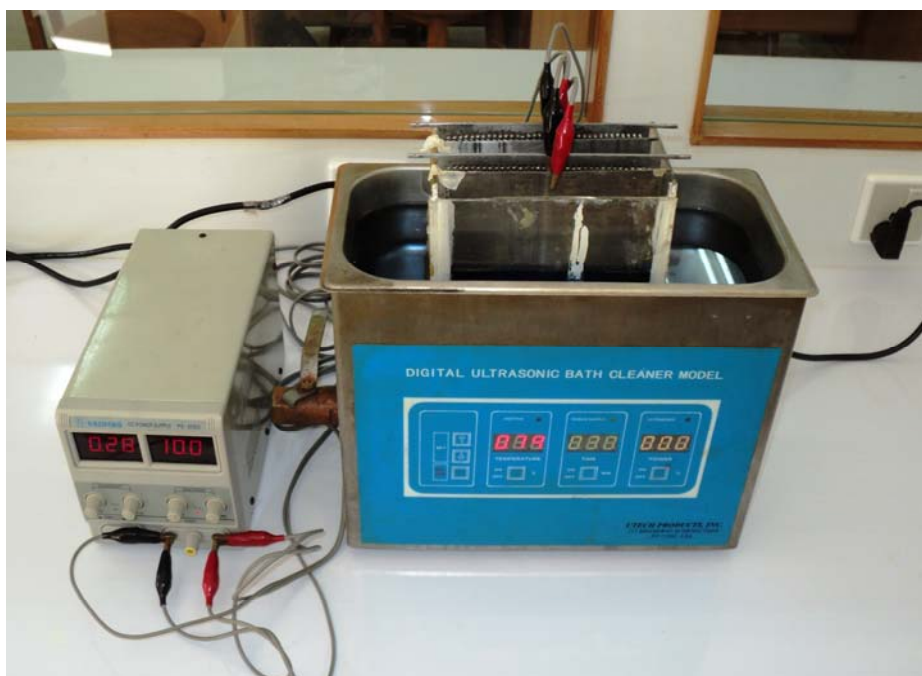


Figure 7: Sonoelectrochemical reactor



Figure 8: Photocatalytic reactor

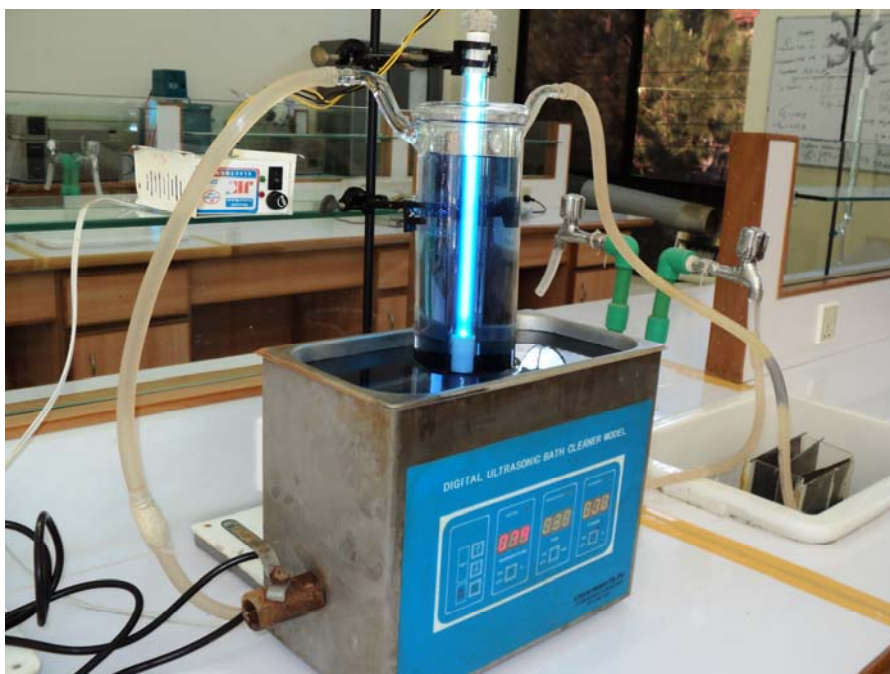


Figure 9: Sonophotocatalytic reactor

Appendix IV