PROCEEDINGS BOOK

St. Petersburg | 2018

ICNTC CONFERENCE

4th INTERNATIONAL CONFERENCE ON NEW TRENDS IN CHEMISTRY

4th International Conference on New Trends in Chemistry

St. Petersburg | 2018

ICNTC CONFERENCE

4th INTERNATIONAL CONFERENCE ON NEW TRENDS IN CHEMISTRY

MAY 11-13 2018
Original Sokos Hotel Olympia Garden – St Petersburg/Russia
http://www.icntcconference.com/

ICNTC'2018

4th International Conference on New Trends in Chemistry
St Petersburg/Russia

Published by the ICNTC Secretariat

Editors:
Assoc. Prof. Dr. Dolunay Sakar Dasdan

ICNTC Secretariat
Büyükdere Cad. Ecza sok. Pol Center 4/1 Levent-İstanbul
E-mail: aioc.chemistry@gmail.com
http://www.icntcconference.com

ISBN: 978-605-67476-2-5

Conference organised in collaboration with Smolny Institute of the Russian Academy of Education

SCIENTIFIC COMMITTEE

Prof. Dr Josef Trna,
Masaryk Univerzoty – Czech Republic

Prof.Dr.Frieder W. Scheller,
Institute of Biochemistry and Biology, University of Potsdam, Potsdam, Germany

Assoc. Prof. Dr. Dolunay Sakar Dasdan,
Yıldız Technical University – Turkey
Conference Chair

PhD Dr. Habil. Agnieszka Kaczor,
Medical University of Lublin, Department of Medical Analytics,
Faculty of Pharmacy, Poland

PhD Dr. Habil. Daniel Ayuk Mbi Egbe,
Linz Institute for Organic Solar Cells, Linz,
Austria

Dr. Aysu Yarman,

Dr. Decha Dechechtrirat,
Department of Materials Science,
Faculty of Science, Kasetsart University, Thailand

Dr. Eduardo V. Ludeña,
Escuela Superior Politecnica del Litoral Ecuador
Center of Nanotechnology Research and Development (CIDNA), Guayaquil, Ecuador

Dr. Mauricio Heriberto Cornejo Martinez,
Escuela Superior Politecnica del Litoral Ecuador
Center of Nanotechnology Research and Development (CIDNA), Guayaquil, Ecuador

ORGANIZATION COMMITTEE

Assoc. Prof. Dr. Dolunay Sakar Dasdan
Yıldız Technical University – Turkey
Conference Chair

Assoc. Prof. Dr. Yelda Yalcin Gurkan
Namik Kemal University – Turkey
Chemistry Department

Dear Colleagues,

I am honoured to invite and send you this call for papers on behalf of Conference Organisation Board of "***4th International Conference on New Trends in Chemistry***", to be held at St. Petersburg dates between 11 – 13th of May 2018

A limited number of Papers and Posters with the below mentioned topics will be accepted for our conference:

- Polymer Chemistry and Applications
- Pharmaceutical Chemsitry
- Computational Chemistry
- Bio Chemistry
- Physical Chemistry
- Analytical Chemistry
- Inorganic Chemistry
- Organic Chemistry
- Material Chemistry
- Environmental Chemistry

The most distinctive feature of ICNTC Conferences from other conference organizations is that the academicians working interdisciplinary can also attend to presentations performed in different speciality fields and they will also have the opportunity to meet with other academicians coming from various parts of the world.

Selected Papers presented as Oral Presentation in conference will be published in **Special Issue Edition of Bulgarian Chemical Communications**. **(ISSN:0324-1130)**

Web site of journal : http://www.bcc.bas.bg/

Bulgarian Chemical Communications is indexed by Science Citation Index Expanded (SCI-E).

We kindly wait for your attendance to our congress to be held on 11–13th of May 2018, with a hope to realize a satisfactory conference with it's social activities as well as the scientific ones and leaving a trace on your memories.

Respectfully Yours,
On Behalf of the Organization Committee of ICNTC Conference
Assoc. Prof. Dr. Dolunay SAKAR DASDAN
4th ICNTC 2018 | Conference Chair
Yıldız Technical University – Istanbul / Turkey
Chemistry Department

This Conference is organized in cooperation with **Smolny Institute of the Russian Academy of Education, St. Petersburg.**

SCIENTIFIC PROGRAM

10 MAY 2018 THURSDAY

18:00 – 21:00 : REGISTRATION

11 MAY 2018 FRIDAY

08:00 - 17:00 : REGISTRATION

MAIN HALL

09:00 – 09:30 : GRAND OPENING CEREMONY

09:30 – 09:40	B R E AK

HALL 1

09:40 – 09:50

Welcome Speech ***by Conference Chair***

Assoc. Prof. Dr. Dolunay SAKAR DASDAN / Yıldız Technical University , Turkey

HALL 1 / KEYNOTE SPEAKER

09:50 - 10:40	DR.AGATA BARTYZEL, Department of General and Coordination Chemistry, Faculty of Chemistry, Maria Curie-Sklodowska University, Poland Lecture Title: "Multifunctional N,O-donor ligands and their complexation abilities toward d-block metal ions"

10:40 – 11:00	C O F F E E / T E A B R E AK

HALL 1 / SESSION A

SESSION CHAIR	Dr.Agata BARTYZEL Maria Curie-Sklodowska University, Poland	
TIME	PAPER TITLE	PRESENTER / CO AUTHOR
11:00 – 11:20	EFFECT OF CHEMICAL TREATMENT ON THE PROPERTIES OF CHITOSAN MULTIWALL CARBON NANOTUBES NANOCOMPOSITE.	A. GOMEZ SANCHEZ, Evgen PROKHOROV, G. LUNA BARCENAS, E. M. RIVERA MIÑOZ; M. GRAZIA RAUCCI, G. BUONOCORE. *Cinvestav, Unidad Querétaro, Querétaro, MÉXICO.*
11:20 – 11:40	INVESTIGATION OF *IN-VITRO* SALT STRESS ON PEROXIDASE ENZYME OF *AMSONIA ORIENTALIS*	Yonca Avcı DUMAN, Arda ACEMİ, Yonca YUZUGULLU, Mustafa YILMAZ Fazıl ÖZEN

	AND PURIFICATION OF PEROXIDASE FROM NON-STRESSED AND SALT-STRESSED PLANTS	*Kocaeli University, Kocaeli, Turkey*
11:40 – 12:00	BIOSORPTION OF REACTIVE DYES BY KEFIR GRAINS	Ali Osman ERDOĞDULAR, Dilek KILIÇ APAR *Yıldız Technical University, Istanbul, Turkey*
12:00 – 12:20	ALGINATE AND CHITOSAN HYDROGELS AND THEIR COMPOSITES IN DRUG DELIVERY, WASTE WATER TREATMENT, FOOD COATING AGENTS AND WOUND DRESSINGS	F.Bedia ERİM *Istanbul Technical University, Istanbul, Turkey*
12:20 – 12:40	HOT-AIR DRYING OF KUMQUAT SLICES IN CONVECTIVE CABINET DRYER	İlknur KÜÇÜK, İbrahim DOYMAZ *Yıldız Technical University, Istanbul, Turkey*
12:40 – 13:00	SYNTHESIS AND FLUORESCENCE PROPERTIES OF SCHIFF-BASE FLUORINE-BORON COMPLEXES	Pınar ŞEN *Uskudar University, Istanbul, Turkey*

13:00 – 14:00	LUNCH

HALL 1 / SESSION B

SESSION CHAIR	PROF.DR. F.BEDIA ERIM Istanbul Technical University,Turkey	
TIME	PAPER TITLE	PRESENTER / CO AUTHOR
14:00 – 14:20	CONTROLLED RELEASE OF DONEPEZIL HYDROCHLORIDE FROM PEG-DA HYDROGELS UNDER UV IRRADITION	Şebnem ŞENOL, Emel AKYOL *Yıldız Technical University, Istanbul, Turkey*
14:20 – 14:40	AXIALLY CHIRAL QUINAZOLINE-4-ONES	Şule Erol GÜNAL, Ari HAKGÖR, Ilknur DOĞAN *Bogazici University, Istanbul, Turkey*
14:40 – 15:00	APPLICATIONS OF CORE-SHELL COMPOSITE HYDROGELS IN DRUG DELIVERY SYSTEMS	Büsra BODUR, Özlem DOGAN *Yıldız Technical University, Istanbul, Turkey*
15:00 – 15:20	SYNTHESIS AND CHACTERISATION OF NEW 2D OXALAMIDE FUNCTIONALIZED METAL ORGANIC FRAMEWORKS	Fatih SEMERCI, Yunus GÜÇLÜ, Seda KESKIN, Alper UZUN, Yunus ZORLU, Hakan ERER *Kırklareli University, Kırklareli, Turkey*
15:20 – 15:40	SYNTHESIS AND CHARACTERIZATION OF COBALT (II) COMPLEX AND ITS CATALYTIC ACTIVITY ON ALCOHOLS/ALKENES OXIDATION	Yalçın KILIÇ, İbrahim KANİ *University of Economics, İzmir, Turkey*

15:40 – 15:50	C O F F E E / T E A B R E AK

HALL 1 / SESSION C

SESSION CHAIR	Assit.Prof.Dr.Emel AKYOL, *Yıldız Technical University, İstanbul, Turkey*	
TIME	PAPER TITLE	PRESENTER / CO AUTHOR
15:50 – 16:10	A NOVEL SANDWICHED COMPOSITE ELECTRO-SPUN	Havva TUTAR KAHRAMAN, Şeyma DAĞDUR,

	MEMBRANE FOR FAST OIL-WATER SEPARATION	Tuğçe DEDE, Ahmet AVCI, Erol PEHLİVAN *Selcuk University, Konya, Turkey*
16:10 – 16:30	STEREOISOMERIC ASSIGNMENTS TO HEMIAMINALS OF HETEROCYCLIC COMPOUNDS	İlknur DOĞAN, Sevgi SARIGÜL, Şenel TEKE TUNÇEL *Boğaziçi University, İstanbul, Turkey*
16:30 – 16:50	POSSIBLE REACTION PATHWAYS of THE OXYDIBENZENESULFONYL HYDRAZIDE (OBSH) MOLECULE ACCORDING TO THE DFT CALCULATION METHOD	Yelda YALÇIN GÜRKAN , Bahar EREN *Namık Kemal University,Tekirdag, Turkey*
16:50 – 17:10	pH EFFECT ON THE PARTICLE SIZE AND ZETA POTENTIALS OF POLY (ETHYLENE GLYCOL) AND POLY EHTYLENE-BLOCK-POLY(ETHYLENE GLYCOL) WITH VARIOUS MOLECULAR WEIGHTS	Dolunay ŞAKAR DAŞDAN, Gamze Tosun, Yeşim Karahan Yıldız Technical University, Istanbul, Turkey

17:10 – 17:45	LIVE CONCERT by CONFERENCE PARTICIPANTS

17:45 – 19:30	HOTEL DEPARTURE FOR BOAT TOUR (Incl. into Registration Fee)

12 MAY 2018

08:30-17:00 : REGISTRATION

HALL 1 / KEYNOTE SPEAKER

09:00 – 09:30	PROF. DR MUSTAFA ERSÖZ SELCUK UNIVERSITY, KONYA TURKEY Lecture Title: “NANOSTRUCTURED FUNCTIONAL MATERIALS BASED ON SELF-ASSEMBLY OF BLOCKCOPOLYMERS”

HALL 1 / SESSION D

SESSION CHAIR	PROF. DR VURAL BÜTÜN ESKİŞEHİR OSMAN GAZI UNIVERSITY, ESKIŞEHIR, TURKEY	
TIME	PAPER TITLE	PRESENTER / CO AUTHOR
09:30 – 09:50	STRUCTURAL CHARACTERIZATION and *IN VITRO* BIOACTIVITY of TITANIUM-DOPED 45S5 BIOGLASSES	Sevil YÜCEL, Burcu KARAKUZU İKİZLER, Pınar TERZİOĞLU, Yeliz ELALMIŞ *Yıldız Technical University, İstanbul, Turkey*
09:50 – 10:10	AMPEROMETRIC DETECTION OF CADAVERINE WITH c-MWCNTs-CO_3O_4 MODIFIED SCREEN-PRINTED ELECTRODE	Ceren KAÇAR *Ankara University, Ankara, Turkey*
10:10 – 10:30	EFFECT of PROCESS PARAMETERS on the PRODUCTION of METAL INCORPORATED SILICA AEROGELS	Pınar TERZİOĞLU, Burcu KARAKUZU IKIZLER, Tülay Merve TEMEL, Sevil YÜCEL *Muğla Sıtkı Koçman University, Muğla, Turkey*
10:30 – 10:50	THE RELATIONSHIP BETWEEN SEA SURFACE TEMPERATURES AND RAINFALL OVER TURKEY	Esin BOZKURT KOPUZ *Marmara University, Istanbul,Turkey*

10:50 – 11:00	C O F F E E / T E A B R E AK

HALL 1 / SESSION E

SESSION CHAIR	PROF. DR MUSTAFA ERSÖZ SELCUK UNIVERSITY, KONYA, TURKEY	
TIME	PAPER TITLE	PRESENTER / CO AUTHOR
11:00 – 11:20	CHELATING BENZIMIDAZOLE FUNCTIONALIZED PERYLENE DIIMIDE DERIVATIVES WITH DIFFERENT BAY-SUBSTITUENTS	Abdurrahman ŞENGÜL, Fatih PEKDEMİR *Bülent Ecevit University,Zonguldak, Turkey*
11:20 – 11:40	VOLTAMMETRIC SENSING OF TRICLOSAN BASED ON THE ENHANCEMENT EFFECT OF THE CATIONIC SURFACTANT AT CATHODICALLY PRETREATED BORON-DOPED DIAMOND ELECTRODE	Nurcan ALPAR, Yavuz YARDIM, Zühre ŞENTÜRK *Van Yüzüncü Yıl University, Van, Turkey*
11:40 – 12:00	ADSORPTION CAPACITIES OF NOVEL ECO-FRIENDLY BIOSORBENTS IN REMOVAL OF CONTAMINANTS IN AQUEOUS SOLUTIONS	Elif Hatice GÜRKAN, Berkay İLYAS *Ondokuz Mayis University Samsun Turkey*
12:00 – 12:20	THE FT-IR, NMR SPECTROSCOPY AND COMPUTATIONAL STUDY OF THE SUBSTITUTED CARBAZOLE USED IN SYNTHESIZING OF THE STRYCHNOS ALKALOIDS	Goncagül SERDAROĞLU, Nesimi Uludağ *Cumhuriyet University, Sivas, Turkey*
12:20 – 12:40	ADSORPTION OF Th(IV) ONTO CHEMICALLY MODIFIED ACTIVATED CARBON	Özlem SELÇUK ZORER, Çiğdem ÖTER *Van Yüzüncü Yıl University, Van, Turkey*
12:40 – 13:00	DETERMINATION OF WATER CONTENT IN APROTIC SOLVENT BY ANTRAQUINONE-MODIFIED MULTI-WALLED CARBON NANOTUBES	İzzet KOÇAK *Bulent Ecevit University, Zonguldak Turkey*

13:00 – 14:00	LUNCH

HALL 1 / KEYNOTE SPEAKER

14:00 – 14:30	PROF. DR VURAL BÜTÜN Lecture Title: STIMULI-RESPONSIVE POLYMERS: INTELLIGENT, SURFACE-ACTIVE, SCHIZOPHRENIC, AND SUPERB SOURCE FOR VARIOUS NANOSTRUCTURES “

HALL 2 / SESSION F

SESSION CHAIR	Prof.Dr. Sevil YÜCEL YILDIZ TECHNICAL UNIVERSITY, ISTANBUL, TURKEY

TIME	PAPER TITLE	PRESENTER / CO AUTHOR
14:30 – 14:50	INHIBITION EFFECT OF POLYACRYLIC ACID AND ITS MIXTURE WITH POTASSIUM IODIDE ON MILD STEEL CORROSION IN ACID SOLUTION	İlyas DEHRİ, Gökmen SIĞIRCIK, Ayşen SARI, Mehmet ERBİL *Çukurova University, Adana, Turkey*
14:50 – 15:10	SYNTHESES AND SPECTROSCOPIC CHARACTERIZATIONS OF MONO CYCLO-2,2'-DİHYDROBIPHENYLPHOSPHAZENE BEARING VANILLINATO GROUPS	Yasemin TÜMER, Sinan Ziya ÖZDEMİR *Karabük University,Karabük, Turkey*
15:10 – 15:30	ELECTROCHEMICAL BEHAVIOUR OF OFLOXACIN IN PHARMACEUTICAL AND BIOLOGICAL SAMPLES USING A BORON-DOPED DIAMOND ELECTRODE IN USING ANIONIC SURFACTANT	Pınar TALAY PINAR, Zühre ŞENTÜRK *Van Yüzüncü Yıl University, Van, Turkey*
15:30 – 15:50	CONTROLLED RELEASE OF DRUG FROM A NEW PLATFORM BASED CALIXARENE NANOFIBER	Esra MALTAS CAGIL, Othman HAMEED, Fatih OZCAN *Selcuk University, Konya, Turkey*
15:50 – 16:10	DEVELOPMENT OF DISPOSABLE AMPEROMETRIC PUTRESCINE BIOSENSOR USING METHYLENE BLUE AS A MEDIATOR	Berna DALKIRAN *Ankara University, Ankara, TURKEY*

16:10 – 16:30	C O F F E E / T E A B R E AK

HALL 1 / SESSION G

SESSION CHAIR	Prof.Dr.İlyas DEHRİ, Çukurova University, Adana, Turkey	
TIME	PAPER TITLE	PRESENTER / CO AUTHOR
16:30 – 16:50	SPECTROSCOPIC AND PHOTOPHYSICAL PROPERTIES OF TWISTED PERYLENE DIIMIDES APPENDED WITH CHELATING N-HETEROCYCLES	Abdurrahman ŞENGÜL, Sebile Işık BÜYÜKEKŞİ, Nursel ACAR, Ahmet ALTINDAL, Ali Rıza ÖZKAYA *Bülent Ecevit University, Zonguldak, Turkey*
16:50 – 17:10	IMMOBILIZATION OF LIPASE-PRODUCING BACTERIA *Acinetobacter Haemolyticus* ON EGGSHELL MEMBRANE	Ceyhun IŞIK, Nurdan SARAÇ, Mustafa TEKE, Aysel UĞUR *Mugla Sıtkı Koçman University, Muğla, Turkey*
17:10 – 17:30	NEW SYNTHETIC METHODS FOR PYRAZOLE FUSED HETEROCYCLIC COMPOUNDS	Meltem TAN *Van Yüzüncü Yıl University , Van, Turkey*
17:30 - 17:50	NOVEL METAL-BASED ANTICANCER DRUGS: SYNTHESIS AND A NEW APPROACH TO DRUG DELIVERY	Ayşegül GÖLCÜ *Istanbul Technical University, Turkey*
17:50 – 18:10	ELECTROCHEMICAL PROPERTIES OF LANTHANIDE SERIES BIS-PHTHALOCYANINES	Efe B. ORMAN, Emre GÜZEL, Baybars KÖKSOY, Ali R.ÖZKAYA *Marmara University.,Istanbul, Turkey*

18:10 - 18:30	COST AND INTERNATIONAL NETWORK WORKSHOP	Mustafa Ersöz, *Selcuk University, Konya, Turkey*

18:30 – 18:40	B R E AK

HALL 1 / POSTER SESSION H

SESSION CHAIRS	Assoc.Prof.Dr.Dolunay ŞAKAR DAŞDAN Yildiz Technical University,Istanbul, Turkey	Assoc.Prof.Dr.Yelda YALÇIN GÜRKAN Namık Kemal University, Tekirdağ, Turkey
18:40 – 19:40	PAPER TITLE	PRESENTER / CO AUTHOR
PREPARATION OF AMINO MODIFIED RECYCLED POLYETHYLENE TEREPHTHALATE NANOFIBERS AND INVESTIGATION OF USAGE IN WASTE WATER FILTRATION		Yaşar Can AYRA, Memet Vezir KAHRAMAN, Bahattin YALÇIN *Marmara University, Istanbul, Turkey*
POLY(METHACRYLOYLOXY ETHYL PHOSPHATE) GRAFTED PVDF POLYMER ELECTROLYTE MEMBRANES VIA SURFACE INITIATED ATRP		Nilhan Kayaman Apohan, Burcu OKTAY, Mustafa H. UĞUR *Marmara University, Istanbul, Turkey*
THE PREPARATION OF FLUORINE AND GRAPHENE OXIDE CONTAINING HYDROPHOBIC NANOCOMPOSITE COATINGS		Nilhan Kayaman Apohan, Seda Akhan, Burcu OKTAY, Seyfullah MADAKBAŞ *Marmara University, Istanbul, Turkey*
DIELECTRIC PROPERTIES OF POSS/ POLYIMIDE NANOCOMPOSITES		Seyfullah MADAKBAŞ, Hatice BİRTANE, Kadir ESMER, Memet Vezir KAHRAMAN *Marmara University, Istanbul, Turkey*
FLUORIMETRIC SENSOR FOR CYANIDE IONS		Soner ÇUBUK, Aykut KAPLAN, Ece KÖK YETİMOĞLU, M. Vezir KAHRAMAN *Marmara University, Istanbul, Turkey*
COMPREHENSIVE SCREENING OF BEE PRODUCTS FLAVONOID CONTENTS WITH TIME EFFECTIVE AND SENSITIVE HPLC-UV METHODOLOGY		İsmail Emir AKYILDIZ, Soner ÇUBUK, Ece KÖK YETİMOĞLU, Özge ERDEM *Marmara University, Istanbul, Turkey*
A TURN OFF FLUORESCENT SENSOR FOR ALUMINIUM IONS		Ece KÖK YETİMOĞLU, Pelin ATBAŞ, Soner ÇUBUK, M. Vezir KAHRAMAN *Marmara University, Istanbul, Turkey*
A NOVEL APPROACH FOR QUANTITATIVE ANALYSIS OF UNCONJUGATED BISPHENOL A LEVELS IN MATERNAL AND UMBILICAL CORD BLOOD		İsmail Emir AKYILDIZ, Ece KÖK YETİMOĞLU, Soner ÇUBUK, Sezer ACAR *Marmara University, Istanbul, Turkey*

A COMPUTATIONAL APPROACHES ON THE STRUCTURAL, ELECTRONIC AND SPECTROSCOPIC PROPERTIES OF THE PHENYLHYDRAZINE	Goncagül SERDAROĞLU, Nesimi ULUDAĞ *Cumhuriyet University, Sivas, Turkey*
PREPARATION OF REDUCED GRAPHENE OXİDE-CLAY NANAOCOMPOSİTE AND INVESTIGATION OF ITS PROPERTIES	Sevil ÇETİNKAYA, Nurşah KÜTÜK *Cumhuriyet University, Sivas, Turkey*
PREPARATION AND CHARACTERIZATION OF POLY(SODIUM 4-STYRENESULFONATE)-DECORATED SnO_2 NANOPARTICLES BY HYDROTHERMAL METHOD	Filiz BORAN, İmren TAŞKIRAN Sevil ÇETİNKAYA *Cumhuriyet University, Sivas, Turkey*
THE MODIFICATION OF THE SURFACE OF POLYACRYLONITRILE FIBER BY GRAFTING OF GLYCIDYL METHACRYLATE MONOMER	Meral ŞAHİN, Nihan SEVEN, Meryem KALKAN ERDOĞAN, Mehmet SAÇAK *Ankara University, Ankara Turkey*
EDIBLE FILMS BASED ON CHITOSAN: PREPARATION AND PHYSICO-CHEMICAL EVALUATION	Fatmagül ŞAHİN, N. Gayenur HUT, G. Helin ÖZÇELİK, İlknur KÜÇÜK, İbrahim DOYMAZ *Yıldız Technical University, Istanbul Turkey*
ADSORPTION OF BOVINE SERUM ALBUMIN ONTO HYDROXYAPATITE	Imren EKINGEN, Özlem DOGAN *Yıldız Technical University, Istanbul Turkey*
INTERMOLECULAR INTERACTIONS BETWEEN SULFADIAZINE AND SACCHARIN	Nursel ACAR, Emine COŞKUN *Ege University, İzmir, Turkey*
INTERMOLECULAR INTERACTIONS BETWEEN SEROTONIN AND PROMAZINE USING COMPUTATIONAL METHODS	Tuğçe ŞENER RAMAN, Nursel ACAR *Ege University, İzmir, Turkey*
ELECTROCHEMICAL INVESTIGATION OF INTERACTION BETWEEN NIMESULIDE AND Cd(II) IONS IN THE ABSENCE AND PRESENCE OF HYDROGEN PEROXIDE	Emine COŞKUN, Nursel ACAR *Ondokuz Mayıs University, Samsun,Turkey*
PRECONCENTRATION OF COPPER, LEAD, GOLD AND PALLADIUM BY MICROEXTRACTION TECHNIQUE BASED ON IONIC LIQUID	Ümit DİVRİKLİ, Burak AKSOY, Mustafa SOYLAK, Latif ELÇİ *Pamukkale University, Denizli, Turkey*
SELECTIVE EXTRACTION OF IRON, GOLD AND PALLADIUM WITH DISPERSIVE LIQUID LIQUID MICROEXTRACTION METHOD	Ümit DİVRİKLİ, Mustafa SOYLAK, Latif ELÇİ *Pamukkale University, Denizli, Turkey*
DEGRADATION RATE OF PAPER DYED WITH *RHEUM RIBES* L.	Pınar ÇAKAR, Emel AKYOL *Yıldız Technical University, Istanbul, Turkey*
ANODICALLY PRETREATED BORON-DOPED DIAMOND ELECTRODE FOR ANTITHYROID DRUG METHIMAZOLE DETERMINATION IN THE PHARMACEUTICAL FORMULATIONS	Safanur Seyidahmet, Fatih Dönmez, Yavuz YARDIM, Zühre Şentürk *Van Yuzuncu Yil University,Van, Turkey*
EXTRACTION OF PHENOLICS IN CARROT WITH METHANOL SOLVENTS HAVING DIFFERENT pH VALUES	Fatma ISIK ‘Unkan URGANCI, Figen TURAN, Cansu TOPKAYA *Pamukkale University, Denizli, Turkey*
ANTHOCYANINS and DIFFERENT METHODS OF EXTRACTION from SOME FRUITS and VEGETABLES	Cansu TOPKAYA, Unkan URGANCI, Fatma IŞIK, Figen TURAN *Pamukkale University, Denizli, Turkey*
DETERMINATION THE ANTIOXIDANT ACTIVITIES OF VARIOUS DRIED GOJI BERRIES PROVIDED FROM DENIZLI MARKETS	Ünkan URGANCI, Figen TURAN, Fatma IŞIK’ Cansu TOPKAYA *Pamukkale University, Denizli, Turkey*

DETERMINATION THE COLOR VALUES OF RED CABBAGE EXTRACTS HAVING DIFFERENT pH VALUES	Figen TURAN, Fatma ISIK, Unkan URGANCI, Cansu TOPKAYA *Pamukkale University, Denizli, Turkey*
EXCELLENT CORROSION INHIBITION PERFORMANCE PYRAZINECARBOXAMIDE ON MILD STEEL IN 0.5 M HCl	Ayşen SARI, İlyas DEHRİ *Çukurova University, Adana, Turkey*
THE INVESTIGATION OF STRUCTURAL ALTERATION OF RAW MATERIALS USED TO ATTAIN GRAPHENE QUANTUM DOT IN DIFFERENT PROLYSIS CONDITIONS	Şifa KIR, Ilyas DEHRİ, Yunus ÖNAL, Ramazan ESEN *Çukurova University, Adana,Turkey*
NEW IMPROVEMENTS ON SUPERCRITICAL DYEING MACHINES	Nalan DEVRENT, Sema PALAMUTCU *Pamukkale University, Denizli, Turkey*
APPLICATION OF SUPERCRITICAL FLUID DYEING PRINCIPLE FOR THE SYNTHETIC TEXTILE FIBERS	Nalan DEVRENT , Sema PALAMUTCU *Pamukkale University, Denizli, Turkey*
ELECTROCHEMICAL DETERMINATION OF LUTEOLIN IN BIOLOGICAL SAMPLE AT A CATHODICALLY PRETREAMENT BORON-DOPED DIAMOND ELECTRODE IN THE PRESENCE CATIONIC SURFACTANT USING SQUARE-WAVE ADSORPTİVE STRIPPING VOLTAMMETRY	Melike KENDİRCİ, Pınar TALAY PINAR, Zühre ŞENTÜRK *Van Yüzüncü Yıl University, Van, Turkey*
ENYZMATIC TREATMENT ALTERNATIVES IN TEXTILE	Nalan DEVRENT, Sema PALAMUTCU *Pamukkale University, Denizli, Turkey*
APPLICATION OF SUPER ABSORBENT POLYMERS IN TEXTILE PRODUCTS	Nalan DEVRENT, Sema PALAMUTCU *Pamukkale University Denizli, Turkey*
BIOLOGICAL ACTIVITY OF AMIDE DERIVATIVES SYNTHESİZED FROM BENZOCAINE	Fatma ESEN, Kader GÜNDÜZALP, Meltem TAN *Van Yüzüncü Yıl University, Van, Turkey*
MOLECULER MODELING of CAPSAICIN MOLECULE	Yelda YALCIN GURKAN, Bahar EREN, Yasemin IYIDOGAN *Namık Kemal University, Tekirdag, Turkey*
ELECTROCHEMICAL, SPECTROELECTROCHEMICAL AND ELECTROCOLORIMETRIC CHARACTERIZATION OF NOVEL PT(II) AND PD(II) COMPLEXES OF PYRIDINE APPENDED PERYLENE DIIMIDE FOR ELECTROCHROMIC APPLICATIONS	Efe Baturhan ORMAN, Ali Rıza ÖZKAYA, Sebile Işık BÜYÜKEKŞİ, Abdurrahman ŞENGÜL *Marmara University, Istanbul, Turkey*
ELECTROCHEMICAL, SPECTROELECTROCHEMICAL AND ELECTROCATALYTIC CHARACTERIZATION OF NOVEL PHTHALOCYANINE COMPOUNDS INCLUDING 1,1'-THIOBIS (2-NAPHTOL) MOIETIES	Sevinç ARUCU, Efe Baturhan ORMAN, Ali Rıza ÖZKAYA, Meltem Betül SAĞLAM *Marmara University, Istanbul, Turkey*
COMPARISON OF U(VI) ADSORPTION ONTO DIFFERENT ADSORBENTS	Özlem SELÇUK ZORER, Çiğdem ÖTER *Van Yüzüncü Yıl University, Van, Turkey*
DETERMINATION OF PARTICLE SIZES OF NANOPARTICLES BY NMR SPECTROSCOPY	Gökhan DİKMEN *Eskisehir Osmangazi University, Eskisehir, Turkey*
INVESTIGATION OF INTERACTION BETWEEN 2-THIOURACIL AND TIO_2 THROUGH NMR, FT-IR, RAMAN SPECTROSCOPIC METHODS AND DFT	Gökhan DİKMEN *Eskisehir Osmangazi University, Eskisehir, Turkey*
INVESTIGATION OF SUPEROXIDE DISMUTASE ACTIVITY, GLUTATHIONE AMOUNT AND PROTEIN CARBONYL LEVEL AT *Cyprinidae Family* EXPOSED TO	Şenay AKKUŞ ÇETİNUS, Mustafa Doğan BEDİR

VARIOUS STRESSORS	*Cumhuriyet University, Sivas, Turkey*
IMMOBILIZATION OF CATALASE IN PARAFFIN WAX	Burcu EROL, Şenay AKKUŞ ÇETİNUS *Cumhuriyet University, Sivas/ Turkey*
ELECTROSPUN POLYVINYL ALCOHOL/ZNO NANOFIBER AS A NEW CARRIER FOR LIPASE IMMOBILIZATION: AN OPTIMIZATION STUDY	Ceyhun IŞIK, Gökmen ARABACI, Yasemin İspirli DOĞAÇ, İlyas DEVECİ, Mustafa Teke *Muğla Sıtkı Koçman Üniversitesi, Muğla, Turkey*
LIPASE IMMOBILIZED ELECTROSPUN POLYVINYL ALCOHOL/ALGINATE NANOFIBERS FOR EFFECTIVE AND ENHANCED STABILITY	Yasemin İSPİRLİ DOĞAÇ, İlyas DEVECİ, Bedrettin MERCİMEK, Mustafa TEKE *Muğla Sıtkı Koçman University, Muğla , Turkey*
EFFECT OF BENZOPHENONE DERIVATIVE SCHIFF BASE TO CONTAINING METAL SALTS LYOTROPIC LIQUID CRYSTAL	Seher MERAL, Seda Nur AYGUN, Aysen ALAMAN AGAR, Erbil AGAR *Ondokuz Mayıs University, Samsun, Turkey*
EFFECT TO LYOTROPIC LIQUID CRYSTAL MEDIA AND ELECTROCHEMICAL PROPERTIES OF SCHIFF BASE METAL COMPLEX	Nihal ERMIİŞ, Seher MERAL, Nihat TINKILIC, Ayşen ALAMAN AGAR *Ondokuz Mayıs University, Samsun, Turkey*
REDUCTION OF PYRIDINE COMPOUNDS TO THEIR HEMIAMINAL DERIVATIVES	Senel Teke TUNCEL, Ilknur DOĞAN *Bogazici University, Istanbul, Turkey*
ADJUSTABLE AC CONDUCTIVITY IN ARDEL/MWCNT COMPOSITES	Dolunay ŞAKAR DAŞDAN, Banu SÜNGÜ MISIRLIOĞLU, Zeynep GÜVEN ÖZDEMİR, Pelin KAVAK, Jürgen PIONTECK, Petra PÖTSCHKE, Brigitte VOIT *Yıldız Technical University, Istanbul, Turkey*
ZETASIZER MEASUREMENTS OF CO-RELEASING ORGANOMETALLIC COMPLEX: [Mn(phenylimidazole)(2,2-bipyridyl)$(CO)_3$]OTf	Dolunay ŞAKAR DAŞDAN, Yeşim KARAHAN, Elvan ÜSTÜN *Yıldız Technical University, Istanbul, Turkey*
PARTICLE CHARGE and STABILITY BEHAVIOUR OF [Mn(2-mercaptobenzimidazole)(2,2-bipyridyl)$(CO)_3$]OTf IN DIFFERENT pHs and SIMULATED BODY FLUIDS	Ecem AKSOY, İmren ÇOTUK, Dolunay ŞAKAR DAŞDAN, Elvan ÜSTÜN *Yıldız Technical University, Istanbul, Turkey*
ZETA POTENTIAL, MOBILITY and PARTICLE SIZE OF [Mn(2-isopropylbenzimidazole)(2,2-bipyridyl)$(CO)_3$]OTf IN DIFFERENT pHs and SIMULATED BODY FLUIDS	Gizem Yadigar ECE, İmren ÇOTUK, Dolunay ŞAKAR DAŞDAN, Elvan ÜSTÜN *Yıldız Technical University, Istanbul, Turkey*
NOVEL TETRAKIS 4-(1-(PYRIDIN-4-YL)ETHOXYL) SUBSTITUTED METALLOPHTHALOCYANINES: SYNTHESIS AND ELECTROCHEMISTRY	Aleyna ÇAVUŞ, Betül ÖZDEMİR, Tuğçe AKBAL, Efe Baturhan ORMAN, Metin ÖZER, Bekir SALİH, Ali Rıza ÖZKAYA *Marmara University, Istanbul, Turkey*
SYNTHESIS AND ELECTROCHEMISTRY OF NOVEL TETRAKIS 2-DİBENZYLAMINOETOXYL SUBSTITUTED METALLOPHTHALOCYANINES	Sema ŞENOĞLU, Efe Baturhan ORMAN, Metin ÖZER, Bekir SALİH, Ali Rıza ÖZKAYA, Özer BEKAROĞLU *Marmara University, Istanbul,Turkey*
PARTICLE SIZE PREDICTION OF COPOLYMER-DRUG CONJUGATE USING PARTIAL LEAST SQUARES REGRESSION	Fatma Noyan Tekeli, Dolunay ŞAKAR DAŞDAN, Gülderen KARAKUŞ

	Yıldız Technical University, Istanbul, Turkey
MEMBRANES ANTIBIOTICS RETENTION	Andreea Madalina PANDELE, Stefan Ioan VOICU, *University Politehnica of Bucharest, Bucharest, Romania*
FUNCTIONALIZED CELLULOSE ACETATE MEMBRANES. SYNTHESIS, CHARACTERIZATION AND APPLICATIONS	Stefan Ioan VOICU *University Politehnica of Bucharest, Bucharest, Romania*

13 MAY 2018

HALL 1 / SESSION I

SESSION CHAIR	Assist.Prof.Dr.Esin BOZKURT KOPUZ Marmara University, Istanbul,Turkey	
TIME	PAPER TITLE	PRESENTER / CO AUTHOR
09:00 – 09:20	MECHANISM OF THE ELECTRON-EXCHANGE REACTIONS BETWEEN MIXED LIGAND Fe(III) COMPLEXES AND CYANO COMPLEX OF Fe(II)	R. Khattak, I. I. Naqvi *Shaheed Benazir Bhutto Women University, Peshawar, Pakistan*
09:20 – 09:40	GENOTOXIC EVALUATION OF ALCOHOLIC AND HEXANE EXTRACTS FROM AN ENDEMIC PLANT *THERMOPSIS TURCICA* ON LIVER CANCEROUS CELL LINE	Muhammad Muddassir Ali, İbrahim Hakkı CİĞERCİ *University of veterinary and animal sciences Lahore Pakistan*
09:40 – 10:00	NEW ELECTRODE MATERIALS AND ARRANGEMENTS FOR MONITORING OF TRACE CONCENTRATIONS OF BIOLOGICALLY ACTIVE ORGANIC COMPOUNDS	Jiri BAREK, Hana DEJMKOVA, Jan FISCHER, Karolina PECKOVA, Vlastimil VYSKOCIL *Charles University, Czech Republic*
10:00-10:20	EXPERIMENTAL AND COMPUTATIONAL CHEMISTRY STUDIES ON THE INHIBITION EFFICIENCY OF PHTHALIC ACID (PHA) FOR THE CORROSION OF ALUMINUM IN HYDROCHLORIC AND TETRAOXOSULPHATE (VI) ACIDS	Paul Ocheje Ameh *Nigeria Police Academy, Wudil, Kano, Nigeria*
10:20-10:40	RECOGNITION OF A BROMIDE ION BY THE PROTONATED FORM OF 2-(1H-IMIDAZOL-2-YLTHIO)-3-METHYLNAPHTHALENE-1,4-DIONE)	Bigyan Ranjan Jali *VSSUT Burla, Sambalpur Odisha*

10:40 – 11:00	CLOSING

NOVEL METAL-BASED ANTICANCER DRUGS: SYNTHESIS AND A NEW APPROACH TO DRUG DELIVERY

Aysegul GÖLCÜ

Istanbul Technical University, Faculty of Science and Letters, Department of Chemistry, Maslak, Istanbul, Turkey.
aysgolcu@itu.edu.tr

Abstract

Cis-platinum ([$Pt(NH_3)_2Cl_2$]), developed by Rosenberg in 1969 and used for cancer treatment has led many research group to synthesize metal-based drugs (metallo-drugs) since those years. Pt(II), Zn(II), Ru(III), Cu(II), Mn(III) and Au(I/IV) are mostly used as the metal ion for the drug development. In all of those studies, the drug molecules act as ligands and form mostly mono-dentate or bidentate molecular structures by offering pair of electrons to metal atoms. The studies of this topic over the last forty years have been gathered under the roof of "Medicinal Chemistry". The main objective of Medicinal Chemistry is to identify new anticancer agents and put them into clinical practice procedures. However, as the synthesis of metal-based drugs increases, the problems of water solubility and pharmacological evaluation have come to the fore. Apparently, the solutions to overcome these problems lie not in the synthesis of new anticancer drugs, but in the discovery of appropriate drug delivery strategies.

Keywords: Metal-based drugs, complex, drug delivery

1. Introduction

According to the American Cancer Society, cancer continues to be the second most common cause of death in the world, despite the advances in diagnosis and treatment of the last decade. Cisplatin, which was discovered in 1965 by Rosenberg [1] and was used as a chemotherapeutic agent alone or in combination with other drugs in 1978, was used to treat various cancers (ovarian, head and neck, bladder, testicular and lung cancers etc.). etc.) has proven high effectiveness against. However, the high cisplatin power in oncology has potentially increased interest in metal-based drugs as chemotherapeutics. Interestingly, the metals can form a variety of novel metal-based compounds for the design of anticancer agents on organic compounds, due to their ability to bind to a wide variety of coordination numbers, redox and ligands in different ways. All these features offer a wide range of structural variations that can be utilized for oncology treatment. However, cisplatin has some major disadvantages, including major successes, as well as serious toxic side effects such as neurotoxicity, hepatotoxicity, and nephrotoxicity [2-5], and a drug resistance phenomenon leading to unsuccessful treatment [6]. Recent research is a metallo-drug that focuses on mechanisms of action involving other targets, such as proteins or enzymes that interact with different types of DNA, such as classical platinum drugs, or which can lead to the death of tumor cells. Currently, studies related to metal-based compounds have focused on studies that can bind to different types of DNA, such as cisplatin, and may also have anticancer activity against various cells. Drug delivery systems that can target a tumor site and/or prevent binding to non-pharmacological targets are beneficial in reducing drug toxicity and resistance. However, in order to improve the aqueous solution reaction in the human body and specific environment pHs, controlled release systems, the mechanism of transmission to specific tumors, and the long-term anti-cancer activity of metal-containing compounds, the researchers had to focus on drug delivery strategies. Therefore, with the help of molecular biology and chemical approaches, drug release studies should be extended to understand the scenarios of the underlying biological, pharmacological and chemical mechanisms of the cellular fate of the metal-based drugs.

Materyal and Method

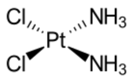
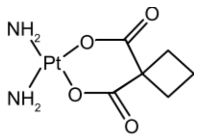
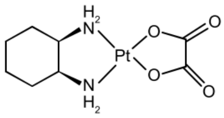
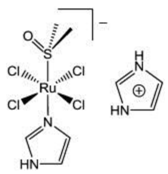
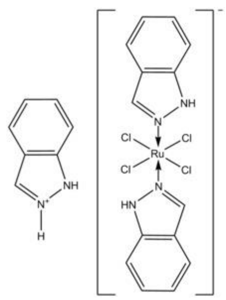
In complexation studies using drug-active substances, these substances are supplied from pharmaceutical companies or they are purchased from local pharmacies. The metal ions are in the form of their salts and are dissolved in water or high polarity solvents such as ethanol/ methanol (at a certain concentration). In each reaction, the analytical parameters such as pH, temperature, waiting time, concentration of reacted species are kept under control [7-10].

In delivery studies, chitosan dissolves in 1% acetic acid and drug containing chitosan solution was added dropwise to 5% sodium triphosphate solution. After crosslinking chitosan beads washes with water and dried at room temperature during 12 hours [11].

Results and Discussion

The Table below gives some metal-based drugs that are in clinical use or in the trial phase.

Table: Some metal-based compounds used in cancer treatment

Compound	Chemical structure
Cis-platin	
Carboplatin	
Oxaliplatin	
NAMI-A	
KP1019	

Delivery systems

Despite the advances in chemotherapy of cancerous diseases, antitumor drugs in current clinical use suffer from major pharmacological deficiencies. The family of platinum drugs represented by cisplatin, the parent drug, directly enters this category with toxicity and resistance problems, which are the main factors leading to suboptimal therapeutic efficacy. Polymer drug conjugation is one of the most promising tools in advanced drug research to increase the therapeutic index of a drug by modification of the pharmacokinetic pathway, a technique comprising a biologically reversible drug that is conveniently linked to water-soluble carrier polymers. The conjugate acts as a prodrug, transporting the bioactive constituent from central circulation to, and into, the transformed target cell, where it is released from the carrier for biological action. This technique is used as a means to enhance the therapeutic efficacy of the platinum drug species selected herein.

For nearly two decades, new metal-based drug compounds have been synthesized and their biological activity has been evaluated in our laboratory [7-10]. The ligands which make complexes with metal ions are active pharmaceutical active ingredients. This group includes antihypertensive drugs, antibacterial drugs, antiviral drugs and anticancer drugs. The metal ions used are transition metal ions such as Cu(II), Zn(II), Pt(II), Ru(III), Fe (II/III).

For example, the Cu (II) and Zn (II) complex of the anticancer 5-fluoracil was synthesized and the biological activity of these complexes in the cervical cancer cell line was investigated in three different concentrations [7]. Our research group now strives for controlled release of these compounds due to the particularly toxic side effects of the aforementioned metal-based compounds. For this purpose, methotrexate (anticancer) and its Cu (II) and Zn (II) metal complexes were synthesized and developed green carriers for Cu(II) and Zn(II) complexes using methotrexate and chitosan hydrogels.

Acknowledgments
This work was supported by a Scientific Research Project Unit of ITU, Project ID: 40917.

References

1- Rosenberg B, VanCamp L, Trosko JE, Mansour VH: Platinum compounds: a new class of potent antitumour agents. *Nature* 1969;**222**:385-386.
2- van Rijt SH, Sadler PJ: Current applications and future potential for bioinorganic chemistry in the development of anticancer drugs. *Drug Discov Today* 2009;**14**:1089-1097.
3- Sandler A, Graham C, Baggstrom M, Herbst R, Zergebel C, Saito K, Jones D: An open-label, multicenter, three-stage, phase II study of s-1 in combination with cisplatin as first-line therapy for patients with advanced non-small cell lung cancer. *J Thorac Oncol* 2011;**6**:1400-1406.
4- Jung Y, Lippard SJ: Direct cellular responses to platinum- induced DNA damage. *Chem Rev* 2007; 107:1387-1407.
5- Pabla N, Dong Z. Cisplatin nephrotoxicity: mechanisms and renoprotective strategies. *Kidney Int* 2008, 73;994-1007.
6- Dempke W, Voigt W, Grothey A, Hill BT, Schmoll HJ. Cisplatin resistance and oncogenes-a review. *Anticancer Drugs* 2000, 11;225-236.
7- Golcu, A, Muslu, H, Kilicaslan, D, Cesme, M. Eren, O, Atas, F, Demirtas, I. The new generation drug candidate molecules: Spectral, electrochemical, DNA-binding and anticancer activity properties. *Journal of Molecular Structure* 2016;**1119**:96-109.
8- Muslu A and Golcu A. New metal based drug as a therapeutic agent: Spectral, electrochemical, DNA-binding, surface morphology and photoluminescence properties. *Journal of Molecular Structure* 2015; **1092**:22-33.
9- Cesme M and Golcu A. Metal-based molecular compounds: Structure, analytical properties, dsDNA binding studies and in vitro anticancer activity on selected cancer cell lines, *Pharmaceutical Chemistry Journal*, 2018 (Accepted for publication).
10- Tumer F, Golcu A, Tumer M, Bulut S and Kose M. Multifunctional metallo porphyrin-imine conjugates: Photophysical, electrochemical, DNA binding and SOD enzyme mimetic studies. 2017;**346**:236-248.
11- Kahya N, Cesme M, Golcu A and Erim FB. Release kinetics of methotrexate and its metal complexes from chitosan hydrogels. 1st Balkan Chemistry Congress, 2018; 17-20 Sep, Edirne, Turkey.

CONTROLLED RELEASE OF DONEPEZIL HYDROCHLORIDE FROM PEG-DA HYDROGELS UNDER UV IRRADITION

Sebnem SENOL[a], Emel AKYOL[b]

[a]*Yıldız Technical University, Istanbul 34210, Turkey*
[b]*Yıldız Technical University, Istanbul 34210, Turkey*

Abstract

The aim of the present investigation was to prepare of PEG-DA based hydrogels. To modify PEG-DA hydrogels, rutile titanium oxide and hydroxyapatite (HAp) were used. The influence of experimental conditions such as pH, rutile titanium dioxide, Hap, type of photo-initiators were investigated on the release profiles of Donepezil Hydrochloride from hydrogels. For characterizing hydrogels, FT-IR and digital misrocope were used. Swelling and release analysis were done at pH 1.2, pH 6.8 and pH 7.4. PEG-DA hydrogels are investigated useful for release of Donepezil HCl.

Keywords: Alzhemier diasease; PEG-DA based hydrogels;photopolymerization; TiO_2; HAp

Introduction

Drug delivery systems have been gained attention for the past few decades because of effective and targeted drug delivery in the field of pharmaceutics. Hydrogels are used control drug release due to their gel structure in response to environmental situation. Their high water content, biocompatibility and flexibility give rise to potential applications in topical, transdermal, sustained drug delivery and medicine. [1-2].

PEG-DA based hydrogels are a class of cross-linked polymers and generally used in biomaterial science because they are non-toxic, low immunogenicity, and can be easily chemically modified and ease of use [3-4]. Photopolymerization technique has been used in a lot of fields such as coatings, inks, adhesives, and biomedical materials. Photopolymerization technique provide lots of advantages such as low energy consumption, environmental friendly and high efficiency [5].

Hydroxyapatite (HAp) is a type of biomaterial with excellent biocompatibility and tissue bioactivity. Furthermore, It is used in drug delivery systems and drug carrier as well [6]. Hydroxyapatite particles have been encapsulated in hydrogels to control drug release for drug delivery applications, improve the mechanical properties. TiO_2 belongs to the class of transition metal oxides and has four types of polymorphs such as anatase (tetragonal), brookite (orthorhombic), rutile (tetragonal) and TiO_2 (monoclinic). TiO_2 nanoparticles have been prepared in different forms such as powder, thin film, crystal, nano tubes and nano rods. TiO_2 nanoparticles are known as promising candidates in various fields, because of their simple synthesis methods, low price and low toxicity [7].

Alzhemier disease (AD), the most common cause of dementia, is a neurodegenerative disease that leads to decline in cognitive function, impaired learning and memory and decline in attention, planning, spatial orientation and language. Donepezil HCl (DH) is the second drug approved by the FDA for the treatment of mild to moderate dementia of the Alzheimer's type. [8-10].

In this presented study; donepezil hydrochloride (DH) which was encapsulated in to PEG-DA hydrogels which were combined with HAp and TiO_2 in via photopolymerization. Fourier transform infrared (FT-IR) spectroscopy and digital microscope were used to characterize the hydrogels. Swelling and release analyses were completed.

Experimental

Materials

Polyethylene glycol diacrylate (PEG-DA, Mn=700), ethylene glycol dimethacrylate, 2,2-Dimethoxy-2-phenyl-acetophenone (Irgacure 651, 99% purity), 1-Hydroxycyclohexyl phenyl ketone (Irgacure 184, 99% purity), 2-Hydroxy-4'-(2-hydroxyethoxy)-2-methylpropiophenone (Irgacure 2959, 98% purity), Hydroxyapatite (powder, 5µm and surface area≥100m2/g), were purchased from Sigma-Aldrich. Donepezil HCl was a kind gift from Abdi İbrahim Company. Titanium powder was provided by Alfa Aesar

Synthesis and Characterization of Hydrogels

Photo-initiators (Irg 184, Irg 651, Irg 2959)and cross-linking agent (ethylene glycol dimethacrylate) were used for pereparing hydrogels which shown in Table 1. Rutile TiO_2 and Hap were choosed for modifying hydrogels. Glass molds (diameter of 15 mm, depth of 1 mm) were used for photopolymerization reaction and photopolymerization was contiuned at for 40 s at 365 nm under UV irradiation. During photopolymerization nitrogen gas was used.

Table 1. Synthesis conditions of hydrogels

HYDROGELS	PEG-DA MN=700	EGDMA	IRG 651	IRG 184	IRG 2959	TIO_2	HAP
HYDROGEL 1 (H1)	50 %	1 %	0,5 %	-	-	-	-
HYDROGEL 2 (H2)	50 %	1 %	0,5 %	-	-	-	
HYDROGEL 3 (H3)	50 %	1 %	-	0,5 %	-	-	
HYDROGEL 4 (H4)	50 %	1 %	-	-	-	0,05 %	-
HYDROGEL 5 (H5)	50 %	1 %	-	-	0,5 %	-	0,05 %

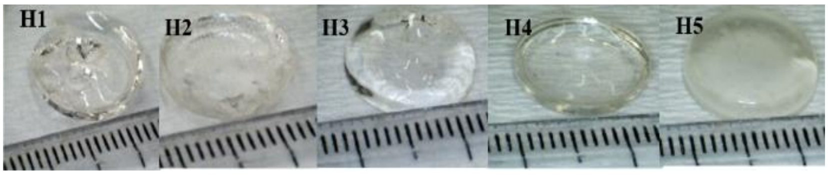


Fig.1. Image of PEG-DA based hydrogels

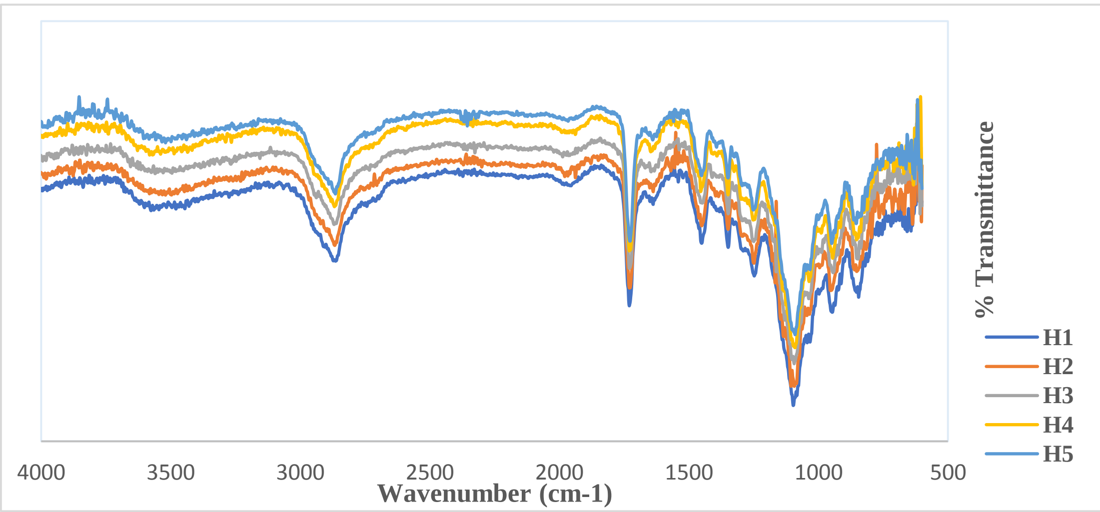


Fig.2. FT-IR analysis of PEG-DA based hydrogels

Swelling Tests

Swelling curves of hydrogels in deionized water and in solutions with of pH 1.2, pH 6.8, pH 7.4 at 37 C are shown in Figs. 3.

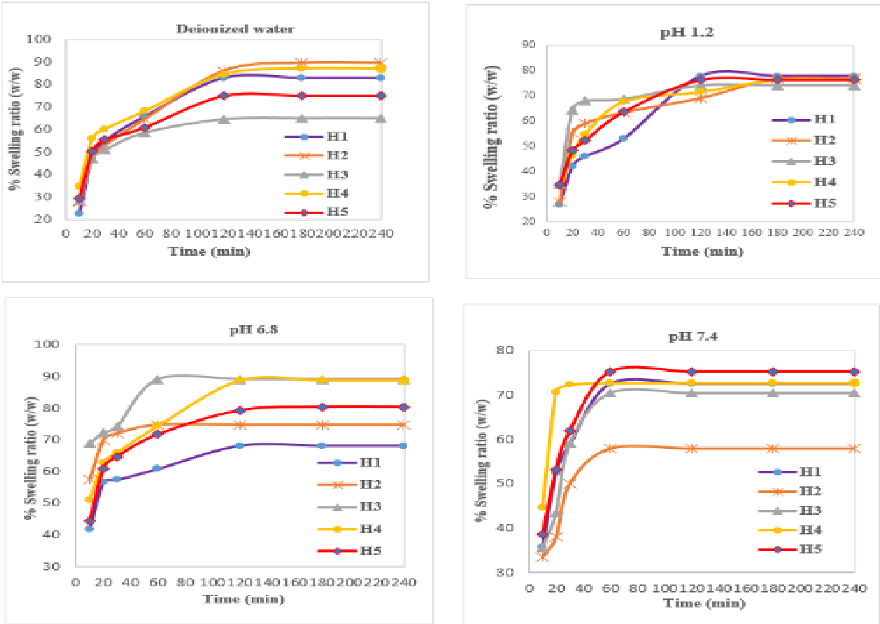
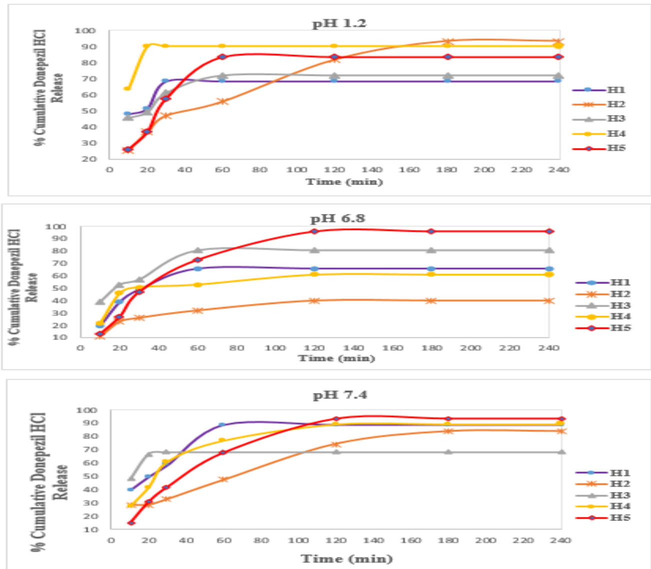


Fig.3. FT-IR analysis of PEG-based DA hydrogels

Release Tests

Cumulative Donepezil HCl release of hydrogels in deionized water and in solutions with of pH 1.2, pH 6.8, pH 7.4 at 37 C are shown in Figs. 4.



Acknowledgements

This work was supported by Research Fund of the Yildiz Technical University. Project Number: FDK-2017-3029.

References

[1] Senol S, Akyol A. Synthesis and characterization of hydrogels based on poly(2-hydroxyethyl methacrylate) for drug delivery under UV irradiation. *J Mater Sci* 2018;**53**:14953-14963.
[2] Akyol E, Senol S, Dogan O. Controlled release of donepezil hydrochloride from the ternary sodium alginate based hydrogels. Bulgarian Chemical Communications 2017;**49**: 57-63.
[3] Kraut G, Yenchesky L, Prieto F, Tovar E.M.G, Southan A. Influence of shear thinning and material flow on robotic dispensing of poly(ethylene glycol) diacrylate/poloxamer 407 hydrogels. *Journal of Applied Polymer Science* 2017; 45083-45091.
[4] Lv G, Xia H, Shi Q, Wang Y-S, Chen Q-D, Zhang Y-L, Liu L-Q, Sun H-B. Sensitively Humidity-Driven Actuator Based on Photopolymerizable PEG-DA Films.*Adv. Mater. Interfaces* 2017 **4**:1601002.
[5] Wang K, Jiang S, Yu Q. Sesamin as a Co-Initiator for UV Photopolymerization. *Polymer Science* 2011; **53**176–180.
[6]Cao X-Y, Wen F, Bıan W, Cao Y, Pang S-J, Zhang W-K. Preparation and comparison study of hydroxyapatite and Eu-hydroxyapatite. *Front. Mater. Sci.*2009;**3**:255–258.
[7] Aaditya V.B, Bharathesh B.M, Harshitha R, Chaluvaraju B.V, Raghavendra U.P, Murugendrappa M.V. Study of dielectric properties of polypyrrole/titanium dioxide and polypyrrole/titanium dioxide-MWCNT nano composites. *J Mater Sci* 2018; **29**: 2848-2859.
[8] Oboh G, Ogunsuyi O.B, Olonisola O.E. Does caffeine influence the anticholinesterase and antioxidant properties of donepezil? Evidence from in vitro and in vivo studies. *Metab Brain Dis* 2017;**32**:629–639.
[9]Singh B.K, Srivastata R.K, Kumar S, Dutta P.T. Stability-indicative hplc determination of donepezil hydrochloride ın tablet dosage form. *Pharmaceutical Chemistry Journal* 2011***;*** **45**: 766.770.
[10]Das J.R, Tizabi Y. Additive Protective Effects of Donepezil and Nicotine Against Salsolinol-Induced Cytotoxicity in SH-SY5Y Cells. *Neurotox Res* 2009;**16**:194–204.

ALGINATE AND CHITOSAN HYDROGELS AND THEIR COMPOSITES IN DRUG DELIVERY, WASTE WATER TREATMENT, FOOD COATING AGENTS AND WOUND DRESSINGS

F.Bedia ERİM

Istanbul Technical University, Department of Chemistry, Istanbul, 34496, Turkey

Abstract

Alginate and chitosan based materials has gained importance as promising materials in biomedicine, pharmacology and waste water treatment due to their biocompatible, biodegradable and non-toxic characteristics. In the present study, it is given the results of our studies on alginate beads in drug delivery and waste water treatment and alginate and chitosan films as food coating and wound dressing materials.

Keywords: Biopolymers; Films; Drug; Controlled Release; Removal

1. Introduction

Alginate is a polysaccharide bio-copolymer consisting of monomeric units of 1–4 linked β-D-mannuronate (M) and α-L-guluronate (G) in different proportions in the chain. Alginate is obtained from marine brown algae. Chitosan is a polysaccharide composed of β-(1–4)-d-glucosamine and β-(1–4)-N-acetyl-d-glucosamine, produced by alkaline deacetylation of chitin. Chitin is a natural biopolymer derived from exoskeletons of crustaceans. Both biopolymer have been widely used in food and pharmaceutical industries. Alginate and chitosan play a significant role in the design of controlled release drugs. The excellent film forming properties of both biopolymers allow their use as food packaging or wound dressing material. Furthermore, as adsorbents in removal of pollutants, alone or in combination with other materials, is another area of their applications.

2. Controlled Drug Release From Alginate Beads

2.1. Protein Release

The instability and degradation of protein drugs in the acidic medium of the stomach is the major drawback in oral-delivery of protein drugs. Alginate is a pH-sensitive hydrogel and shrinks in acidic condition, so that the diffusion of encapsulated protein drug in alginate gels is comparatively low in gastric fluid. However, the low entrapment efficiency of alginate beads and the dissolution of alginate gel in basic media resulting in the burst release of entrapped protein in basic intestine medium are the main limitations of alginate gels for oral delivery of protein drugs. In order to compensate these limitations, alginate–clay composite gels were prepared and the model protein drug bovine serum albumin (BSA) was entrapped in alginate beads. Alginate beads were obtained by dropping alginate solution (2 % w/v) containing montmorillonite (MMT) type clay through a syringe needle into aqueous calcium chloride solution (3% w/v). The spherical beads formed were dried and the release kinetic of BSA from beads to simulated gastric fluid (SGF) and simulated intestinal fluid (SIF) were investigated. Fig. 1 shows the SEM images of the beads. The spherical shapes of beads improved with the addition of MMT. The incorporation of MMT into alginate substantially increases the entrapment efficiencies of BSA from 40% for alginate beads to 78% for MMT-alginate composite beads. As seen from Fig.2, BSA release from alginate beads began immediately at the first contact time in the SGF, however no BSA release was detected until 90 min after the first contact time of beads containing MMT. Very low release ratio of protein in gastric medium prevented protein degradation in acidic solution. On the other hand, contrary the burst release rate of BSA from pure alginate beads, incorporation of MMT exhibited a controlled release system in intestinal medium [1].

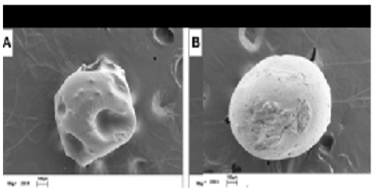


Fig.1. Scanning electron microscopy images of alginate and composite beads, (A) Alginate bead (B) Alginate with 2% MMT

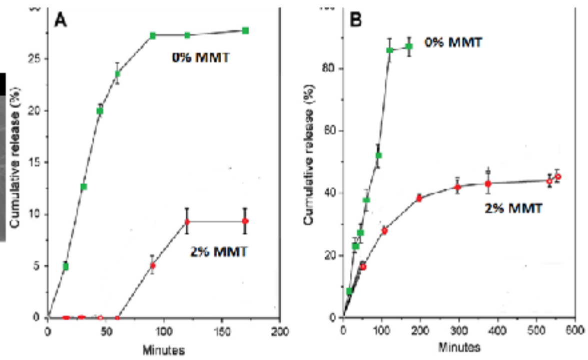


Fig.2. Cumulative release profiles of bead formulations in (A) simulated gastric fluid and (B) simulated intestinal fluid

2.2. Small drug release

Alginate-montmorillonite composite beads crosslinked with calcium and barium ions showed high encapsulation efficiency (EE) for vitamin B2 (riboflavin). The EE value in beads with 0.2% MMT (w/v) reaches up to 93.7% and 98.1% for calcium and barium beads, respectively. Whereas, EE of alginate beads for vitamin B2 were only 49.9% and 55% for calcium and barium beads, respectively. MMT addition to the beads slows down the release rate of both formulations in both SGF and SIF media significantly. No significant difference was observed between calcium and barium alginate beads, except for the greater stability of barium alginate beads in the release media [2].

3. Waste Water Treatment with Alginate Gels

3.1. Effects of crosslinking cations for alginate gelation to removal efficiencies of pollutant ions

Chromium compounds are widely used in numerous industrial processes. Hexavalent chromium compounds are highly toxic and carcinogen for humans. Thus, the removal of Cr (VI) ions from waters has become an important environmental issue. Although the most commonly used ion is calcium, the alginate form hydrogel with divalent or trivalent metal ions. Calcium alginate beads have been used as adsorbent for the effective removals of toxic metal ions, however negatively charged chromate ions do not show any attraction to the calcium alginate beads. Due to the strong affinity between barium and chromium (VI) ions, barium ion cross-linked alginate beads were prepared as low cost, and easily prepared adsorbent candidates for the hexavalent chromium species. Barium ion cross-linked alginate beads have shown great affinity to toxic hexavalent chromium ions in aqueous solution, in contrast to the traditionally used calcium alginate beads as seen from Figure 3. Adsorption experiments were carried out by the batch contact method. The optimal pH for removal was found to be pH 4. The equilibrium was established in 4 h, and the removal efficiency of chromium (VI) was found to be 95 %. The high maximum chromium (VI) adsorption capacity was determined from the Langmuir isotherm as 36.5 mg/g dry alginate beads [3].

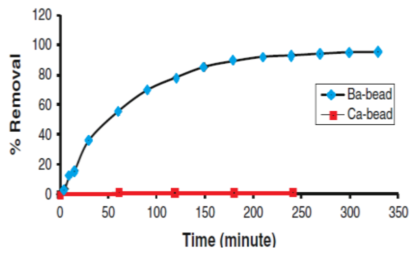


Fig. 3. Uptake % of Cr(VI) ions as a function of the contact time.

The excess amount of fluoride in water causes dental fluorosis, brittle bones, osteoporosis, and cancer. Adsorption methods are accepted as the most effective and economical method in fluoride removal processes. The effective adsorbents for removal of fluoride ions from water are aluminum-enriched materials. High affinity of aluminum for fluoride ion is the main features of these adsorbents. Thereby, aluminum cross-linked biodegradable alginate beads were used in this study for fluoride removal from aqueous solutions taking advantage of high affinity of aluminum for fluoride. Adsorption experiments were carried out by batch contact method. The equilibrium was achieved in 4 h. Optimal conditions were found to be pH 2 at 25°C, giving rise to 99.5% removal of fluoride The maximum adsorption capacity was determined as 75.2 mg/g from the Langmuir isotherm. This study suggests that aluminum alginate beads can be used as efficient, cheap and eco-friendly adsorbents for the removal of fluoride from contaminated water [4].

3.1. Effect of surface morphology to removal efficiency of a dye

Dyes constitute a large part of pollutants in nature. Among the conventional dye removal techniques, adsorption is prominent. Research challenges are on developing low-cost, biodegradable and efficient adsorbents. In order to remove methylene blue dye from aqueous medium, alginate–montmorillonite composite beads were prepared with a novel cryogelation-like strategy. Fort this purpose, alginate-clay beads after ionic gelation with calcium ions were filtered and placed in distilled water and the mixture was deep-frozen at −21 °C for 24 h. Subsequently, the mixture was defrozen, filtered, and dried at room temperature. Alginate-clay beads maintain spherical shape after drying; however, freeze dried alginate-clay beads have more pellet like shape. Freezing the beads produced significant cracks and pores on the surface of the bead, resulting in an increased surface area without losing the bead integrity. This process increased the adsorption capacity of beads for the dye [5].

3.2. Antibacterial alginate films cross-linked with cerium ions and chitosan

Wound dressings require good antiseptic properties, mechanical strength. Alginate films crosslinked with calcium ions do not have antibacterial properties. On the other hand, antimicrobial properties of cerium ions and chitosan are known. Moreover, cerium (III) nitrate has been successfully used in clinics for burn treatment. In this study, it was combined the antibacterial properties of Ce(III) ions and chitosan with flexible and hydrophilic properties of alginate films in order to develop novel, biodegradable films that have the potential to be used as wound dressing. For this purpose, alginate films were crosslinked with cerium(III) solution and chitosan added cerium(III) solution Both cerium ion crosslinked and cerium ion-chitosan crosslinked alginate films gained antibacterial activity against gram-negative (Escherichia coli) and gram-positive (Staphylococcus aureus) bacteria. The elastic modulus values of cerium ion crosslinked films are significantly higher than the elastic modulus of films crosslinked with Ca (II) ions [6].

3.3. Antibacterial chitosan films incorporated with turmeric extracts

Food packages extend the shelf life of the food product protecting them from external factors such as micro-organisms, moisture, and ultraviolet light. Recently, incorporation of antimicrobial agents into biodegradable food packaging systems in order to prevent microbial growth on the food surface has gained a significant interest. Turmeric is very popular worldwide as a spice, food preservative, and coloring material. In the present study, turmeric containing chitosan-based film was produced with casting procedure and cross-linked with sodium sulfate solution. The addition of turmeric to chitosan film significantly increased the tensile strength of the film and improved the ultraviolet-visible light barrier of the film. Antimicrobial activity of the chitosan films was studied against *Salmonella* and *Staphylococcus aureus* and a better antimicrobial activity was observed with turmeric incorporation. Turmeric incorporated chitosan films with enhanced antimicrobial activity and film stiffness can be suggested as a promising application for food packaging [7].

Acknowledgements

Experimental studies were financially supported by Research Foundation of Istanbul Technical University.

References

[1] Kaygusuz H, Erim FB. Alginate/BSA/montmorillonite composites with enhanced protein entrapment and controlled release efficiency. *Reactive and Functional Polymers* 2013; **73**: 1420-1425

[2] Kaygusuz H, Uysal M, Adımcılar V, Erim FB. Natural alginate biopolymer montmorillonite clay composites for vitamin B2 delivery. *Journal of Bioactive and Competible Polymers* 2015; **30**:48-56

[3] Uzaşçı S, Tezcan F, Erim FB. Removal of hexavalent chromium from aqueous solution by barium ion cross-linked alginate beads. *International Journal of Environmental Science and Technology* 2014: **11**:1861-1868

[4] Kaygusuz H, Uzaşçı S, Erim FB. Removal of Fluoride from Aqueous Solution Using Aluminum Alginate Beads. *Clean-Soil Air Water* 2015; **43**:724-730

[5] Uyar G, Kaygusuz H, Erim F.B. Methylene blue removal by alginate–clay quasi-cryogel beads. *Reactive and Functional Polymers* 2016;**106**:1-7

[6] Kaygusuz H, Torlak E, Akın-Evingür G, Özen İ, von Klitzing R, Erim FB. Antimicrobial cerium ion-chitosan crosslinked alginate biopolymer films: A novel and potential wound dressing. *International Journal of Biological Macromolecules* 2017;**105**: 1161-1165

[7] Kalaycıoglu Z, Torlak E, Akın-Evingür G, Özen İ, Erim FB. Antimicrobial and physical properties of chitosan films incorporated with turmeric extract. *International Journal of Biological Macromolecules* 2017; **101**:882-888

STEREOISOMERIC ASSIGNMENTS TO HEMIAMINALS OF HETEROCYCLIC COMPOUNDS

Sevgi SARIGÜL, Şenel Teke TUNÇEL and İlknur DOĞAN*

Boğaziçi University, Department of Chemistry, 34342 Bebek, İstanbul, Turkey

Abstract

Hemiaminals (N,O-hemiacetals) are tetrahedral intermediates during imine and enamine formation reactions and are usually not isolable. Thus, the synthesis of hemiaminals is a challenging task for organic chemists. The present work describes stereoselective reductions of several heterocyclic compounds to produce hemiaminals and their stereoisomeric assignments. Some of the hemiaminals have been found to be exeptionally stable. Some others have been found to eliminate water with time to produce eneamidines. The elimination products have been exploited to assign configurations to the chiral carbons at C-4 of the heterecyclic ring. The NMR analyses of the hemiaminals showed that the *cis* and *trans* hydrogens of the heterocylic ring have different coupling constants (Figure 1). The C-4 hydrogen of the major isomer had a very small coupling constant (2.0 Hz), whereas the minor one of the same proton coupled with a larger *J* (6.4 Hz). To assign with certainty the *cis* and *trans* isomeric products, the bromination reaction of compound **2** has been used (Figure 2). Based on the the found NMR results, the smaller coupling constant has been assigned to the *cis* and the larger to the *trans* isomer. The **M** and **P** isomeric assignments have been done based on the anisotropic effects of the *o*-aryl substituent.

Keywods: Hemiaminals; $LiAlH_4$ reductions

Introduction

Hemiaminals are tetrahedral intermediates during imine and enamine formations and are usually not isolable. Thus, the synthesis of hemiaminals is a challenging task for organic chemists [1]. We [1.2,3] and others [4,5] synthesized stable hemiaminals from heterocyclic compounds. Hemiaminals have been postulated to be tetrahedral intermediates during some enzymatic reactions, that involve cleavage of biochemically important amides[6], and during some natural product syntheses [7]. Therefore, isolating hemiaminals as stable compounds and elucidating their chemical structures is important for understanding the related biochemical processes. In the present presentation, I will show the synthesis of several hemiaminals via $LiAlH_4$ reduction of heterocyclic compounds and talk about how their stereochemical assignments have been done.

Results and Discussion

All hemiaminals were synthesized from the corresponding heterocyclic compounds via $LiAlH_4$ reductions followed by an electrophilic quench with water (Fig.1). The hemiaminal **4**, from the thiazolidin-4-one, **1**, showed a ^{1}H NMR spectrum where the proton at C-4 gave a signal at 5.6 ppm and showed a coupling with one of the geminal hydrogens at C-5, but not with the other. A similar result was obtained for the hemiaminals **6** and **7** synthesized from the compound **3**. The C-4 proton of **6** which appeared at at 5.0 ppm (the major isomer) gave a small coupling (J=2 Hz, 400 MHz instrument) with the proton at C-5 but the C-4 proton of **7** which appeared at 5.2 ppm (the minor isomer), showed a larger coupling with C-5-H (6.4 Hz, , 400 MHz instrument).

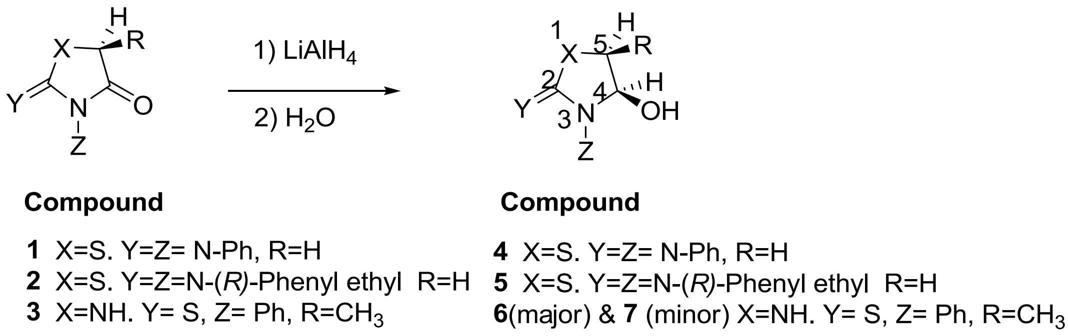


Fig. 1. Synthesis of the hemiaminals from heterocyclic compounds.

To be able to find out whether the smaller coupling isomers belonged to the compound having hydrogens trans with respect to each other at C-4 and C5-positions of the heterocyclic ring, we performed the following experiment:

The hemiaminal **5** obtained from the heterocyclic compound **2**, underwent a dehydration reaction to give a thizol-imine as a single enantiomer (Fig. 2 (a)). We thought of doing a simple bromination reaction over the single enantiomer thiazol-imine. The bromination reaction has a known stereochemistry. It is an *anti* addition reaction. When we did the bromination, we obtained two isomers; one major, one minor. They are diastereomers of each other therefore have different NMR spectra (Fig. 2 (b). For both isomers the coupling constant of C5-H with C4-H is zero. The two hydrogens are necessarily *trans* to each other. So this was a proof that small J isomers were the ones where the C-5 and the C-4 hydrogens were *trans* with respect to each other.

The ^{1}H NMR of the hemiaminals obtained from **2**, showed the presence of a 70:30 ratio of major to minor ratio (Fig. 2 (b). The value was obtained from the integral ratio of the C-4H singlets. The same ratio was seen in the CH_3 doublets as well. CH_3 doublets resonate with quite different chemical shift values because of the amidine conjugation (Fig.3) within the molecule. Because of this, CH_3 in the imine moiety appeared more shielded. Plus the fact that bromine has a long-rage anisotropic effect on the protons which are on the same side with it, the CH_3 signal of the minor isomer appeared more upfield.

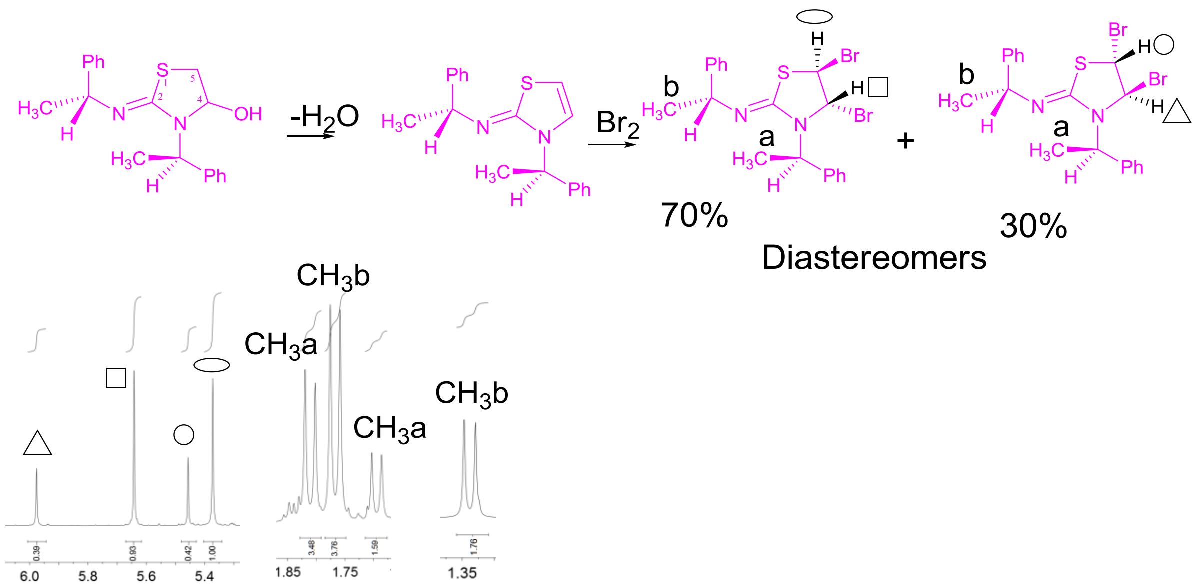


Fig. 2. (a) Bromination rection done on (*R*)-1-phenyl-*N*-3- ((*R*)-1-phenylethyl)thiazol-2(3H)ylidine)ethanamine (b) the partial ^{1}H NMR spectrum of the minor and the major diastereomers.

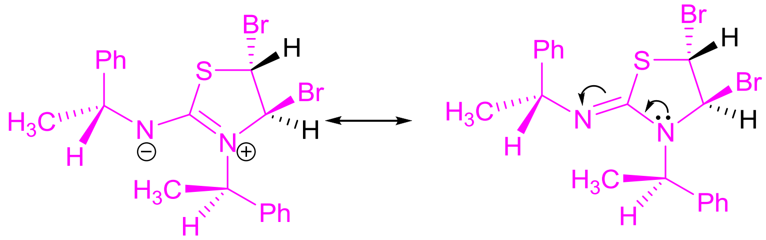


Fig. 3. The amidine conjugation present in compound **2**.

Conclusion

Stable hemiaminals were synthesized by $LiAlH_4$ reductions of the corresponding heterocyclic compounds and their stereochemistries were identified.

Acknowledgements

The financial support from Boğaziçi University Research Fund (BAP) with project number *17B05P2* is greatly acknowledged.

References

[1] Gunal, SE., Gurses, GS., Erdem, SS, Dogan, I. **'**Synthesis of stable tetrahedral intermediates (hemiaminals) and kinetics of their conversion to thiazol-2-imines' *Tetrahedron* 2016;**72**:2122-31.
[2] Demir-Ordu, Ö, Doğan, İ. **'**Axially chiral N-(o-aryl)-4-hydroxy-2-oxazolidinone derivatives from diastereoselective reduction of N-(o-aryl)-2,4-oxazolidinediones: Thermally interconvertible atropisomers via ring-chain-ring tautomerization' *Chirality* 2010;**22**:641-54.
[3] Yildirim, A., Sungur-Konuklar, FA., Catak, S., Van Speybroeck, V., Waroquier, M., Dogan, I., Aviyente, V. 'Solvent-Catalyzed Ring-Chain-Ring Tautomerization in Axially Chiral Compounds' *Chem. Eur. J* 2012;**18**: 12725-32.
[4] Evans, DA., Borg, G., Scheidt, K.A. **'**Remarkably Stable Tetrahedral Intermediates: Carbinols from N-Acylpyrroles*' Angew. Chem. Int. Ed.* 2002;**317**:493-96.
[5] Subik, P., Welc, B., Wisz, B., Wolowiec, S. 'Stable hemiaminals attached to PAMAM dendrimers' *Tetrahedron Lett*. 2009;**50**6;512-14.
[6] Petrillo, T., O'Donohoe, C.A., Howe, N., Malthouse, JPG. **'**Importance of Tetrahedral Intermediate Formation in the Catalytic Mechanism of the Serine Proteases Chymotrypsin and Subtilisinoles *Biochemistry.* 2012;**51**:6164-70.
[7] Szostak, M., Aube, J. 'Chemistry of Bridged Lactams and Related Heterocycles'Chem. Rev. 2013;**113;5701**-65.

PREPARATION OF AMINO MODIFIED POLYETHYLENE TEREPHTHALATE (PET) NANOFIBERS AND INVESTIGATION OF THEIR WASTE WATER FILTRATION PERFORMANCE

Yaşar Can AYRA[ab], Memet Vezir KAHRAMAN[a], Bahattin YALÇIN[a]

[a]Marmara University, Chemistry Department, Istanbul 34722, Turkey.
[b]Koc University, Chemistry Department, Istanbul 34450, Turkey.

Abstract

Nanotechnology has become the most important development in this decade and its effectiveness is nothing like seen before. For several years, electrospinning has become the most important tool for production of nanofibers. Due to the known fact that membranes must have porous pattern, nanofibers and their intensive properties are always one step ahead. There are many advantages compare to common filtration techniques such as disuse of additional chemical agents or high-pressure necessity.

In this study, it is aimed to preparation of PET nanofibers using electrospinning method, pre-modification with branched polyethylene imine and production of modified nanofibers. PET source was chosen as water bottles. Consequently, this source allows us to solve an environmental problem with another problem maker material. Obtained polyethylene imine covalently bonded nanofiber networks were tested in waste water filtration.

The amount of heavy metal concentration in waste water were investigated by Inductively Coupled Plasma Mass Spectrometry and compared before and after the filtration process. Nanofiber morphology investigated by Scanning Electron Microscope images. Amino modified and unmodified nanofibers chemical properties analysed by Fourier Transform Infrared Spectroscopy. Nanofiber wettability performance detected by contact angle measurement. Thermal properties of nanofibers determined by Thermal Gravimetric Analysis. Modified nanofiber membrane characterized by Fourier-Transform Infrared Spectroscopy (FTIR). Nanofiber morphology were analysed by Scanning Electron Microscopy (SEM). Thermal property of membranes was examined by Thermogravimetric Differential Thermal Analysis (TGA). The amount of heavy metal ions in waste water were investigated by Inductively Coupled Plasma Mass Spectrometry (ICP-MS) before and after the filtration process. Results of the filtered waste water metal concentration indicates that amino modified polyethylene terephthalate nanofiber matrix can be suitable for the wastewater applications.

Keywords: nanofiber; pet; waste water; filtration; modification

Introduction

Clean water accessibility is a global problem that caused by rapid urbanization, industrial and domestic waste water. Inorganic contaminants such as heavy metals are the preeminent factor in toxicological perspective. Unlike organic contaminants, heavy metals are not biodegradable and they have an inevitable attribute like quite rapid biomass transfer. Due to these facts, waste water treatment has an important role for next generations of human population. [1-3]

Another problem with a huge environmental impact is the pollution caused by polymeric materials. Polyethylene terephthalate is a widely used polyester. PET water bottles, depending on the end use, constitute a serious waste problem. It is a well-known fact that conventional recycling methods for PET cause the reducing of molecular weight and loss of economical product grade. Also, these recycling methods depend on high energy consumption and/or additional chemical agents. [4,5]

In this study, it was aimed to solve these environmental problems side by side, while waste PET water bottles are being converted into high value-added goods. Within this scope, heavy metal contaminants were chosen as the main problem to be solved and PET polymeric nanofiber was modified with polyethylene imine by pre-modification method. The filtration process was applied with the use of basic filter paper as a supporting layer.

Experimental

Well known property of PET is that highly resistance to most of known solvent. Major solvents for PET are TFA and HFIP. Both solvents tested for R-PET that originating from used water bottles. %10wt PET solutions were prepared and used for manufacturing nanofibers via electrospinning device. All nanofiber samples were dried out at 30°C after the process. SEM images showed that TFA was more efficient to obtain nanofibers that has smaller diameter. TFA was used for all next steps without further purification.

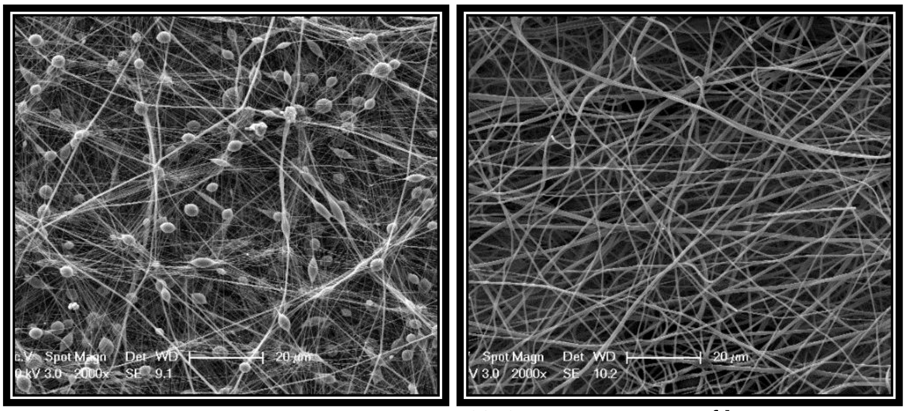
Polyethylene imine that is purchased from Sigma-Aldrich was %30 percent in aqueous medium. Water is a precipitating agent for PET in both of two solvents. For that reason, PEI solution dried in freeze-drier. Thus, dried PEI was used in all modification steps.

PET water bottles were cut into 1x1cm pieces and simply washed with purified water, acetone and water again. Strips were dried in mild conditions at 30°C.

Main PET-TFA (%10wt) solution divided in reaction flasks and PEI was added in order to their PET concentration as respectively 0, 20, 30 and 40 percent. Reflux apparatus were attached in order to avoid decrease any solvent amount. Aminolysis reaction has occurred in 90°C for 30 minutes for all samples.

Results and Discussion

Figure 1 show the fiber and bead distribution difference under effect of TFA and HFIP.



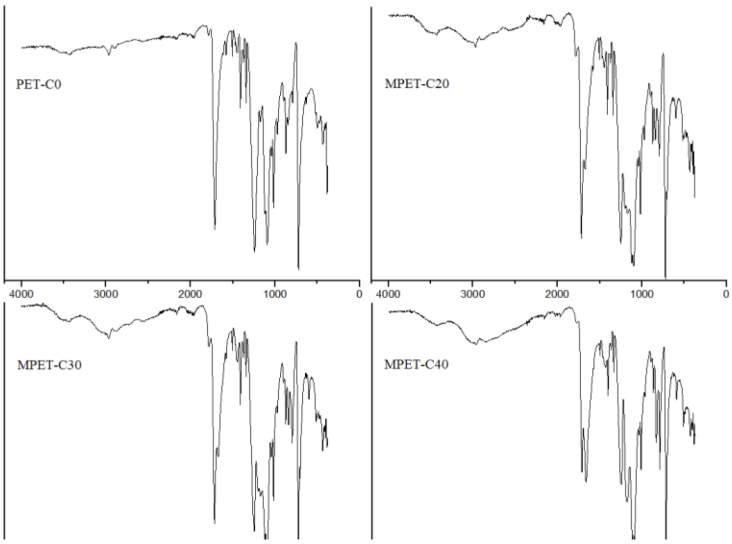
%10 PET- HFIP Nanofiber SEM image (10000x)

%10 PET- HFIP Nanofiber SEM image (10000x)

Figure 1: Solvent effect on fibers

e
r

Fig. 2. FTIR spectra of (a) PET-C0, (b) MPET-C20, (c) MPET-C30, (d) MPET-C40



The FTIR spectra of PET and M-PET nanofibers are given in Figure 2. The peaks at around 1712 cm^{-1} and 1720 cm^{-1} were attributed to the ester carbonyl parts of the polymeric structure. Characteristic amide bond was observed at around 1665 cm^{-1}.

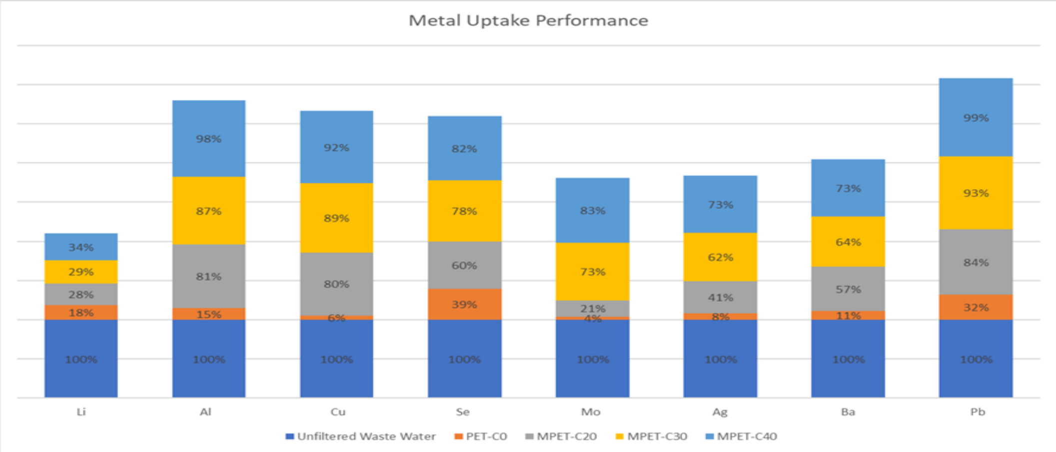


Fig. 3. Metal Uptake Performance of Nanofibers

Conclusion

In the comparison made with PET and MPET samples, it was determined that the wettability performance was improved by the increase in the amount of modification, and the PET based nanofiber has become super hydrophilic after the modification step. Modified nanofibers showed the best metal uptake performance in removal of aluminum, copper and lead contaminants from the industrial waste water.

Acknowledgements

This work is supported by Marmara University BAPKO. (Grant No. FEN-C-YLP-081117-062)

References

[1] Ramakrishna S., Shirazi M.M.A., (2015), “Electrospun membranes: Next generation membranes for desalination and water/wastewater treatment,” p. 2.
[2] Wang X. Hsiao B.S., (2016), “Electrospun nanofiber membranes,” Current Opinion in Chemical Engineering, vol. 12, pp. 62–8.
[3] Fu F., Wang Q., (2011), “Removal of heavy metal ions from wastewaters: A review,” Journal of Environmental Management, vol. 92, no. 3, pp. 407–418.
[4] Awaja F., Pavel D., (2005), “Recycling of PET,” European Polymer Journal, vol. 41, no. 7, pp. 1453–1477
[5] Sinha V., Patel M. R., Patel J.V., (2010), “Pet Waste Management by Chemical Recycling: A Review,” Journal of Polymers and the Environment, vol. 18, no. 1, pp. 8–25

THE PREPARATION OF FLUORINE AND GRAPHENE OXIDE CONTAINING HYDROPHOBIC NANOCOMPOSITE COATINGS

Nilhan Kayaman APOHAN[1], Seda AKHAN, Burcu OKTAY, Seyfullah MADAKBAŞ

Marmara University, Department of Chemistry, 34722 Goztepe-Istanbul, Turkey

Abstract

Hydrophobic composite coatings can be used in wide range of applications such as corrosion resistant coatings. In this study, it was aimed to prepare new fluorine and graphene oxide based hydrophobic polyurethane-PDMS nanocomposite coatings. To improve the compatibility between organic and inorganic phases, PDMS based polyurethane prepolymer was synthesized. The nanocomposite coatings were prepared by using an anhydrous sol-gel, the alkoxysilane modified polyurethane-PDMS prepolymer and perfluorooctylalkoxysilane. Structure analysis of alkoxysilane modified polyurethane-PDMS was confirmed by FTIR. The surface morphology of the nanocomposite coatings was investigated by Scanning Electron Microscopy analysis. The contact angle results show that the obtained coatings have good hydrophobic properties. Thermal properties of the coatings were investigated by Thermal Gravimetric Analysis (TGA).

Keywords: Hydrophobic surface; hybrid coating; polyurethane

Introduction

The development of polymer nanocomposites with hydrophobic properties has become a prominent area of current research and development. Flourine containing nanocomposites have been attracted great attention by owing to the characteristics of fluorine atoms such as excellent surface properties, water resistance, corrosion resistance, low refractivity and low dielectric constant [1]. In addition excellent physical and mechanical properties of graphene and its derivatives as nano fillers make it more preferable for designing the corrosion resistant coatings than the other nano-materials. Graphene oxide has high surface area and nanometric thickness, which shows the barrier property preventing oxygen and water permeability of the coating [2].

In this study, a new fluorine and graphene oxide based hydrophobic polyurethane-silicone nanocomposite coatings were developed. The nanocomposite coatings were prepared by using a sol-gel process from the alkoxysilane modified polyurethane prepolymer and perfluorooctylalkoxysilane. In addition, graphene oxide was added into the prepared sol-gel mixture. Hydrophobic coatings were fabricated with incorporation of the mixture of the graphene oxide and sol-gel into nanocomposite formulations. Structure analysis of alkoxysilane modified polyurethane was confirmed by FTIR. The surface morphology of the nanocomposite coatings was investigated by Scanning Electron Microscopy. The contact angle results show that the obtained coatings have good hydrophobic properties.

Experimental

Materials

Poly(propylene glycol (PPG) (Sigma), poly(dimethyl siloxane (PDMS) (Sigma), isophorone diisocyanate (IPDI) (Fluka), graphene oxide (GO) (Sigma), tetraethyl ortosilicate (TEOS) (Sigma) and 1H,1H,2H,2H-Perfluorooctyltriethoxysilane (PFO-Silane)(Sigma) were used.

Synthesis of isocyanate-terminated Polyurethane (PU) resin

Synthesis of isocyanate-terminated PU was carried out by reaction of poly(propylene glycol), poly(dimethyl siloxane) and isophorone diisocyanate (IPDI) [3]. The product was clear viscous liquid.

* Corresponding author. Tel.: -+90 216 347 96 41; fax: +90 216 3478783.
E-mail address: napohan@marmara.edu.tr

Modification of isocyanate-terminated PU with NH_2

Prepared PU prepolymer from the previous step of the experiments were reacted with amino propyl triethoxy silane (APTES). APTES was slowly introduced in the reaction medium and stirred continuously at room temperature for 5 h. The reaction scheme was shown in Fig. 1.

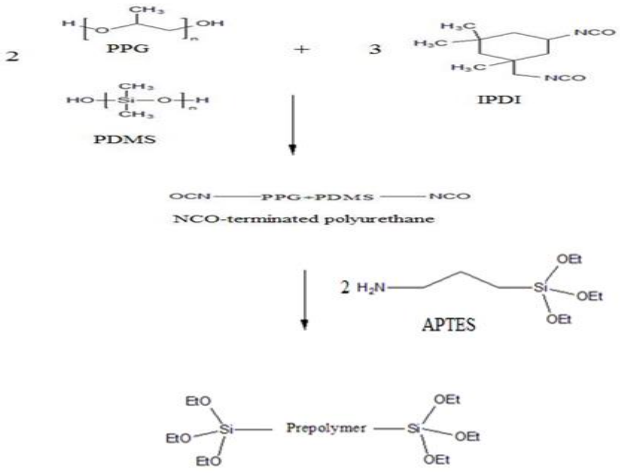


Fig. 1. Preparation of silane modified Polyurethane

Preparation of Anhydrous Sol-gel

An anhydrous sol–gel process was performed with boric acid and tetraethyl orthosilicate (TEOS) according to literature [4].

Preparation of Nanocomposite Coatings

The formulations named as C1, C2 and C3 were prepared by mixing the calculated amounts. The compositions are shown in Table 1. After homogenization, the formulations were pouring into the Teflon mold. Then the coating formulations were cured stepwise at 70, 100 and 120 ˚C for 1 h at each temperature.

Table 1. Composition of nanocomposite coatings

Sample codes	NCO-terminated polyurethane (%)	Silane modified polyurethane (%)	PFO-Silane (%)	GO (%)	Sol-Gel (%)
C1	90	-	-	-	10
C2	88	2	1	-	9
C3	87	2	1	1	9

Results and Discussions

The chemical structures of PU prepolymer and modified PU prepolymer were confirmed with FT-IR. Figure 2a show FTIR spectrum of NCO terminated polyurethane. The peak at 2970-2870 cm^{-1} is related to C-H stretching. The characteristic NCO peak of IPDI observed at 2270 cm^{-1}. C-O bending and stretching were assigned at 1258 and 1087 cm^{-1}, respectively [5]. The peak at 2270 cm^{-1} disappeared by reaction between NCO of prepolymer and NH_2 of APTES (Figure 3b).

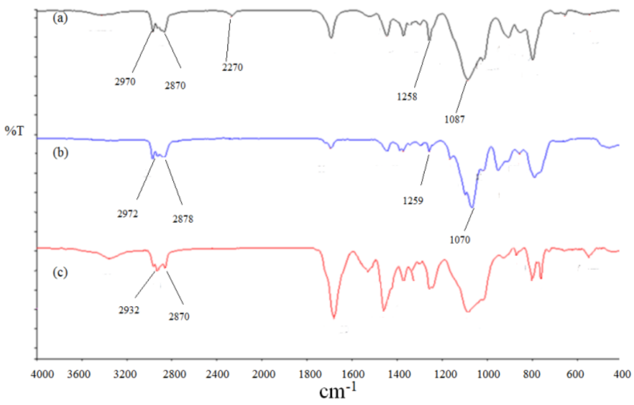


Fig. 2. FTIR spectra of (a) NCO terminated PU, (b) silane modified PU, and (c) C3 sample.

The morphology of the coatings was investigated by SEM. In fig. 3, the fractured surfaces of C1, C2, and C3 samples can be seen, respectively. Silane coupling agent and graphene oxide did not show agglomeration in polymer matrix. The incorporation of graphene oxide morphology has not changed much.

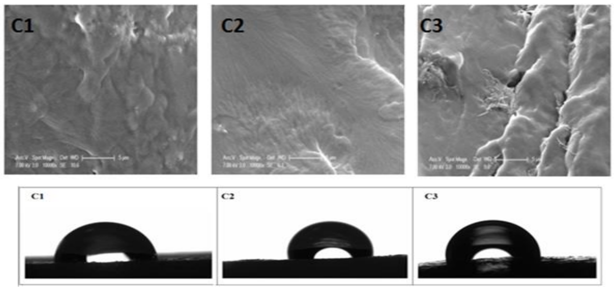


Fig. 3. SEM images and contact angles of C1, C2 and C3 samples

The surface of coatings was evaluated using contact angle measurements. The contact angle values of C1, C2 and C3 are 87, 92 and 100˚, respectively. The contact angle of the coatings increased the addition of silane coupling agents and perfluorooctyltriethoxysilane .
Thermal properties of the composite films were evaluated by thermogravimetric analysis (TGA) under air atmosphere as shown in Fig 4. Silica sol–gel containing samples have higher decomposition temperature.

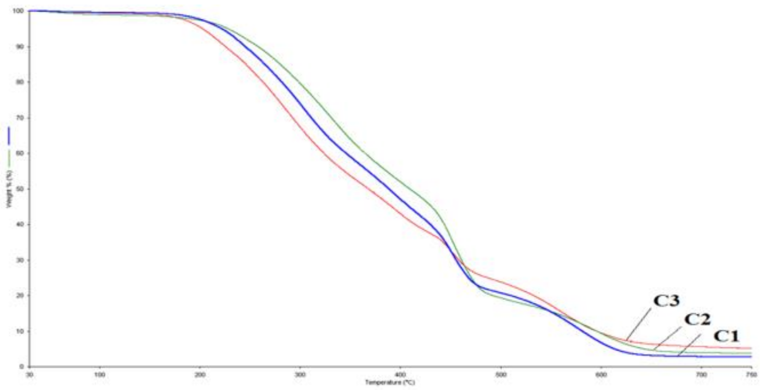


Fig. 4. TGA thermograms of the C1, C2 and C3 samples

Conclusions

Fluorine and graphene oxide containing polyurethane-PDMS hybrid coatings were prepared as indicated on Fig.1. Silica particles homogeneously dispersed in polymer matrix. Hydrophobicity of coatings improves with fluorine incorporation into the coating. Contact angle increased from 87˚ to 100˚. On the other hand graphene oxide addition can thermally protect the nanocomposite coating at high temperatures > 400 ˚C and it provided an effective heat transfer. Graphene oxide containing coating showed high mass residue.

Acknowledgements

This work was supported by Marmara University, Commission of Scientific Research Project (M.U.BAPKO) FEN-C-YLP-090518-0256.

References

[1] S. Liu, X.Liu, S.S. Latthe, L.Gao, S.An, S.S.Yoon, B.Liu , R. Xing, *App Surface Sci.* 2015; **351**(1) 897-03.
[2]B. Ramezanzadeh, E.Ghasemi, M.Mahdavian, E.Changizi, M. H. Mohamadzadeh Moghadam, *Carbon* .2015; **93**, 555-73.
[3] B.Oktay, N.Kayaman Apohan, *J Coat Techn Res.* 2013; **10** (6), 785-98.
[4]E. Çakmakçı, Z. Altıntaş, M. Vezir Kahraman, N. Kayaman Apohan, J Vinyl Add Techn. 2015; **21**, 272-77
[5] B. Oktay, N.Kayaman Apohan *Advan. Polym. Techn.* 2013; **32** (2), 21341- 51.

INTERMOLECULAR INTERACTIONS BETWEEN SEROTONIN AND PROMAZINE USING COMPUTATIONAL METHODS

Tuğçe ŞENER RAMAN, Nursel ACAR
Ege University, Chemistry Department, Bornova 35100 İZMİR, TURKEY

Abstract

Serotonin (5-Hydroxytryptamine) (SE) has been implicated in a broad range of behavioural disorders involving the sleep cycle, eating, the sex drive and mood [1]. Promazine (PZ) is a psychotropic drug which is used extensively in mental disorders and anticancer activities. Its interactions in metabolism with the serotonin are important in terms of its biological activity. In this study, intermolecular interactions between photophysically excited promazine and naturally occurring hormone (serotonin) in the human body at ground-state will be investigated using computational tools. Conformational analyses have been performed to determine the initial structures for promazine and hormone (serotonin) using Spartan 08 [2]. Ground state geometry optimizations are first performed with Gaussian 09 [3] at the ω-B97XD/6-31G(d,p) level of DFT theory without symmetry constraint in gas phase and aqueous phase, solvation calculations were performed by Tomasi's Polarizable Continuum Model (PCM) [4,5]. The electronic transitions were calculated by the time-dependent density functional theory (TD-DFT) with CAM-B3LYP, B3LYP and ωB97XD methods using 6-311++G(d,p) basis set in gas phase and in water. Molecular orbitals, energy differences of frontier orbitals and electrostatic potentials for studied molecules were investigated. Intermolecular charge transfer between HOMO-LUMO orbitals of SE-PZ complex was observed in both media.

Keywords: Density functional theory (DFT), UV-Vis absorption spectra, Promazine, Serotonin

Introduction

Photophysically excited electron transfer processes play an important role in many scientific fields. Charge transfer complexes and energy transfer processes formed by this mechanism is significant in biochemical processes. Serotonin (5-Hydroxytryptamine) (SE) has been implicated in a broad range of behavioural disorders involving the sleep cycle, eating, the sex drive and mood [1]. Promazine (PZ) is a psychotropic drug which is used extensively in mental disorders and anticancer activities. In this study, intermolecular interactions between photophysically excited promazine and naturally occurring hormone (serotonin) in the human body at ground-state will be investigated using computational tools.

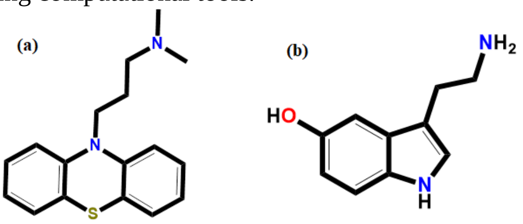


Fig.1. Investigated compounds; Acceptor (a) Promazine-PZ, donor (b) Serotonin-SE

Method

Ground state geometry optimizations of promazine and serotonin are performed by using Density Functional Theory (DFT/ωB97XD/6-31G(d,p)) for determining minimum energy geometries in gas phase and aqueous phase. The optimized initial structures for possible donor–acceptor complexes were obtained by using different orientations of the donor and acceptor molecules. Frequency analyses have been carried out to verify the nature of all optimized geometries. Promazine, Serotonin and their complex were investigated to Time-Dependent Density Functional Theory (TD-DFT) with CAM-B3LYP, B3LYP and ωB97XD methods using 6-311++G (d,p) basis set in aqueous phase. All calculations have been carried out with Gaussian09 [2].

Results and Discussion

Structures of the optimized ground state PZ, SE and PZ-SE complex at ωB97XD/6-31G(d,p) level in gas and aqueous phases are shown in Fig. 2. While serotonin is interacted with ring structure of promazine in gas phase, it is interacted with amino group of promazine in aqua phase. Especially, complex is formed mainly by conjugated parts: N….H-N aqueous phase. Also, there may be attributed to both the presence of H-bonds and π-π* interactions in aqueous phase.

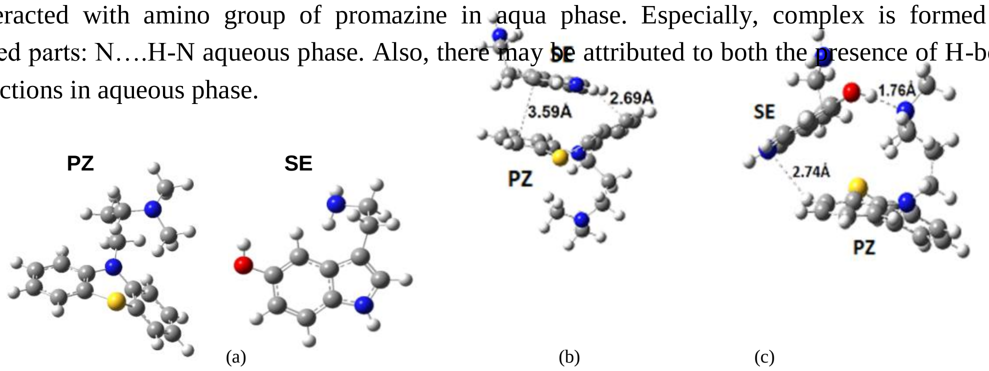


Fig.2 The optimized ground state structures of studied (a) monomers in water, (b) complexes in gas and (c) in water at ωB97XD/6-31G(d,p) level

Results in Table 1, molecules form stable complexes (ΔE_C) in gas phase and in water. As the interactions between molecules to form complexes are much easier in gas phase, complexation occurs easier compared to solution. There are complex forms by overlapping of the conjugated by π-π* interactions in gas phase.

Table 1. Dipole moments (μ, Debye), sum of electronic energies and zero point energies (E_{elec}+ZPE, Hartree), sum of electronic energies and free energies ($E_{elec}+\Delta G$, Hartree), complexation (ΔE_C) and complexation free energy changes ($\Delta\Delta G_C$) of investigated molecules in gas phase and in water, calculated at ωB97XD /6-31G(d,p) level.

		μ (D)	E_{elec}+ZPE (Hartree)	$E_{elec}+\Delta G$ (Hartree)	ΔE_C[a] (kcal/mol)	$\Delta\Delta G_C$[b] (kcal/mol)
in gas	PZ	2.36	-1166.96082	-1167.00629		
	SE	3.03	-572.64054	-572.677370		
	PZ-SE	2.02	-1739.62521	-1739.68689	**-14.97**	**-2.03**
in water	PZ	3.65	-1166.96830	-1167.01335		
	SE	4.15	-572.65363	-572.69053		
	PZ-SE	3.08	-1.739.64459	-1739.70646	**-14.22**	**-1.62**

[a] $\Delta E_C = E_{Complex} - (E_{PZ} + E_{Hormones})$; [b] $\Delta\Delta G_C = \Delta G_{Complex} - (\Delta G_{PZ} + \Delta G_{Hormones})$

Table 2 and Fig. 3 display electronic transitions of the studied molecules. When the electronic transitions were examined for CAM-B3LYP, B3LYP and ωB97XD methods using 6-311++G(d,p) basis set, the most appropriate method was found to be B3LYP compared with experimental. All calculations were carried out using the Polarizable Continuum Model (PCM) [4,5].

Table 2. Excited state properties of studied molecules calculated at B3LYP/6-311++G(d,p) level in gas phase (g) and in water (w).

	$S_0 \rightarrow S_n$	ΔE (eV)		λ_{ex} (nm)		f		Predominant Transitions		Character[a]	
		g	w	g	w	g	w	g	w	g	w
PZ	S_1	3.81	3.80	325	326	0.0004	0.0021	H→L+1	H→L	ICT	ICT
	S_2	3.98	3.98	311	312	0.0184	0.0287	H→L	H→L+1	ICT	ICT
	S_3	4.17	4.18	297	297	0.0746	0.1176	H→L+2	H→L+2	ICT	ICT

	S_4	4.26	4.37	291	284	0.0013	0.0018	H-1→L	H-1→L	ICT	ICT
	S_5	4.27	4.38	290	283	0.0093	0.0038	H-1→L+1	H-1→L+1	ICT	ICT
SE	S_1	4.34	4.31	285	288	0.0628	0.0703	H→L	H→L	ICT	ICT
	S_2	4.48	4.60	277	270	0.0004	0.1252	H→L+1	H-1→L	ICT, LE	LE
	S_3	4.65	4.74	267	262	0.0816	0.0029	H-1→L	H→L+1	LE	ICT, LE
	S_4	4.67	4.97	266	249	0.0093	0.0056	H→L+2	H→L+2	ICT	ICT
	S_5	4.73	5.07	262	245	0.0042	0.0025	H-1→L+1	H-1→L+1	ICT	ICT
PZ-SE	S_1	3.67	3.64	338	340	0.0024	0.0045	H→L	H→L	ICT,CT1	LE1, CT2
	S_2	3.84	3.82	323	325	0.0029	0.0221	H-1→L+1 H→L	H→L+1	CT1,ICT ICT,CT1	LE1
	S_3	3.88	4.04	320	307	0.0273	0.0884	H→L+1	H→L+3 H-1→L+2	CT1,ICT	LE1,CT2 LE2,CT2
	S_4	3.98	4.11	311	302	0.0048	0.0064	H-1→L+1	H-1→L	ICT,CT1	LE2,CT1
	S_5	4.06	4.14	305	299	0.0016	0.0115	H-2→L	H-2→L+1	ICT,CT2	CT1

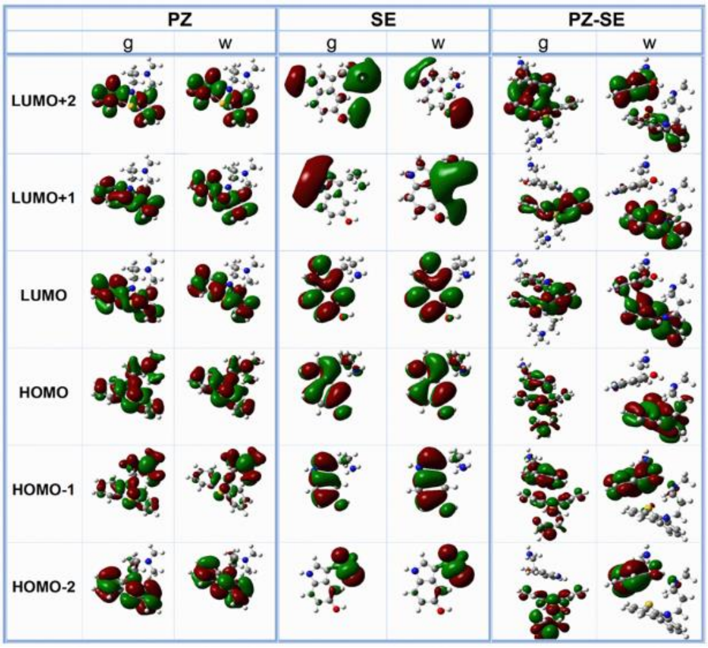


Fig. 3. Molecular orbitals and energy differences of frontier orbitals for studied molecules calculated at B3LYP/6-311++G(d,p) level in gas phase and in water.

PZ-SE complex has charge transfer from SE to PZ (CT1). This result agrees with the selection of donor-acceptor system. An intermolecular full charge transfer for PZ-SE complex was found at 299 nm for S_5 excited state and this is in agreement with experimental results.

Conclusion

Investigated molecules forms charge transfer complexes in gas phase and in water. Complexes form by overlapping of the conjugated by π-π* interactions in gas phase. Also, this may be attributed to both the presence of H-bonds and π-π* interactions in water. PZ-SE complex shows charge transfer transition at 323 nm and 325 nm in gas phase and in water, respectively. This charge transfer property between HOMO and LUMO orbitals makes it suitable for photosensitive material design.

Acknowledgements

We acknowledge computer time on FenCluster provided by Ege University Faculty of Science.

References

[1] Jacobs, B. L.,1994. Serotonin, Motor Activity And Depression-Related Disorders: Clues To The Origin And Treatment Of Depression And Obsessive-Compulsive Disorders Can Be Found In The Role Of Serotonin Neurons In The Brain. American Scientist, 82,5, 456.
[2] Gaussian 09, Revision C01, M. J. Frisch et al., Gaussian, Inc., Pittsburgh PA, 2009.
[3] J. Tomasi, B. Mennucci, and Cancès E., 1999. J. Mol. Struct. (Theochem) 464, 211-226.
[4] J. Tomasi, B. Mennucci, and Cammi R., 2005. Chem. Rev. 105, 2999-3093.

REDOX REACTIONS BETWEEN SELECTED FE(III) AND FE(II) COMPLEXES: KINETIC STUDY

Rozina KHATTAK[a,b]2, Iftikhar Imam NAQVI[b]

[a]Department of Chemistry, Shaheed Benazir Bhutto Women University, Peshawar, Pakistan.
[b]Department of Chemistry, University of Karachi, Karachi-75270, Pakistan.

Abstract

This study surfaces the kinetics of the reduction of the mixed ligand Fe(III) complexes; $[Fe^{III}(diimine)_2(CN)_2]^+$ by the hexacyano complex of Fe(II); $[Fe^{II}(CN)_6]^{4-}$. The reactions were performed under the controlled condition of pseudo-first order at constant ionic strength and temperature in the aqueous medium. The progress of the reaction was monitored by the formation of the product species; $[Fe^{II}(diimine)_2(CN)_2]$ at 510 nm and 522 nm, respectively in the visible region. The increase in absorbance with respect to time was recorded. Integration method was implemented to determine the order of reaction with respect to the reactants. A complex kinetics was observed for each of the reaction. Each of the reaction completed into three phases and each phase had different kinetic orders. The effect of a couple of parameters such as the concentration of acid and ionic strength on the rate constant was studied in each phase to draw a clear conclusion.

Keywords: Hexacyanoferrate(II); dicyanobis(diimine)iron(III); complex kinetics; redox reaction

1. Introduction

The redox chemistry of Fe(III) and Fe(II) complexes have been of interest for decades. The mixed ligand complexes of Fe(III) and Fe(II) were first synthesized in the 1960s [1]. Later on, the kinetics of the redox reactions of these newly synthesized complexes of Fe(III)/Fe(II) was studied, but this arena could not take enough attention of the investigators [2-6]. We were interested in the selected mixed ligand complexes of Fe(III) due to their several properties such as the high stability in aqueous medium, substitution inertness with a sufficiently high value of the reduction potential (0.80 - 0.74 V) to oxidize other coordination compounds without any external trigger and without substitution of the ligands [7]. Dicyanobis(phenanthroline)iron(III) and dicyanobis(bipyridine)iron(III) were selected to oxidize hexacyanoferrate(II). Hexacyanoferrate(II) has been oxidized by various other coordination complexes [8-10], but its kinetics of the oxidation by our selected coordination complexes was unknown before this work. Our recent publications explain the kinetics and mechanism of the oxidation of the selected derivatives of ferrocene by dicyanobis(phenanthroline)iron(III) in dioxane-aqueous medium [11-12]. In this study, we oxidized hexacyanoferrate(II) by two different mixed ligand complexes of Fe(III), which contained two molecules of cyanide as a ligand and two molecules of the chelate either of 1,10-phenanthroline or 2,2'-bipyridine as the ligand to form octahedral geometry. The focus was to study the effect of ligand substitution on the redox chemistry of the octahedral compounds, which are outer-sphere oxidants or reductants.

2. Experimental

All the reagents and solvents used for this study were of the Analar grade. They were purchased from either of Merck, Sigma Aldrich, and or, BDH depending upon the availability with the company. Distilled and deionized water was used for this study to maintain the aqueous medium. The complexes such as dicyanobis(phenanthroline)iron(III) and dicyanobis(bipyridine)iron(III) were synthesized and crystallized out as reported earlier [7]. The instrumental setup was home-built to probe the rapid reactions in solution [11]. The experimental setup was maintained at the pseudo-first order condition with the excess concentration of hexacyanoferrate(II) over the dicyano(diimine)iron(III) complex. The reaction was probed at constant ionic strength (I) 0.06 and temperature. The increase in absorbance with respect to time was recorded at 510 nm and 522 nm upon formation of the dicyanobis(phen)iron(II) and dicyanobis(bpy)iron(II), respectively. The integration method was employed to determine the order of reaction and the rate constant, and to differentiate

* Corresponding author. Tel.: +92-91-9224706.
E-mail address: e-mail: rznkhattak@sbbwu.edu.pk, rznkhattak@yahoo.com

among the different phases of each reaction. All the data such as the rate constant are the average of 3-6 experimental trials with r^2 = 1.00 - 0.99.

3. Results and Discussion

The redox reaction of $[Fe^{III}(diimine)_2(CN)_2]^+$ with $[Fe^{II}(CN)_6]^{4-}$ was completed into three phases in the aqueous medium at constant ionic strength 0.06. In the first phase of the reaction, the reaction followed an overall zeroth order kinetics. In the second phase of the reaction, the reaction followed an overall second order kinetics. The third phase was named as the competition phase due to the competition between the rate of the redox reaction and the rate of the insolubility of dicyanobis(diimine)iron(II). The word 'diimine' corresponds to 1,10-phenanthroline and 2,2'-bipyridine molecule collectively. The order of reaction was determined with respect to each of the oxidizing and the reducing agent in each reaction. The value of the observed-zeroth, and or, observed pseudo-first order rate constant such as k_{obs} and k'_{obs} were determined by treating the recorded absorbance data according to the integration method. The slope of the plot of absorbance at time point 't' versus time yielded the multiplication product of molar absorptivity (ε) of $[Fe^{II}(diimine)_2(CN)_2]$, path length of the cuvette (b = 1 cm) and the observed zeroth order rate constant (k_{obs}) with an overall dimension 's^{-1}'. We used this value in order to determine the effect of the reaction parameters on the rate constant as this value is "ε" times greater than the actual k_{obs}, and "ε" is added as a constant in each reading of the slope in the first phase of the reaction. The plot of log natural of the absorbance at time point 't' versus time yielded the value of the slope, which corresponds to the observed pseudo-first order rate constant 'k'_{obs}' with dimension 's^{-1}'.

The effect of variation in the concentration of the oxidizing agents such as $[Fe^{III}(phen)_2(CN)_2]^+$ or $[Fe^{III}(bpy)_2(CN)_2]^+$ was studied over the observed rate constant in each phase of the reaction. Meanwhile, the effect of variation in the concentration of the reducing agent such as $[Fe^{II}(CN)_6]^{4-}$ was also studied upon the observed rate constants. Upon increasing the concentration of $[Fe^{III}(phen)_2(CN)_2]^+$ or $[Fe^{III}(bpy)_2(CN)_2]^+$, the value of the rate constant in each phase remained unchanged, we observed. This helped to conclude a zeroth order kinetics as well as the appropriateness of the pseudo-first order condition to follow the reactions. However, in the first phase of the reaction, the rate constant remained neutral or unchanged and showed a sign-wave pattern in the second phase of the reaction upon increasing the concentration of $[Fe^{II}(CN)_6]^{4-}$ and keeping all other parameters constant. The results have been shown in Figs. 1-2.

The effect of variation in the concentration of acid (HNO_3) or protons (H^+) and ionic strength (I) has been measured over the observed rate constant in each phase of the reaction and for each of the reaction. The observed rate constant in the second phase of the reaction decreased with increasing acidity, and it remained constant in the first phase in each of the redox reaction.

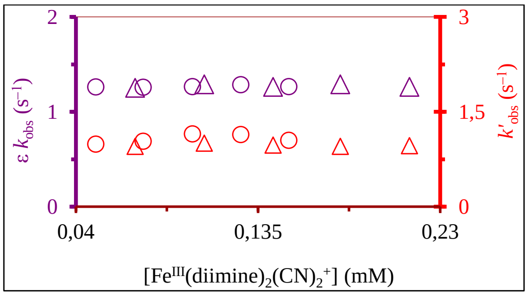


Fig. 1. Effect of $[Fe^{III}(diimine)_2(CN)_2^+]$ (o phenanthroline, Δ bipyridine) on the rate constants at 298 ± 0.5 K and $[Fe^{II}(CN)_6^{4-}]$ = 1.8/1.3 mM respectively.

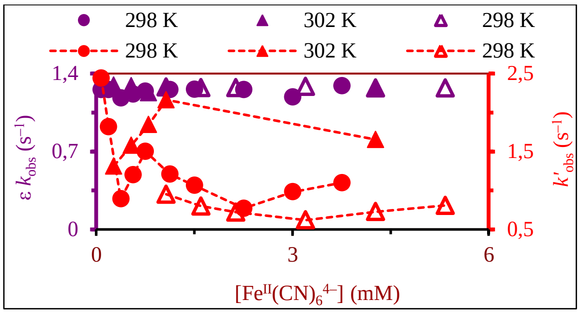


Fig. 2. Effect of $[Fe^{II}(CN)_6^{4-}]$ (● phenanthroline, Δ/▲ bipyridine) on the rate constants at 298/302 ± 0.5 K,

and $[Fe^{III}(diimine)_2(CN)_2^+]$ = 0.08/0.11 mM respectively.

The results show monoprotonated hexacyanoferrate(II) as the retarding species in the reaction mechanism of the electron transfer during the second phase of the reaction. The unchanged behaviour of the rate constant was expected in the first phase of each reaction due to the zeroth order kinetics, which confirms our finding. The dicyanobis(diimine)iron(III) does not become protonated under the experimental conditions, we employed. We did not find any support from experiments and literature regarding its protonation. The results are shown in Fig. 3.

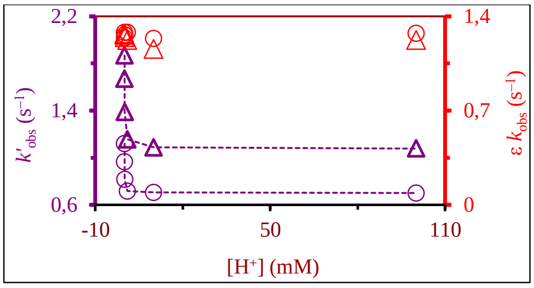


Fig. 3. Effect of $[H^+]$ on the rate constants (o phenanthroline, Δ bipyridine) at 298/302 ± 0.5 K, I = 0.12, $[Fe^{III}(diimine)_2(CN)_2^+]$ = 0.08/0.11 mM, and $[Fe^{II}(CN)_6^{4-}]_T$ = 0.8/1.1 mM respectively.

The ionic strength was varied by adding the aqueous solution of potassium nitrate (KNO_3) in the reaction mixture to maintain the desired value of ionic strength and keeping the other parameters constant. The observed rate constant in the second phase of each of the reaction decreased, and the value of the observed rate constant in the first of the reaction remained unchanged for both of the redox reactions when we increased the ionic strength of the reactions (Fig. 4). The zeroth order phenomenon justifies the unchanged observed rate constant in the first phase of each reaction. However, according to the formulation of the transition state theory of reactions in solution, the negative slope with its value approximately 4 confirms that the free hexacyanoferrate(II) ion is getting oxidized during the rate-determining step of the reactions (Fig. 4).

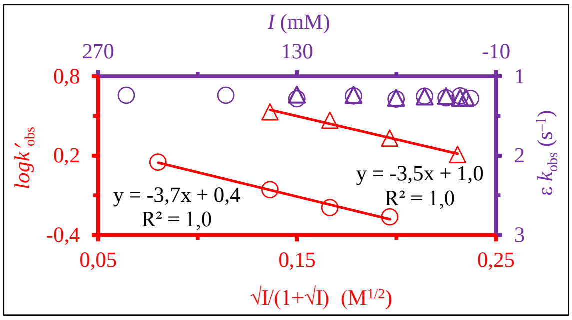


Fig. 4. Effect of ionic strength on the rate constants (o phenanthroline, Δ bipyridine) at 300/302 ± 0.5 K, $[Fe^{III}(diimine)_2(CN)_2^+]$ = 0.08/0.11 mM, and $[Fe^{II}(CN)_6^{4-}]_T$ = 0.8/1.1 mM respectively, in aqueous medium.

4. Conclusion

In the view of our results, we concluded that the rate of redox reactions between the coordination complexes depends upon the binding site(s) of the ligand to the metal ion. The rest of the structure although affect the rate constant but the binding site of the ligand to metal control the mechanism of the electron transfer during the reactions of such complexes.

References

1. Schilt AA. Mixed ligand complexes of iron(ii) and (iii) with cyanide and aromatic di-imines. J Am Chem Soc. 1960;82:3000-5.
2.Takagi HD, Kagayama N, Matsumoto M, Tarumi T, Funahashi S. Mechanistic study of oxidation reactions of hydroquinone, catechol and l-ascorbic acid by dicyanobis(1,10-phenanthroline)iron(iii) in dimethyl sulfoxide. J Mol Liq. 1995;65-66:277-80.
3. Matsumoto M, Tarumi T, Sugimoto K-i, Kagayama N, Funahashi S, Takagi HD. Oxidation reaction of l-ascorbic acid by dicyanobis(1,10-phenanthroline)iron(iii) in dimethyl sulfoxide at elevated pressure: Evidence for adiabatic electron transfer. Inorg Chim Acta. 1997;255:81-5.
4. Wang X, Stanbury DM. Copper catalysis of the oxidation of iodide by $[fe^{iii}(bpy)_2(cn)_2]^+$ in acetonitrile. J Phys Chem A. 2004;108:7637-5.
Wang X, Stanbury DM. Oxidation of iodide by a series of fe(iii) complexes in acetonitrile. Inorganic Chemistry. 2006;45:3415-23.
6. Wang X, Stanbury DM. Direct oxidation of l-cysteine by $[fe^{iii}(bpy)_2(cn)_2]^+$ and $[fe^{iii}(bpy)(cn)_4]^-$. Inorg Chem. 2008;47:1224-36.

7. Khattak R. Comparative kinetic study for the electron transfer reactions of some iron complexes [PhD]. Karachi: University of Karachi; 2011.
8. Kardel DM, Dunford HB, Alexandre S. Kinetics of the oxidation of ferrocyanide by lactoperoxidase compound ii. Eur J Biochem. 1990;194:259-62.
9. Rabai G, Epstein IR. Kinetics and mechanism of the oxidation of hexacyanoferrate(ii) by bromate. Inorg Chem. 1989;28:732-6.
10. Abdel-Hady AEM. Kinetics and mechanism of oxidation of ferrocyanide by n-bromosuccinimide in aqueous acidic solution. Transition Met Chem. 2008;33:887-92.
11. Khattak R, Naqvi II, Summer S, Sayed M. Mechanism of the oxidation of 1-(ferrocenyl)-ethanone/ethanol by dicyanobis(phenanthroline)iron(iii). Arabian Journal of Chemistry. 2016.
12. Khattak R, Nazir M, Summer S, Sayed M, Minhaz A, Naqvi II. Thermodynamic aspect: Kinetics of the reduction of dicyanobis(phen)iron(iii) by acetylferrocene and methylferrocenemethanol. Chemical Papers. 2018;72:883-93.