

Dedicated to the Father of the Nation Bangabandhu Sheikh Mujibur Rahman

**BARISHAL UNIVERSITY JOURNAL OF
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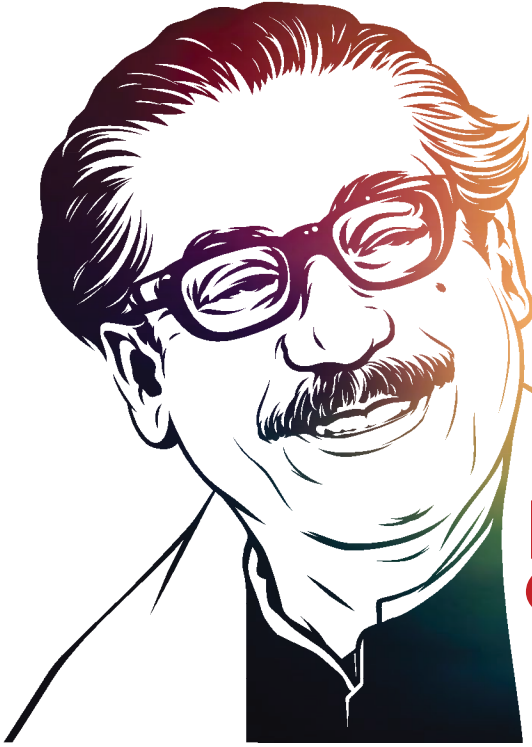
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Barisal University is dedicated in honour of
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Sheikh Mujibur Rahman
on his birth centenary celebration*



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Editorial

It is also our great honor and privilege to declare the Barishal University Journal of Science and Engineering (Volume -7, Issue -1, December 2020) of the faculty of Science and Engineering as the 'Mujib' edition. As the Mujib Year is being fervently observed across Bangladesh and beyond, this particular edition is meant to be an expression of our solidarity with the cherished ideals and vision of Bangabandhu Sheikh Mujibur Rahman, the Father of the Nation, whose glorious presence in our history gives meaning to all our liberation struggles of the past and our independence in 1971. Moreover, our tribute to the Father of the Nation in the Mujib Year will be fulfilling if this special edition ushers in qualitative changes within academia and beyond, and thus, help us realize Bangabandhu's vision of 'Sonar Bangla'- an intellectually independent and culturally liberal Bangladesh.

Science, technology, and engineering are recognized as key interdisciplinary areas. It has been demonstrated that textbook hypotheses do not always provide useful information for learning. As a result, there is a pressing necessity for exemplifying research findings in the form of articles, which could be beneficial in enriching the learning process in grasping fundamental principles to apply scientific and engineering applications. It is my great pleasure to be associated with the process that has successfully brought out the BUJSE Journal- a research Barishal University Journal of Science and Engineering, Volume-7, Issue-1, December-2020.

Barishal University Journal of Science and Engineering is inter-disciplinary and is dedicated to issue quality articles through rigorous and blind review process. It publishes articles in the field of Computer Science & Engineering, Mathematics, Physics, Chemistry, Geology and Mining, and Statistics. The journal aims to open a space of creativity and research of international standards by incorporating innovative modalities of perceptions and ideas. As far as ensuring the quality of the journal is concerned, the editorial panel of the journal has raised the bar. Articles submitted are reviewed with the utmost rigor by eminent scholars corresponding to the field of the articles. The research papers in this journal present relevant research works conducted by our academics in the fields of Science and Engineering. I firmly believe that this journal will flourish over time and be established as one of the finest journals of Science and Engineering in the country.

I would like to take this opportunity to thank everyone who has contributed to the BUJSE in various capacities and urge researchers to continue submitting research articles to the journal. Your cooperation will be highly appreciated. If you have any questions or suggestions, please directly email me or the journal coordinator at: bujournalscience@gmail.com.

I wish this journal and those who worked tirelessly to make it see the light of the day every success.

With thanks,

Professor Dr. Md. Sadequ Arefin

Editor-in-Chief

Barishal University Journal of Science and Engineering
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BANGABANDHU: A PATRON OF SCIENCE-ORIENTED EDUCATION SYSTEM IN BANGLADESH

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Science-oriented Education: Religion, Literature and Science

Let us start with important quotes (inscribed near the Senate Bhavan of Rajshahi University):

First one from Philosopher Socrates (470 BC – 399 BC), the best teacher of all times, who sacrificed his life for the sake of truth, “Unexamined life is not worth living”. The second one from Physicist Albert Einstein (1872-1970), considered best of all times, “I have no special talents. I am only passionately curious.” Both of the quotes indicate that practicing the human qualities in a science-oriented society can help one lead modest and noble life.

There exists the most prevalent slogan in Bangladesh, “we want science-oriented and pro-people education”. To understand the meaning of science-oriented education, let us analyze what Harvard particle physics Professor Lisa Randall tells us about nature and universe. She said that “The universe is humbling. Nature hides many of its most interesting mysteries”. The universe and its nature allure us with the truth and beauty to dissect with spiritual, mental and intellectual pursuits. To unfold the mysteries of the nature around us and universe, qualities needed are: logic, reason and comprehension, irrespective of the viewing perspectives. There are mainly three different viewing attitudes: religion, art and science. As an example, let us consider the case of *Moon*, the natural and only one satellite of our planet Earth. Different religions attribute importance to it by considering its appearance in the sky as deciding the day and time of religious worshiping and festivals. In literature, a poet becomes happy to describe the beauty of the moon like American poet Babatunde Aremu who glorifies the beauty of the Moon as: /There are billions of stars in the sky/ There are trillions of lamps on earth/ None glows like the beautiful moon/ At your up-rise the world glows/ Your appearance reveals God’s glory/ ...

Scientists with their science-cult unfold the mysteries of the moon in its assuming different shapes, its beauty coupled with its cool luster and the composition of its soil and atmosphere. These indomitable aspirations led to the NASA’s Apollo 11 space flight that first landed humans, Neil Armstrong and Buzz Aldrin in 1969. The success of this space-flight encouraged many space-programs, manned and unmanned. Recently NASA’s Perseverance rover landed safely on the planet Mars and started making oxygen [The Daily Star presentation dated 23 April 2021, p. 12]. This is followed by China’s Zhurong rover which has also started roaming on the Martian surface [The Daily Star presentation dated 23 May, 2021,

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page 12]. It is a great stride in finding a future human abode when our earth becomes inhabitable with the sun-temperature rising too high. Thus inquisitiveness about the moon has brought forth phenomenal prosperity in science and associated technologies.

The world during recent years witnessed stupendous scientific achievements. In particular, the experimental confirmations of ‘Higgs Boson’, the so-called God’s particle, in 2012 and gravitation wave, predicted in the century old Einstein’s Relativity theory, in 2016 which could be realized with global collaborations of advanced Science, Technology and Engineering. Furthermore, for survival of human race in a distant future, scientists through collaborated works realize now the need for exploration of an alternative Earth as a future abode of posterity perhaps in a distant galaxy as our earth will go apocalyptic with gradually increasing temperature of our sun in its core. Although our standard of living is greatly improved in numerous ways, we are lagging far behind the developed countries.

Religion, Literature and Science for Patriotism

Religion, literature and science are complementary, provided these are served and practiced by relevant persons with *free minds having adequate human qualities of logic, reason and comprehension*. The ingredients are referred to in the 2010 National Education Policy of Bangladesh. This means that learning and teaching in all traits of education are to be practiced with free minds. In other words, proper education is to be imparted to the students by the teachers with free mind irrespective of its types to awaken interest in them. Nobel Laureate in Physics 1979 Steven Weinberg (born 1933) in an interview on religion and science said to New York Times in 1999 that “With and without religion one can find, good people doing good and bad people doing evil things. But religion takes good people doing evil things”. I, however, believe that this happens due to a wrong interpretation of what religion tells.

Free mind with profundity in human qualities awakens creativity, humanism and patriotism. Persons imbued with such attainments, bear ability to roam across different tiers of topics freely to mitigate tiredness due to monotony resulting from a long stay in a particular topic. Humanism means speaking fearlessly for the downtrodden common mass. Patriotism brings in fearlessness to respect *Trinity of Mothers*: Mother-tongue, Mother-land comprising country including the common mass and child-bearing mothers providing continuity in the human race. Let us examine the life-sketch of Nobel Laureate in Literature 1950 Bertrand Arthur William Russell (1872-1970). Russell with good British education in the UK had a free mind to become a British polymath (having knowledge in multi-dimensional topics) as he could move freely around philosophy, mathematics, history, literature, social criticism and political activity. He was a wrangler in mathematics from Cambridge University. His philosophical essay, *On Denoting*, has been considered as a paradigm of philosophy. He condemned the US involvement in the Vietnam-war. He was always anti-war. He urged that all nuclear-weapons should be banned.



Let us now turn to Nobel Laureate Rabindranath Tagore (1861-1941) who was an Indian polymath as a renowned poet, writer, playwright, composer, philosopher, novelist, social reformer and painter. With his noble patriotic feeling, Kabiguru Rabindranat relinquished the British Knighthood as a mark of protest to the misrule of British-Raj in India. He had weakness over scientific knowledge. His only scientific book, *Vishwa Parichay* (Our Universe), has been dedicated to Scientist Satyendra Nath Bose (1894-1974) universally acclaimed for developing the foundations of the *Bose-Einstein quantum statistics* and the theory of *Bose-Einstein condensation*. In the introduction to the book, Kabiguru expressed, “Needless to say, I am no devotee of science, but since childhood I have always been curious about it, deriving endless pleasure from it.” Scientific mind of Kabiguru had been appreciated by his close friend, Sir Jagadish Chandra Bose (1858-1937). The conversation on July 14, 1930 in Berlin between Albert Einstein and Rabindranath Tagore not only examined science, beauty, consciousness and philosophy but also generated “a curious osmosis of Indian traditions and secular Western scientific doctrine”. I like to discuss a portion of the discourse highlighting the scientific mind of Kabiguru about Truth. Einstein (**AE**): Do you believe in the Divine as isolated from the world? / Tagore (**RT**): Truth of the Universe is human Truth. I have taken a scientific fact to explain this – Matter is composed of protons and electrons, with gaps between them, but matter may seem to be solid The entire universe is linked up with us in a similar manner, it is human universe. I have pursued this thought through art, literature and the religious consciousness of man./ ... / **AE**: I cannot prove scientifically that Truth must be conceived as a Truth that is valid independent of humanity, but I firmly believe it. .../ **RT**: Truth, which is one with the Universal Being, must essentially be human ... at least the Truth which is described as scientific and which can be reached through the process of logic, in other words, by an organ of thoughts which is human./ ... / **AE**: Even in our everyday life we feel compelled to ascribe a reality independent of man to the objects we use ... For instance, if nobody is in this house, yet that table remains where it is./ ... / **RT**: Science has proved that the table, as a solid object is an appearance and therefore that which the human mind perceives as a table, would not exist if that mind were naught. ... In any case, if there is any Truth absolutely unrelated to humanity then for us it is absolutely non-existing. It is difficult to imagine a mind to which the sequence of things happens not in space but only in time like the sequence of notes in music. ... There is reality of paper, infinitely different from the reality of literature. ... Truth which has no sensuous or rational relation to the human mind, ... will ever remain as nothing so long as we remain human beings. / **AE**: Then I am more religious than you are! / **RT**: My religion is the reconciliation of the Super-personal Man, the universal human spirit, in my own individual being./ The discourse between the two scientific and literary giants reveals the *crucial relationship between art, science and religion*.

Sir Jagadish Chandra Bose (1858-1937) and Sir Prafulla Chandra Ray (1861-1944), two compatriot contemporaries of Kabiguru, and their great students Statistician Prasanta



Chandra Mahalanobis (1893-1972), Quantum Physicist Satyendranath Bose (1894-1974), Astrophysicist Meghnad Saha (1893-1956) and Photo-Chemist Jnan Chandra Ghosh (1894-1959) were all polymath with extra-ordinary talents in their respective subjects and patriot of highest order. In the nineteenth century during the British colonial rule in the Indian sub-continent, a group of brave, talented and patriotic personalities appeared in Bengal. They include Michael Modhusudan Dutt (1825-1873), Ishwar Chandra Vidyasagar (1820-1891), Jagadish Chandra Bose (1858-1937), Rabindranath Tagore (1861-1941), Chitta Ranjan Das (1869-1934), Khudhram Bose (1889-1908), Prasanta Chandra Mahalanobis (1893-1972), Meghnad Saha (1893-1956), Surja Sen(1894-1934), Satyendranath Bose (1894-1974), Jnan Chandra Ghosh (1894-1959), Subhas Chandra Bose (1897-1945), Kazi Nazrul Islam (1899-1976), Mohammad Quadrat-e-Khuda (1900-1977) to name a few. The reason behind the concentrated germination of the talents is that *oppression and torture coupled with good education* in the British rule generated braveness, diligence, comprehension, creativity, patriotism and challenges to whip up attainments.

Let us now analyze Satyendranath Bose, to whom Dhaka University owes a big share of its fame as *Oxford of the East*, to adjudge his braveness and patriotism. During his stay in Dhaka, he used to help the students of science irrespective of the subjects from morning to evening in their research works. In 1925, Bose (**SB**) met Einstein (**AE**), considered by Bose as his master (*Guru*), in Berlin. Their conversation went beyond science to politics. Bose recalled their political discourse as the following: “One day Einstein confided to me, ‘I think Englishmen are better than other Western colonial nations, and I feel that they are far better than the French and Dutch. You should not be surprised as a German like me praising the English. Now tell me do you really want that the British should quit your country?’ . I (**SB**) said, ‘Of course, we all want to determine our own destinies ourselves ‘. He (**AE**) was not convinced. ... He said, ‘Really?’ and kept quite a while. I (**SB**) asked him, ‘Well, why do you Jews want to establish a new Israeli state? Even you seem to be fairly inclined in its favour’. He (**AE**) said, ‘Of course, I now understand what you are saying – it is an emotional matter and cannot be understood rationally’.

Bangabandhu’s realization about Science-oriented Education

During partition of the British India in 1947, the standard of education and research in our country was at par with that of India. With passage of time, India is improving in technological developments and trailing China closely. On the other hand, in spite of being the successors of Sir Jagadish Chandra Bose and Sir Prafulla Chandra Ray, the two great pioneers of scientific renaissance in the subcontinent, we are lagging far behind India. Now we are pleased to hear that we are graduated from a “least developed country” (LCD) status to a “developing country”.



Bangabandhu Sheikh Mujibur Rahman, received good education from the teachers of British India. He could realize that after the creation of Pakistan, Government of Pakistan exploited religion to extort our earned foreign currency from export of jute and utilize that for wellbeing of West Pakistan. With good education background he used to possess science-oriented knowledge and used to attach importance to proper education. I can recall two instances:

(i) In January, 1954 when I was a student of class VII, Bangabandhu along with Maulana Abdul Hamid Khan Bhashani and two other leaders of newly formed political coalition in the name of *United Front* visited my school, R. M. Academy (adjacent to Edward College, Pabna) just before Pakistan's first provincial election. I can recall that Maulana Bhasahani and Sheikh Mujibur Rahman in their speeches expressed their concern on the education being imparted to the school students after creation of Pakistan. Both of them stress the need of effective education which can motivate the students to understand what they read and to nurture their ability to differentiate between good and bad. The election resulted in a landslide victory for the United Front and a crushing defeat to the ruling Muslim league which enabled the united front to form the 1954 East Bengal cabinet with A K Fazlul Huq as the Chief Minister and Sheikh Mujibur Rahman as a Minister of Land, Agriculture and cooperative affairs.

(ii) My brother-in-law Professor Dr. Rathindra Nath Bose, who was born in 1952 in a pristine village Kamalapur of Narail in Bangladesh, had been holding a highly visible administrative position as Vice Chancellor/ Vice President for Research and Technology Transfer in addition to his appointment as Professor in simultaneously two Departments: Biology & Biochemistry and Chemistry of Houston University, USA until his premature death on 10 July in 2015. Professor Bose had been honoured with a Distinguished Scholar Award, four Outstanding and Distinguished Teaching Awards. He became a Fellow of National Academy of Inventors, USA in 2013. He was awarded the Distinguished Professorship in Biology and Biochemistry in 2015. He authored more than 175 articles in highly selective International journals and proceedings and 11 (eleven) Patents. He delivered 44 Invited Speeches in Academic Institutions and 13 Keynote/Plenary Lectures in conferences. Professor Bose's research activities encompass a wide variety of interdisciplinary and multidisciplinary aspects of Medical and Material Chemistry. In particular, he postulated a new mechanism for platinum anticancer drugs for ovarian and testicular cancers. He received his Ph.D. degree in 1982 from Georgetown University of Washington, D.C.

Rathindra Bose obtained his B.Sc. (Hons.) and M.Sc. degrees in Chemistry in 1973 and 1975, respectively, with distinctions as recognized by his First Class First merit positions in both degrees from Rajshahi University. He got appointment as a Lecturer in Chemistry



of Dhaka University in 1976. In addition to being academically a meritorious student, Bose had been a powerful orator and one of the most popular student leaders which earned him a victory as General Secretary of the Syed Amir Ali Hall Student Union Election of Rajshahi University.

At the end of 1974, Rathindra sought a valuable advice from Bangabandhu who knew Rathindra very well. When asked by Rabindra about career, Bangabandhu told him, “you are good in both. However, *education, which is more powerful than politics*, should be accepted by you to serve the nation. You should go abroad for higher studies”. Rathindra saluted Bangabandhu and came back to Rajshahi to submit his M.Sc. thesis and to prepare himself for going to the USA to pursue higher studies and research.

Sacrifices of Bangabandhu for Independence of Bangladesh

Bangabandhu noted that our education standard had been declining with the migration of teachers and intellectuals with the advent of Pakistan creation. The misrule of Ayub-Mo-nem regime in the middle of sixties triggered mainly two-fold effect: (1) rise of Bangladesh movement leading to our independence and (2) gradual loss of values in our educated people in all sectors. The final picture stands as ‘values and judgment’ are eroded through the growth of selfishness. This attitude leads ultimately to unlimited ‘material greed’, the most dangerous form of our social virus which infacts our human qualities including judgment. Good education instills free mind with values which acts as an antidote to our immense greed.

Awami League won the 1970 election of Pakistan with overwhelming majority bagging almost all parliamentary seats in East Pakistan and absolute majority in whole Pakistan. Denial of the martial Law Government to hand power over to Awami League, inspired Bangabandhu Sheikh Mujibur Rahman to deliver the Landmark Speech of 7 March 1971 declaring Independence in case the Pakistan Army did not respect democratic result of the election. In response, the Pakistan Army inflicted a brutal genocide in East Pakistan starting on the night of 25 March. Bangabandhu was imprisoned in the morning of 26 March just after he declared independence in the early hours. This triggered the Liberation War as per proclamation of Bangabandhu in his Paltan maidan speech. Emergence of the secular Bangladesh was the culmination of the nine month-long Liberation war at the cost of martyred intellectuals, gallant freedom fighters and lives of 3 million innocent people and brutal raping of our mothers.

On 15 August 1975, some of young army officers, lacking in values and lured by big positions, killed Bangabandhu and his family including 10 years old son Sheikh Russel excepting Sheikh Hasina and Sheikh Rehana who were visiting abroad. In 2004, Bangabandhu Sheikh Mujibur Rahman was adjudged the best Bengali in the 1000 years history of Bengal



and also the best Bengali of all time according to the opinion poll conducted by BBC with Rabindranath Tagore in the second position. The Mahatma Gandhi Peace Prize 2020 has been conferred to Bangabandhu Sheikh Mujibur Rahman in recognition of his outstanding contribution to social, economic and political transformation through non-violent and other Gandhi methods.

The oppression of Pakistan although resulted in a Sovereign Bangladesh, but *their weak and non-secular education system* produced a gradual decline in education standard and eroded the human values. We inherited this decline in human values after our independence. The contamination was so deep rooted that even the 2010 National Education Policy of Bangladesh could not yield a tangible effect.

Education for Realizing Scientific and Technological Advances

Scientific and technological researches, supplemented by researches in other fields, are pivotal to the progress of a country. Course-curricula at different stages of education are designed to prepare the students for the future researches. The primary education, which is most vital, is aimed to train up students for discipline, etiquette and *learning with pleasure*. In the secondary stage, the students are taught with comprehensive education for expression and judgment as a preparation for higher studies and research. As advised by my teacher Makhantal Chakarborty Sir in Edward College in 1957, students in this stage should “try to visualize what you learnt throughout the day. If you can, you can learn. If not, read and think over again. You should be up-to-date at the end of the week. Otherwise you will be unable to cope with the new learning in the next week”. To accomplish this, each student should practice the following steps in reading: (a) to understand the meaning of each of the sentences, (b) to bring out the underlying concept in a paragraph and (c) to dig out the intriguing knowledge provided in a chapter. I followed these steps in practicing the valuable advice of my teacher throughout my life.

In the tertiary stage, the students are equipped with qualities to face the competitions and hardships in livelihood as well as to develop creativity needed for research. In order to impart the above qualities to the students, there must be conformity between the word and action of the teachers. There should also be harmony amongst the teachers, guardians and politicians. All these can be realized only when our material greed can be pacified through acquiring proper knowledge concerning religion, politics and conventional education. Unfortunately, none of the teachings is working effectively. Effective education can act as deterrent to material greed and generate a free mind. The students can only realize their limitations in various aspects at the *fab-end* of their education. They try their utmost but cannot cope with all their weaknesses at this stage. In the sea of their ignorance, they try to seek a straw of any ‘short-cut-way-to-success’ without realizing its consequence that



might befall upon them. Their incapability to face hard competitions lead many of them to drug addiction, terrorism or other activities, that are detrimental to the society. We feel, however, complacent with our few students performing fairly well with their inherent talents -in the developed countries. They are, in fact exceptional, born with the qualities of 'Nobel Laureates'.

However, with the global connectivity through World Wide Web (www), enhanced speed in accessing the treasure trove of information through the installation of 'submarine optical fibre' in the first decade of the twenty first century, and improvement in the digital facilities through ICT centres, Bangladesh in the recent years has made a great stride in many areas as reflected in the recent performance index of global ranking. Tremendous growth in the production of important food items is notable. Tremendous growth in the production of important food items is notable.

Present State of Advances in Bangladesh

The last fifteen years has recorded an average growth rate of more than 11.2% in the annual production of rice, which as the staple food is the main concern in populous Bangladesh. The fish production has gone up so much that its price has gone down substantially over those existed five years ago. People's average life expectancy in Bangladesh has also substantially gone up. Research activities in genome technology gained momentum following the remarkable success in the development of fungus resistant jute in 2010 by the Bangladesh team working under Late Dr Maqsdul Alam, a Bangladesh born Professor of Hawaii University. Biodegradable jute fibre is second only to cotton in making apparels, bags, carpets and other attractive items as exposed in an environment fair at Sher-e-Bangla Nagar. Scientists in Bangladesh have now also sequenced the genome of many agricultural items and protein sources including the much loved Hilsha fish. The dairy firms are now being controlled digitally.

Construction works for two 1200 MW nuclear power plants in Rooppur began on 30 November 2017 and are scheduled to supply us atmospherically cleanest form of 1200 MW electricity in the first phase by 2025 which might be delayed by the recent surge of COVID-19 pandemic. With the successful launching of geostationary communication satellite Bangabandhu-1 on 11 May 2018, Bangladesh now finds its pride position in space. Bangladesh now is in a position to finance the construction of Padma Bridge from its own resources. Our living has also become much more comfortable. Research activities are being pursued at an accelerated rate in all universities and research institutes, albeit with satisfactory quality in only a few. We are going to have a Metro-rail in Dhaka to reduce the traffic jam and to mitigate the inconvenience of commuters in their travel to the working places.



Weaknesses and Problems Impeding the Expected Growth of Bangladesh

In spite of all the above-mentioned developments, Bangladesh received on 4 Feb 2016 a shocking experience of cyber heist of US \$ 101 million from Bangladesh Bank to other countries. Moreover, we had a long-standing problem of ‘question leakage’ of various examinations which concerns the future career of our students. These are harmful examples relating to the abuse of digital facilities made available to the common masses even through cell and smart phones in Bangladesh.

There is yet another disappointing misuse of our digital facility to alarm us before it goes out of control. The young teachers and researchers in Bangladesh have been kept lured for the last decade to publish rubbish articles in the so-called ‘online journals’ with a payment of fees to get their easy promotions. The appointing administrations in most cases are ignorant about the magnitude of damage being caused to our education setup. To our utter disappointment, we also heard of the alleged adulteration of gold in the Bangladesh Bank vault. These are culmination of ‘immense greed’ in educated people. Excessive greed puts creative power in an abyss of despair.

Our main problem is embedded in our mindset to measure dignity in terms of wealth in possession and to derive comfort out of laziness. Moreover, our values are on the wane with the lack of accountability and quality assessment in our systems, academia in particular. As a consequence, job seekers for jobs and service-holders for promotions and money-makers become crazy to welcome any method to give them easy achievements. On the other hand, parents and guardians, in general, are blind to the easy attainments of good grades in the examinations of their children. The chase for comfortable success triggers them to bribe the examiners which results in a business-bonanza of the question leakage. Improper education leads to “big dreams without having matching quality to earn”. These hollow dreams with suspended values lead to dangerous ends, even gruesome killings.

Solution to the Weaknesses in Education Quality in Bangladesh

Pleasure and satisfaction are subjective of mental condition and derivative of knowledge. Only money cannot buy these. Money and material property may be plundered by social unrest and natural calamity, but knowledge is non-perishable. Knowledge with free mind has immense power to decision making and leads to creativity for deriving profound satisfaction. Our children, in general, are no less meritorious than their counterparts in developed countries. Our poor social environment and education system make them weak. If we with our free mind work together, we can win over all kinds of our weaknesses to guide our children in the right direction. Not just instructions and advice, demonstrations with our activities can effectively encourage them to attain proper knowledge-strength, as advised by Sir Prafulla Chandra Ray. Our posterity is our torch-bearer. The successes of our children in the global competitions can give us immense pleasure.



In order to impart the above qualities to the students, there must be conformity between the word and action of the teachers, otherwise the students will be confused. There should be also harmony amongst the teachers, guardians and politicians. If the students are provided with proper education with a focus on values before the tertiary stage, they will have curiosity, creativity and judgment to pursue effective education and good research works. If the selection process of candidates in all kinds of job-positions including those of teachers is made transparent through written examinations and/or fair job tests followed by oral examination, the guardians will refrain from question leakage and bribing the examiners for unreasonable grades to spoil their children. The trinity of qualities, namely honesty, values and judgment instilled in the *youths coupled with free mind*, can morph into a powerful shield against evil deeds including the abuse of ICT. Bangabandhu, in his “Prison Diaries”, expressed, ‘Sacrifice wins idealism’. The combination of the sacrifices of dedicated teachers and quality of the research-works surely can expedite the achievement of *Sonar Bangla*, the long cherished dream of Bangabandhu, for which he sacrificed his life and his family. Quality teachers and researchers should be encouraged to hold the flagship of our country.

At the end of the article, let us remember what Nobel winning Richard Feynman, best teacher of Physics ever born, once said “Science is long history of learning how not to fool ourselves”.

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Dedicated to the loving memories of Prof. Dr. Shishir Kumar Bhattacharjee and Professor Dr. Mohammad Nasser, respectively, of the Departments of Mathematics and Statistics, Rajshahi University for their stupendous contributions to the respective departments.



MORPHO-DYNAMICS OF RIVER BANK AND POPULATION MIGRATION ALONG BHAIRAB, RUPSHA AND MAJUTKHALI RIVERS IN DIGHALIA UPAZILA, KHULNA, BANGLADESH

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Abstract

Bangladesh is the world's largest delta formed by the deposition of sediments carried by the rivers and streams that causing river dynamics. The riverbank erosion and accretion are continuous phenomenon in Bangladesh. This research was performed by calculating Bhairab, Rupsha and Majutkhali river bank's accretion and erosion that causing population displacement in Dighalia upazila, Khulna. Landsat satellite images of 2010 and 2020 were used in the Geographic Information System (GIS) environment to observe the morpho-dynamics change of riverbank. A field visit and a questionnaire survey were also conducted to validate the results and evaluate the effects of erosion on the human being and environment. The riverbank change was measured along eleven cross sections, labeled as A to K in the change map, where notable erosion and accretion was occurring. Among all the cross-sections, near the confluence of Bhairab and Rupsha rivers that marked as section A (South Chandanimahal area), has showed the highest erosion which is 32.02% (100.60m) at the right bank and lowest erosion is 5.35% (10.99m) at the left bank of Bhairab River. Maximum accretion (46.08m) was found at the left bank of cross-section F which is 62.18% (Maheshwarpur area) and minimum accretion (0.10m) was found at the cross-section G (Nandan Pratap Maddyapara area) which is 0.13% of all accretion. This study found that most of the erosional and accretional events occurred along the bank of the Bhairab River. However, the Rupsha River faces a more intense erosion in terms of intensity than the other two rivers. Besides the natural processes, human activities like the plying of ships and cargoes are also responsible for riverbank erosion in these rivers. Due to the riverbank erosion, people in this area loses their home, cattle, land even life. As a consequence, people had to migrate from Dighalia upazila to other places. In addition, people who were still surviving here had to shift their household at least twice in last 10 years.

Keywords: Morpho-dynamics, Change detection, Migration, GIS, RS.

Introduction

Networks of rivers and streams are the natural sources of water on the Earth's surface, which carries sediments with greater geological prominence (Aher et al., 2012). Bangladesh has one of the largest river systems in the world, i.e., Ganges-Brahmaputra, which carries about 1×10^9 tons of sediments every year (Goodbred and Kuehl 1999).

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Free-flowing rivers reach a state of equilibrium by sedimentation in one bank and erosion in the other. Rivers flowing a long way from the source gradually loses its capacity to carry the sediments, thus depositing loads at the river bed, but lateral erosion continuous (Das et al. 2014) resulting in riverbank erosion which is a vicinal and recurring hazard in Bangladesh (Uddin et al., 2011). According to Hassan and Mahmud-ul-Islam 2016, Bangladesh is a victim of 2000-3000 km of riverbank erosion every year. Riverbank erosion is a common phenomenon not only in Bangladesh but also in the world.

Natural and human activities are continually changing the Earth's surface. As a result of these activities, changes such as cut, carry away and deposition of the land surface materials frequently occur at river channel (Aher et al., 2012). Similarly, riverbank changes, including bank erosion, accretion and down cutting are natural for an alluvial river (Kummu et al., 2008). However, development works like sand mining, infrastructure building on the riverbank, artificial cutoffs, bank revetment, construction of reservoirs and land use alterations are the anthropogenic causes for changing the natural geomorphological dynamics of rivers (Fuller et al., 2003; Lane and Richards, 1997; Li et al., 2007; Surian, 1999; and Rinaldi, 2003). These development works by humankind threaten the channel stability and balance (Grant et al., 2013; Kesel, 2003; Rinaldi, 2003; and Fuller et al., 2003). Different environmental and socio-economic consequences in navigation, loss of riparian land and infrastructure, flood hazard and the alteration of aquatic and riparian ecosystems are the results of these human activities (Kummu et al., 2008). So, it has become essential to determine bank erosion, river course change and impact on human life, especially for a country like Bangladesh. For spatiotemporal assessment of the different topographical, geomorphic, geological changes, Geographic Information System (GIS) and Remote sensing (RS) are mostly used techniques (Ahmad F., 2012). Changes in channel configuration and the orientations between the river channel and its embankments can be determined by integrating GIS and RS (Das and Talukdar, 2017). In this study, the GIS and RS techniques along with an extensive questionnaire survey have been used to assess the morpho-dynamics of Bhairab, Rupsha, and Majutkhali river banks in Dighalia upazila, Khulna. This two technique was selected for the study as remote sensing databases are freely available and have some advantages like larger view, multi-temporal and time efficiency etc. (Thi and Binh, 2000). Bhairab, Rupsha, and Majutkhali riverbanks are continually changing due to geomorphic, climatic agents and human activities. These rivers are the waterways that are being frequently used as the route to Mongla port. As a result, artificial waves created by the ships and cargoes damages the bank heavily. Despite being a highly erosion-prone area, no such study has been documented regarding morpho-dynamics of riverbank in Dighalia, Khulna. This study is the first attempt to measure the morpho-dynamics of riverbank in Dighalia upazila, Khulna, using integrated GIS and RS techniques with a field visit and questionnaire survey.

Another objective was to find the impact of this riverbank dynamics to local people migration at different places of the country.

Study Area

Dighalia upazila lies in between $22^{\circ}50'$ and $22^{\circ}59'$ N latitudes and in between $89^{\circ}33'$ and $89^{\circ}40'$ E longitudes. It was established as an upazila on 7 November 1983. The upazila consists of six union parishads, which are Gazirhat, Barakpur, Dighalia, Senhati, Aranghata, and Jogipol. The total area of this upazila is about 86.52 square kilometers. The study area is surrounded by Terokhada and Rupsha upazila in the east; Daulatpur in the west; Kalia, Abhaynagar, Dumuria, Phultala upazilas in the north and Khalispur, Khulna Sadar in the south. Dighalia has an annual average temperature of 26.3°C . Its annual average rainfall is 1809.4 millimeters. (Bangladesh Meteorological Department, Retrieved 31 January 2016). The elevation of Dighalia upazila varies from 2.5 m to 10 m.

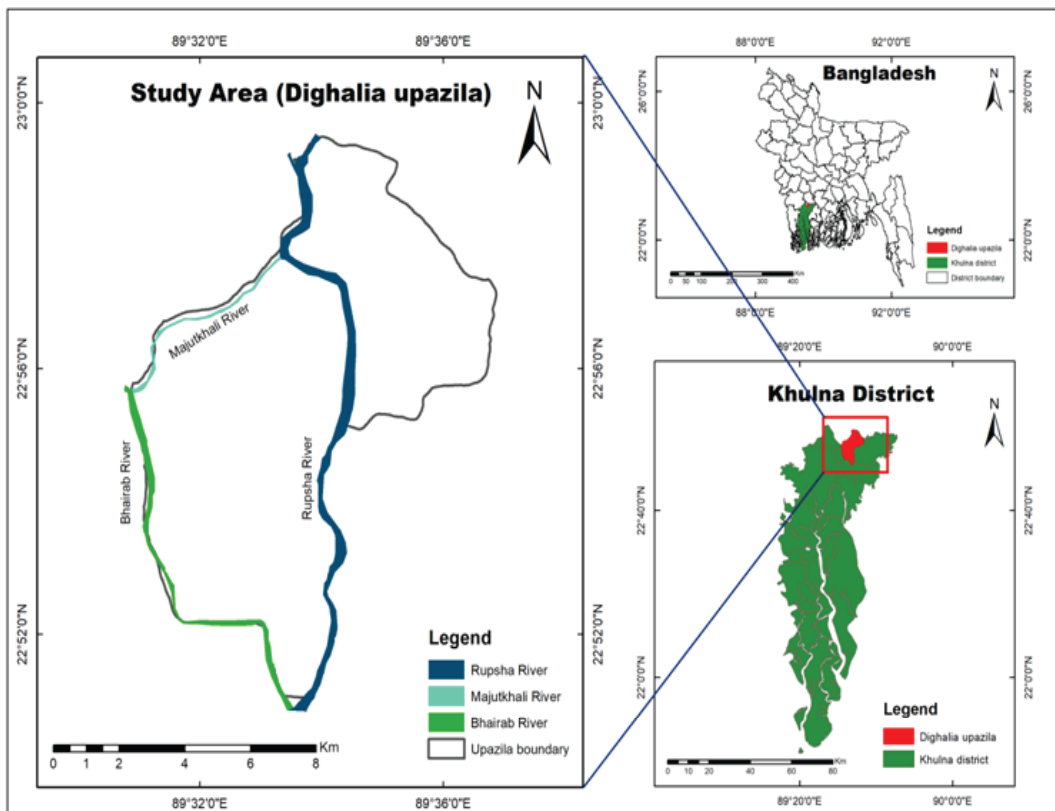


Fig. 1: Map of Dighalia upazila showing the main rivers.



The riverine system of Dighalia upazila is not complex. Three rivers, Bhairab, Rupsha and Majutkhali, are flowing through and around the study area. The Chitra River was renamed as Rupsha River while entering Dighalia upazila. Near Arua Bazar, the Rupsha river has been bifurcated into two tributaries, i.e., Majutkhali River running towards the west and Rupsha River running towards the SW. Bhairab River flows from further east joined the Majutkhali River near Barakpur union and took the name Bhairab River. Near the Chandonimahal area of Senhati union, the Bhairab River joined the Rupsha River and flowed further south towards Khulna Sadar. Bhairab, Rupsha and Majutkhali rivers are 11.7 km, 18.10 km and 6.07 km long respectively at Dighalia upazila.

According to the national census 2011, about 1,53,987 people live in this area, among them, 79,236 are male and 74,751 are female. The population density in Dighalia upazila is 1498 per sq. km. It has a literacy rate of 55.64%. Agriculture 26.81%, non-agricultural laborer 5.85%, industry 5.28%, commerce 13.37%, transport and communication 2.62%, service 34.02%, construction 1.07%, religious service 0.26%, rent and remittance 0.54% and others 10.54% contributes to main sources of income for Dighalia (<http://digholia.khulna.gov.bd>). Kali Mandir (Senhati Shiva Bari), Basu Deva Mandir, Khan Jahan Ali Dighi at Panigati are the main archaeological heritage and relics in this region.

Methodology

Data sources

Riverbank erosion and accretion at Dighalia upazila were calculated by using RS data in the GIS environment. Landsat provides 30m resolution images, which were adequate for this study. So, Landsat OLI-TIRS and Landsat TM images were downloaded from the United States Geological Survey (USGS) website (www.earthexplorer.usgs.gov). Table-01 provides detailed information about the imageries. For satellite image analysis, cloud-free images have preferences because cloud cover can significantly deteriorate image processing accuracy as well as image interpretation. So, the particular focus was that the cloud cover remains below 5% while downloading the Landsat images. It is also imperative to have the same month or season image data to study the river bank dynamics with satellite images because different month or season could show incorrect results. For this study, only the month of January of 2010 and 2020 was considered.

Table-01: Detail information of downloaded satellite imagery.

Satellite	Sensor	Date of acquisition	Path	Row	Source
Landsat 8	OLI/TIRS	17 January 2020	137	44	USGS Landsat level-1 data
Landsat 5	TM	21 January 2010	137	44	



Image Processing

Data processing is needed to metamorphosis the raw, unorganized information into an apprehensible format for further analysis (Puzinas, 2017). After downloading satellite images, a composite band was created using ArcMap 10.7 version software for both images. The color was set to the false-color band known as RGB (Red, Green, and Blue) color formation that helped to identify the target criteria. After completing the preliminary work, the area of interest (AOI) was extracted by a mask, which is the extension of the Spatial Analyst Tool of ArcMap 10.7. The AOI was extracted earlier so that further analysis could be done without spending more time in unwanted areas. The haze or noise was removed from both images by doing the radiometric correction. The whole working procedure has been shown in the flow chart (Fig. 2).

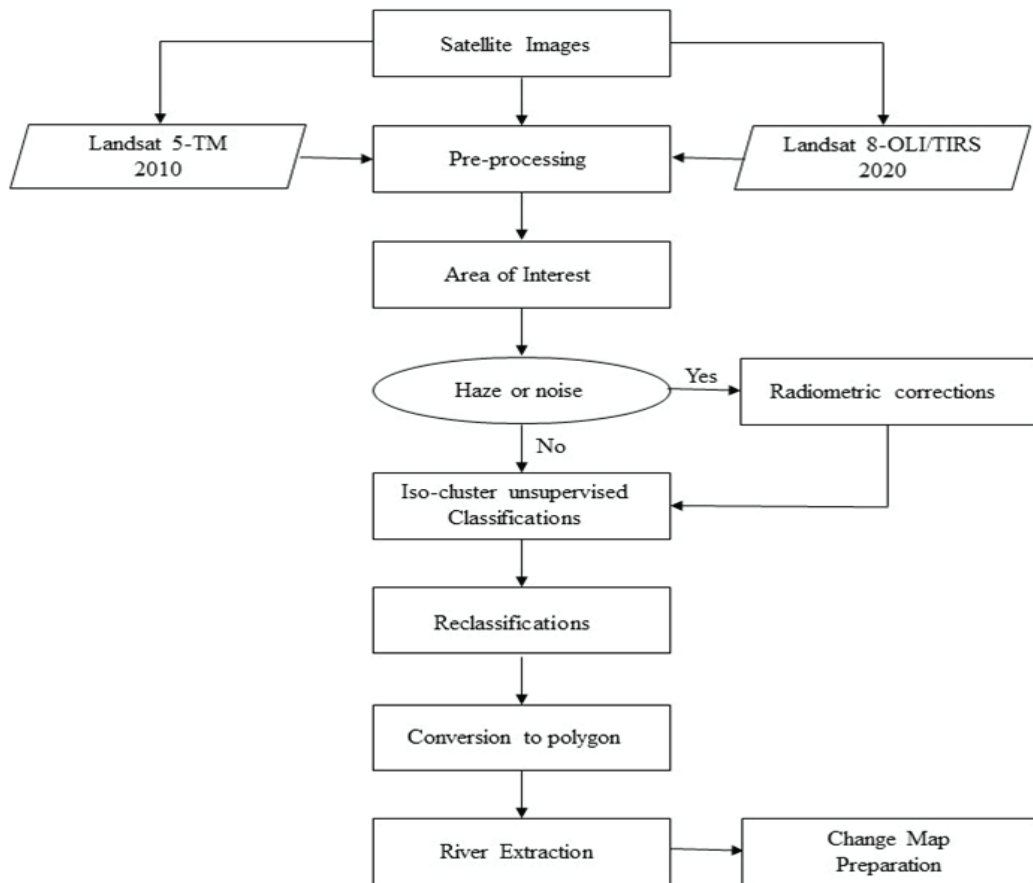


Fig. 2: Working procedure flow chart.

An iso-cluster unsupervised classification was run on AOI using the iso-cluster algorithm in the Spatial Analysis Extension of ArcMap 10.7 (Figure-03a).

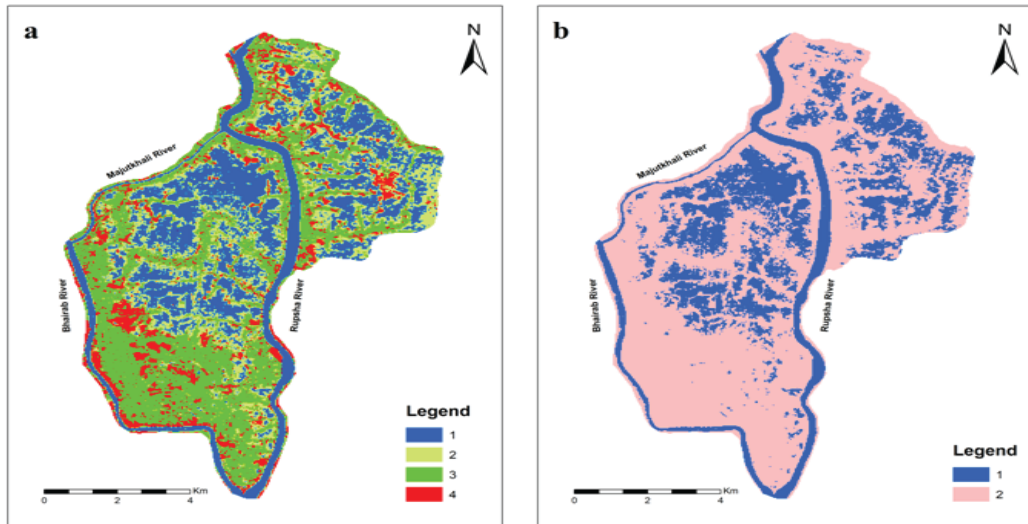


Fig. 3: (a) Unsupervised iso-cluster classification into 4 clusters
(b) Reclassification of the image from 4 clusters to 2 clusters

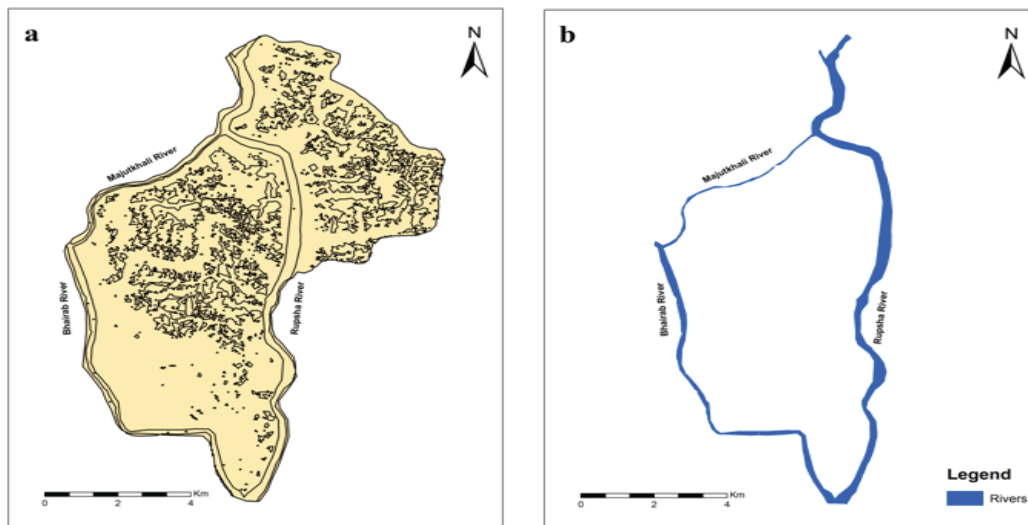


Fig. 4 : (a) Raster to polygon Conversion **(b)** Target Zone (River)



The number of classes or clusters was set to 4 with a minimum class size of 20 and sample interval 10 for taking the sample points to calculate the clusters. These clusters were all specified in the ArcGIS Multivariate Analysis Toolbox. Some researcher may set their cluster class size 30 and sample interval 6, which would have little effect on the results (Abubakar and Ibrahim, 2015).

For understanding, visualizing, identifying and describing spectral changes of each pixel of an image, classification became a medium that gives rise to either increase or decrease in spectral clusters over time. The reclassification functions reclassify or change cell values to alternative values by using a variety of methods. The reclassify dialogue box presented old values of each candidate pixel, after which new values were assigned to each class (Abubakar and Ibrahim, 2015). Reclassification was performed to 2 cluster classes from 4 cluster classes for this study (Fig. 3b) to extract the rivers more efficiently. These 2 cluster classes were created because the majority filter was attached to remove data noise and to provide a single value individually for each given overlay segment.

A polygon layer was created using the 'Raster to Polygon Conversion tool' (Fig. 4a) based on the two cluster classes. Finally, the target zone (rivers) was extracted from the vector image (Fig. 4b).

The same processes were followed by two different Landsat images (Table-01). After getting the vector file of our target zone (rivers) from two images, the change map was created by using ArcMap 10.7. The lateral lengths of riverbank erosion or accretion from 2010 to 2020 were measured from the change map using Measure Tool in ArcMap 10.7.

Results and discussion

Riverbank erosion is a common phenomenon for the rivers in Bangladesh. This study aims at finding the erosion and accretion of the bank of Bhairab, Rupsha and Majutkhali rivers in the last ten years at Dighalia upazila. To measure the change of these three rivers, two images of 2010 and 2020 were superimposed, which were extracted from satellite images. The change was measured along eleven cross-sections (A to K) at the three rivers (Fig. 5). Along Bhairab River, six cross-sections were created which are A (South Chandanimahal area), B (Senhati-Star gate road area), C (Deyara area), D (Dighalia ferry terminal area), E (Dighalia post office area) and F (Moheshwarpur area); two cross-sections were drawn on Majutkhali River which are G (Nandan Pratap Maddhyapara area) and H (Arua Bazar road area) and three cross-sections were drawn on the Rupsha River which are I (Domra Uttarpara area), J (Madhupur Bazar area) and K (Baysormar kheya ghat area). In order to represent erosion and accretion more clearly, individual sections have been shown in Fig. 6.

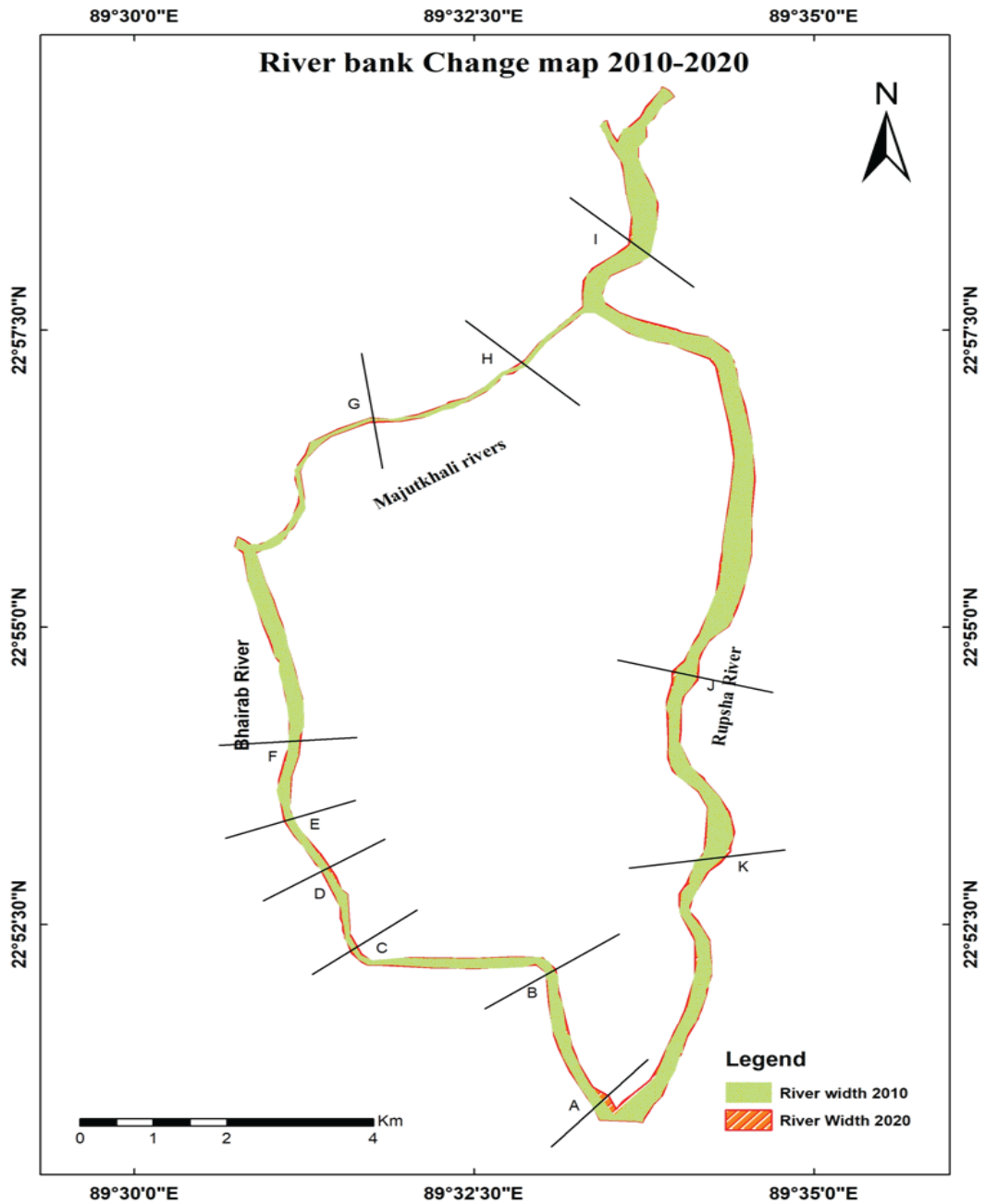


Fig. 5: Riverbank dynamics of three rivers in Dighalia upazila from 2010 to 2020

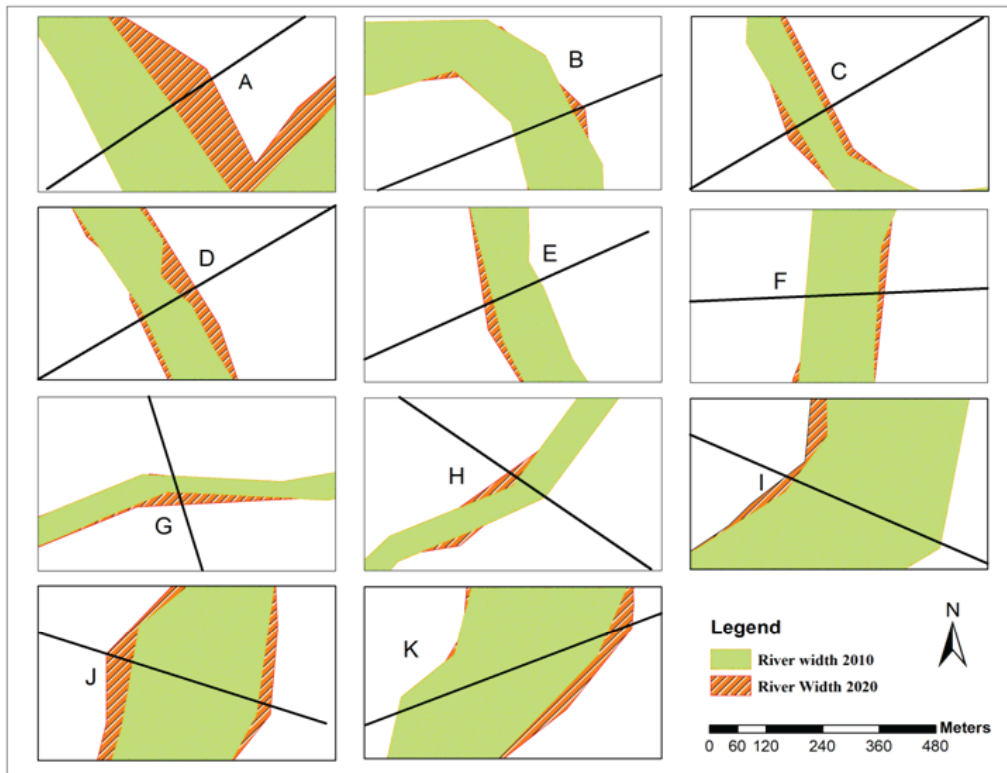


Fig. 6: Cross sections showing erosion and accretion from 2010 to 2020 at three rivers.

Table-02: Change of the channels of the Bhairab, Rupsha, and Majutkhali rivers along both banks from 2010 to 2020 (negative and positive values represent erosion and accretion, respectively)

Section	Left bank (m)	Left bank Erosion (%)	Left bank Accretion (%)	Right bank (m)	Right bank Erosion (%)	Right bank Accretion (%)
A	-10.99	5.35		-100.60	32.02	
B	-23.00	11.19		-24.41	7.77	
C	-28.48	13.85		-24.47	7.79	
D	21.92		29.58	-46.32	14.74	
E	-23.05	11.21		8.48		12.95
F	46.08		62.18	-15.73	5.01	
G	0.10		0.13	-29.32	9.33	
H	-28.28	13.76		37.52		57.28
I	-38.53	18.74		19.50		29.77
J	-53.23	25.9		-28.80	9.17	
K	6.01		8.11	-44.53	14.17	



Riverbank shifting due to erosion has been represented by negative (-) values and accretion by positive (+) values shown in Table-02. The highest and lowest erosion of the Bhairab River was found at the right bank and left bank at cross-section A which were 100.06m (32.02%) and 10.99m (5.35%) respectively. The accretion occurred only at three cross sections at the Bhairab River. The highest accretion was found at cross-section F (46.08m) which is 62.18% of accretion at the left bank and the lowest accretion was 8.48 meter along cross section E which is 12.95% of accretion at the right bank, whereas the left bank of cross-section D showed 21.92m (29.58%) accretion. Fig. 7 represents the clear visualization of bank change along the Bhairab River, whereas the river's right bank exhibits extensive erosion than the left bank. Among six cross-sections, four sections were faced ponderous erosion, including that one which has the highest erosion of all 11 cross-sections.

At Ruphsa River highest and lowest erosion was found at the left bank and right bank of cross-section J, which were 53.23m (25.9%) and 28.8m (9.17%), respectively. The highest accretion was found at cross-section I (19.50m) which is 29.77% of all accretion at the right bank and the lowest accretion was found at the left bank at cross-section K (6.01m) which is 8.11%. Fig. 8 exhibits more visual change of the bank line of Rupsha River where the left bank of the Rupsha River changed more compared to the right bank. Among the three cross-sections, two of them faced significant erosion where the sedimentation was very low along the left bank; in contrast, sedimentation was higher at the right bank of the Rupsha River.

The highest and lowest erosion of Majutkhali River was found at the right bank at cross-section G which is 29.32m (9.33%) and the left bank at cross-section H which is 28.28m (13.76%), respectively. The highest accretion was found at the right bank of cross section H (37.52m) which is 57.28% and the lowest accretion was found at the left bank of cross section G (0.10m) which is 0.13% of all accretion. Fig. 9 shows visual representation of bank line change of Majutkhali River. From the figure, it was evident that the Majutkhali River did not face any extensive erosion; however, the accretion along one cross-section (H) is much higher compare to the Bhairab River.

Overall highest and lowest erosion was found near the junction of Bhairab and Rupsha rivers at South Chandanimahal area which were 100.60m (32.02%) at the right bank and 10.99m (5.35%) at the left bank of Bhairab River. In contrast, the highest accretion was found at Moheshwarpur area (left bank: 62.18%) in Bhairab River and lowest accretion was found at Nandan Pratap Maddhyapara area at Majutkhali River (left bank: 0.13%).

This riverbank erosion caused a significant impact on the people of Dighalia upazila. To understand the impact of riverbank erosion and accretion on the people, a field visit and questionnaire survey was conducted at Dighalia upazila. The questionnaire survey was

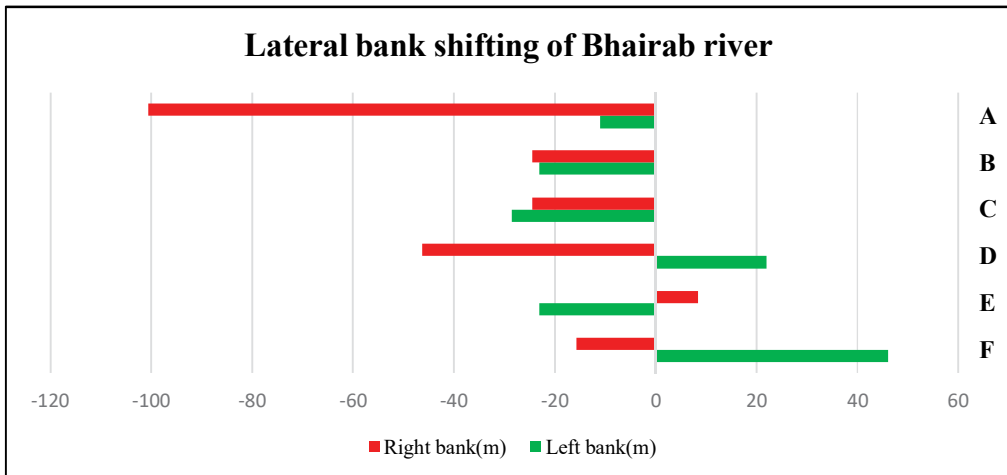


Fig. 7: The erosion and accretion at both banks of Bhairab River from 2010 to 2020

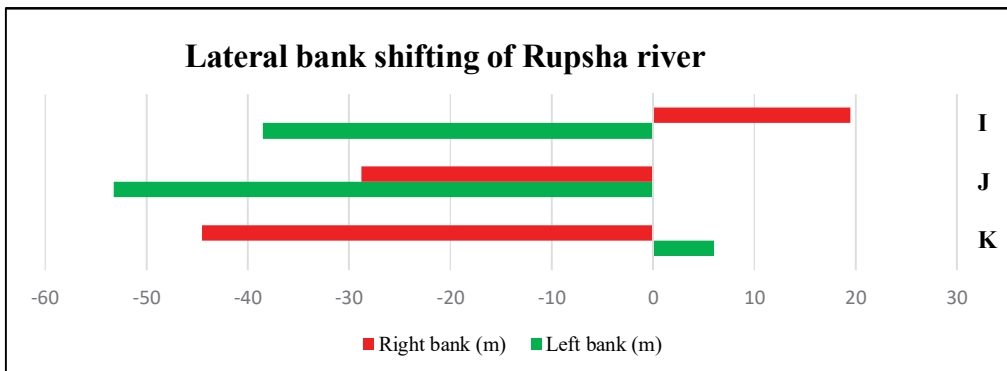


Fig. 8: The erosion and accretion at both banks of the Rupsha River from 2010 to 2020

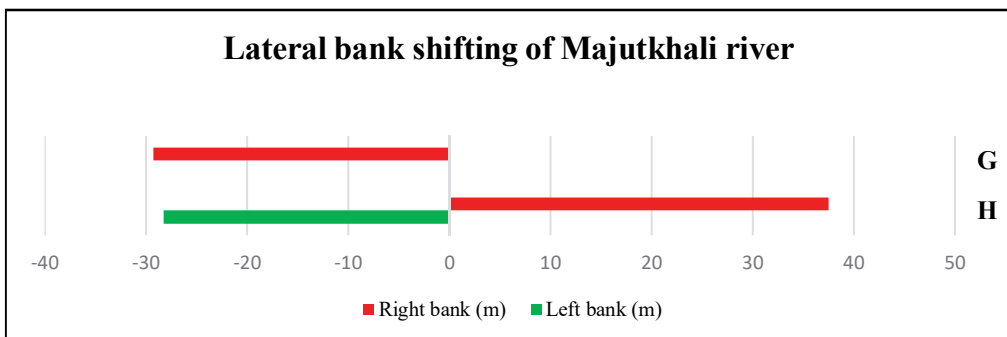


Fig. 9: The erosion and accretion at both banks of Majutkhali River from 2010 to 2020

guided by physically visiting the affected area. The survey points were selected based on image analysis and consulting with the Senhati union parishad chairman. The survey was conducted among 50 families who have been living there for more than ten years. For selecting samples from the population of interest, random sampling is one of the best methods. This method ensures equal chances for the entire target group to be selected (McLeod, 2019). Another advantage of this method is that it requires minimum knowledge of the target population and is very easy to analyze (Acharya et al., 2013). Considering population density, literacy rate, erosion-accretion pattern and other factors, the random sampling method was selected. The targeted and questioned peoples were in between 40 to 60 years of age. According to the survey, about 24 families out of every 100 families (lived near 200 m from the river bank line) faced a major loss due to riverbank erosion in this area. These include loss of patrimony, agricultural land, cattle and even human lives.

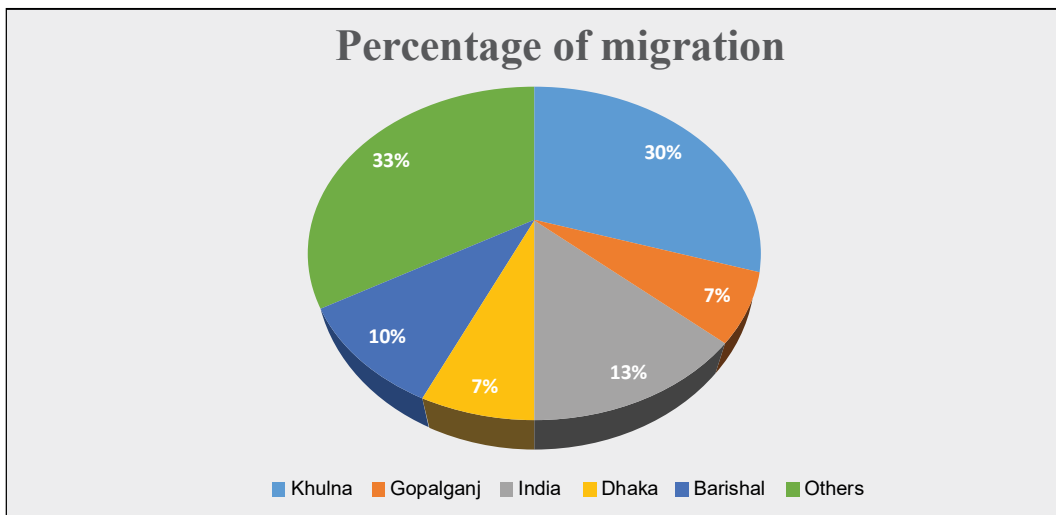


Fig. 10: Pie diagram showing the percentage of population migration from Dighalia upazila to other parts of the country due to riverbank erosion (according to the survey)

The riverbank erosion forced many peoples to migrate at different places. According to people's opinion, the exact number could not be identified. Around 50-60 families migrated to different parts of the country in the last ten years. The survey result shows most of the affected people (about 30% of total migration) migrated to Khulna sadar as it is near (about 12 km) Dighalia upazila and offers more job opportunities. A large number of Hindu communities migrated to our neighboring country India and few people also migrated to Gopalganj, Kushtia, Narail and other districts in Bangladesh. Fig. 10 shows the percentage of people where they migrated.



As a riverine country, riverbank erosion and sedimentation are a natural phenomenon in Bangladesh. However, anthropogenic causes can trigger this phenomenon, which could be more hazardous to people. Riverbank erosion has been becoming a severe issue in this area for many reasons. Climate change and upstream overflow could be one of the leading natural reasons behind erosion in this area; however, artificial causes such as waves created by the ships and cargos increasing riverbank erosion rapidly. Most people think that artificial waves are the leading cause of riverbank erosion in this area. Bhairab, Rupsha and Majutkhali rivers are being used as a pathway for ships to the Mongla port. Our field visit suggests that as the river channels are narrow and the ships come and go regularly, causing water waves, it actually could increase riverbank erosion.

Conclusion

In this study, riverbank erosion and accretion of Bhairab, Rupsha and Majutkhali rivers were measured at eleven cross-sections using integrated RS and GIS technique and result validation was conducted by field visit with a questionnaire survey. The maximum erosion (100.60m) was found near the confluence of Bhairab and Rupsha rivers situated near at South Chandanimahal area which is 32.02% of all erosion at the right bank. The lowest erosion (10.99m) for the Bhairab River was found at the left bank of the same place that is 5.35% of all erosion. Apart from this, the left bank of the Rupsha River faced significant erosion (25.9%) in Madhupur Bazar area. On the other hand, the highest accretion was found on the left bank of the Bhairab River (46.08m) at the Moheshwarpur area which is 62.18% of all accretion, and the lowest accretion (0.1m) was found on the left bank of Majutkhali River which is 0.13% of all accretion at Nandan Pratap Maddhyapara area. According to our questionnaire survey, the erosion caused around 50-60 family migration from Dighalia to other places in the last few years. Many people lost their houses, agricultural land, cattle and even their life. Though both natural and anthropogenic actions were responsible for bank erosion but human activities, i.e., water waves created by ships and cargos, exacerbating the current condition. Overall morpho- dynamic study in this region suggests that the bank accretion was significantly less compared to total erosion. Government and policymakers should take immediate and effective measures to prevent or lessen the current erosion rate at the river banks of Bhairab, Rupsha and Majutkhali rivers in Dighalia upazila, Khulna in order to reduce peoples suffering as well as sustainable development.

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EFFECTS OF CLIMATIC EXTREME INDICATOR ON POTATO YIELD OF BANGLADESH

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Abstract

Extreme climate events have a great impact on the agriculture-based economy like Bangladesh. This study is conducted mainly to gain insight on the overall condition of extreme air temperature of suitable potato growing area in Bangladesh and the effects of some climate extreme indices on potato yield. The result of trend analysis of extreme climate indices indicated that the monthly maximum value daily minimum temperature has continued to increase. While the monthly minimum value of both minimum and maximum temperature has continued to decrease. It is not possible to identify any specific trend for both monthly maximum value of daily maximum temperature. And for precipitation variable, monthly maximum 1-day precipitation also does not follow any particular pattern. Investigating the effects of these extreme indices, it is found that the monthly maximum of daily maximum temperature and monthly maximum of daily minimum temperature has a significant positive impact on potato yield. And other three extreme indicators have negative effects. These positive factors are much more significant on potato yield than those negative factors. Positive factors follows positive trend and negative factors follows negative trend or does not follow any trend at all.

Keywords: Extreme climate indicator, Potato yield, RClimDex.

Introduction

For the past several years in Bangladesh which has six seasons, it felt like the seasons squeezed into two seasons summer and winter. Again, in winter season it does not feel that much of cold either. Not only in Bangladesh but also it observed that since 1950, the number of warm days and nights has increased and the number of cold days and nights has decreased (IPCC 2013). The combined land and ocean temperature have increased at an average rate of 0.07°C (0.13°F) per decade since 1880. However, the average rate of increase since 1981 (0.18°C/0.32°F) is more than twice as great (NOAA 2019). Mearns et al. (1984) and Hansen et al. (1988) concluded that relatively small changes in the mean temperature could produce substantial changes in the frequency of temperature extremes. Any change in the frequency or severity of extreme climate events could have profound impacts on nature and society. Crop yields decreases due to increasing temperature especially night time temperature associated with global warming (Toros et al., 2019).

Bangladesh ranked sixth on Global Climate Risk Index 2017 of the countries most affected by climate change since 1995 (Kreft S. et al 2017). In the widely used ND-GAIN index

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(2017), Bangladesh ranks 160 out of 181 countries for climate vulnerability. Many study had found warming trends throughout the world (e.g., Jones and Moberg 2003; Solomon et al. 2007; Kerr 2009; Abbasnia et al. 2016; Abbasnia and Toros 2018a, b). There had been a strong warming in the warm period compared to the temperatures of the annual and cold period (Toros, 2012). Several studies have been conducted on this regard in Bangladesh. Warm condition in winter with the increase in minimum temperature and more hot summer have been experienced in recent years (Nishat and Mukherjee, 2013). Mia (2003) found an increasing trend of monthly average temperature both in winter and summer seasons. Islam et al. (2004) found increasing trend for monthly maximum temperature but monthly minimum temperature shows both increasing and decreasing trend.

Potato is the fourth major food crop of the world next to rice, wheat and maize and 3rd important crop in Bangladesh next to rice and wheat (Kundu and Kabir, 2012). As Bangladesh is now self-sufficient on potato production, it is considered to be a potential crop to face the challenge of 21st century in Bangladesh and achieved a remarkable success in potato production to take it to 7th rank in the world (FAOSTAT, 2014). A short period of abnormally high or low temperatures can have a significant harmful effect on crop growth and final yield (Mearns et al., 1984). So it is necessary to investigate temperature and precipitation related disasters and assess global warming impacts on crop yields. Therefore, the objective of this study is to find significant trend on temperature extremes and their effect on potato yield in Bangladesh. The information on climatic characteristics of these events and their effects is crucial for decision making with regards to water resources, human health and agriculture.

Materials and Methods

Typically Bangladesh had three types of seasons. From March to June it is hot, humid summer with average maximum temperatures of 37 °C and relatively little rainfall and often drought. From June to September it is cooler monsoon seasons with heavy rainfall frequently resulting in flooding for up to two-thirds of the country. And from October to February it is dry, cooler winters with average maximum temperatures of 28 °C (Karmalker et al, 2012). The highest temperatures are in the southwest, the lowest in the northeast of the country (World Bank, 2011). The average temperature ranges between 13 and 26 degrees °C during the cool season and 25 to 31 °C during the hot season.

Extreme temperature indices were calculated using RCLimDex software which had been developed under R 1.84, can check data quality and computes 27 core indices recommended by the CCI/CLIVAR Expert Team for Climate Change Detection Monitoring and Indices (ETCCDMI). This software uses long-term daily precipitation, maximum and minimum temperature data as input. So weather data of 14 stations which are situated in major potato

growing area or near (namely, Bhola, Bogra, Chandpur, Dhaka, Dinajpur, Faridpur, Ishurdi, Jashore, Madaripur, Mymensingh, Patuakhali, Rajshahi, Rangpur, and Satkhira) were collected from Bangladesh Meteorological Department (BMD) from 1981 to 2018.

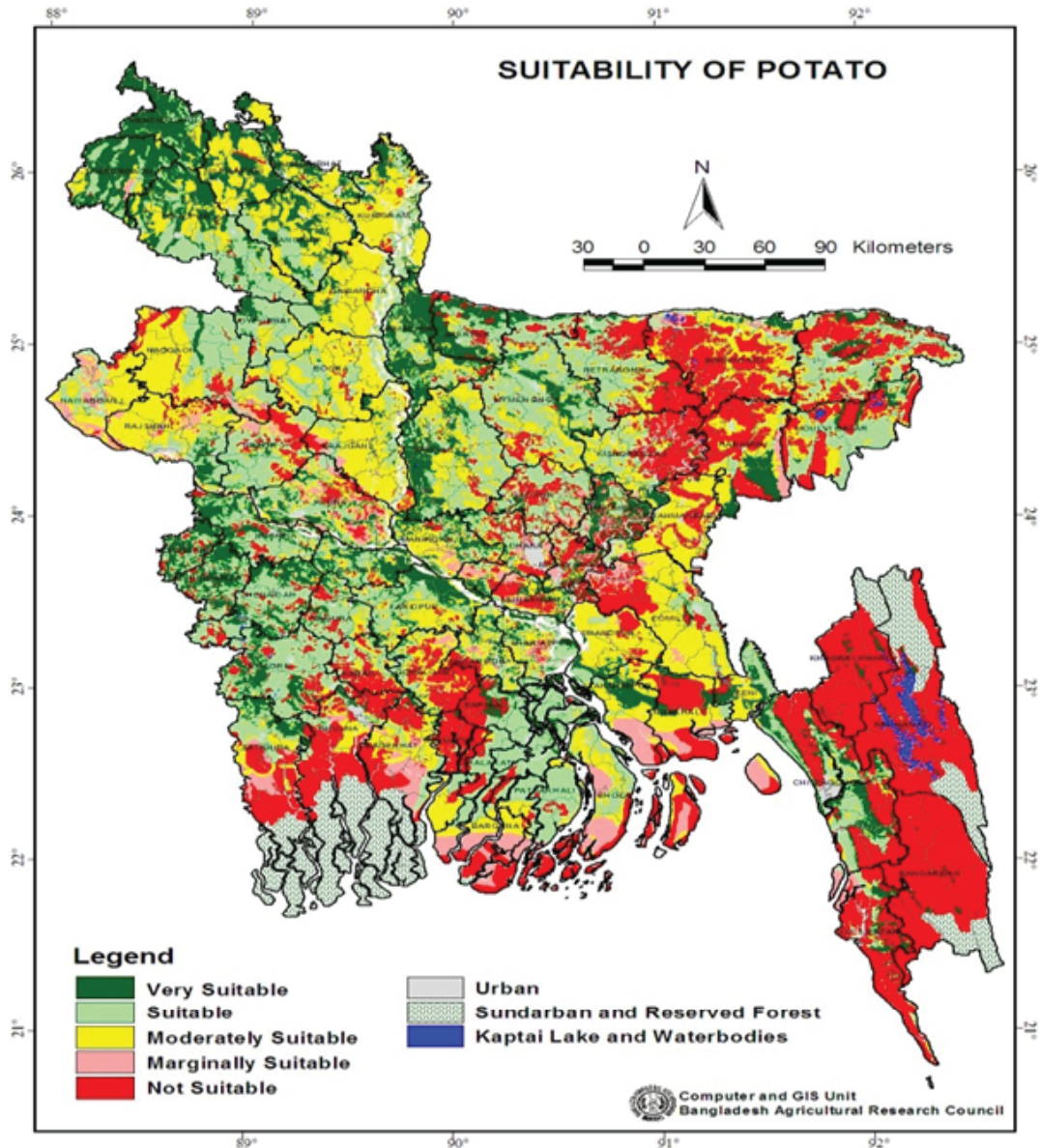


Fig. 1: Suitable land for potato production (Source: Bangladesh Agricultural Research Council)



In this study, four temperature and one precipitation extreme indices (Table 1) had been selected to understand the trending behavior in temperature extreme events in Bangladesh and further investigated their effects on potato yield by simple and multiple linear regression. Kendall's tau-based slope estimator has used to compute the trends as well as their significance.

Table 1. Definition of the selected temperature extreme indices

Index	Indicator name	Definition	Unit
TXx	Max Tmax	Monthly maximum value of daily maximum temp	°C
TXn	Min Tmax	Monthly minimum value of daily maximum temp	°C
TNx	Max Tmin	Monthly maximum value of daily minimum temp	°C
TNn	Min Tmin	Monthly minimum value of daily minimum temp	°C
RX1day	Max 1-day precipitation amount	Monthly maximum 1-day precipitation	Mm

**TXx**

Let be the daily maximum temperatures in month, period. The maximum daily maximum temperature each month is then:

TXn

Let be the daily maximum temperatures in month, period. The minimum daily maximum temperature each month is then:

TNx

Let be the daily minimum temperatures in month, period. The maximum daily minimum temperature each month is then:

TNn

Let be the daily minimum temperatures in month, period. The minimum daily minimum temperature each month is then:

RX1day

Let be the daily precipitation amount on day in period. Then maximum 1-day values for period are:

Results and Discussions

From the output of trend analysis of weather variable of 14 stations from 1981 to 2018, it is found that most of the slope coefficients are negative for TXn and TNn. For TNx most of them are positive. And it is almost evenly distributed for TXx and RX1day (Table-02). The temperature indices were found significant for some of the stations but for precipitation index, none of the stations were found significant. Highest increasing rate of the monthly maximum value of daily maximum temperature was found at Chandpur (0.052) followed by Patuakhali (0.047) and both of them are highly significant. Highest decreasing rate was found at Ishurdi (-0.034) followed by Rangpur (-0.024). Highest increasing rate of the monthly maximum value of daily minimum temperature was found at Mymensingh (0.023) which is significant. Highest decreasing rate of the significant monthly minimum value of both daily maximum and minimum temperature was found at Ishurdi (-0.138) and Jashore (-0.058) respectively. For precipitation variable, highest increasing rate occur at Patuakhali (1.119) and highest decreasing rate occur at Bogra (-1.055). This indicates that the monthly maximum value daily minimum temperature has continued to increase. While the monthly minimum value of both minimum and maximum temperature has continued to decrease. It is not possible to identify any specific trend for both monthly maximum value of daily maximum temperature and monthly maximum 1-day precipitation.

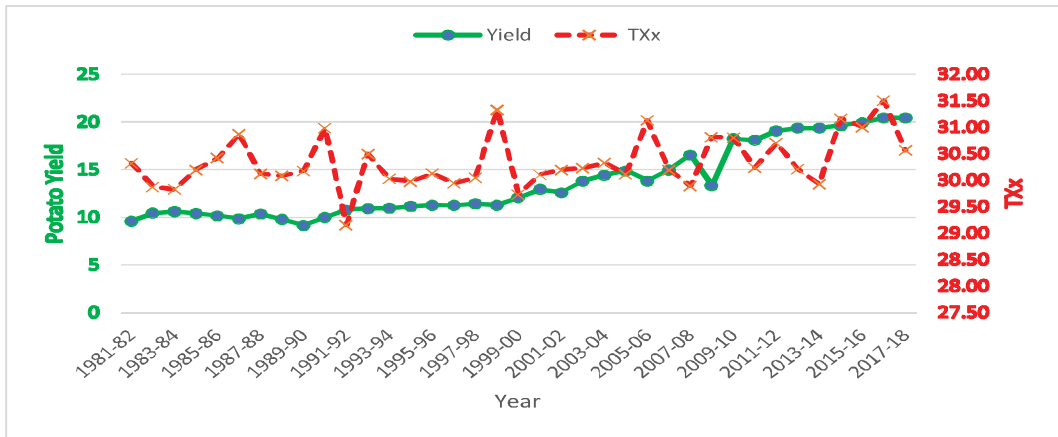


Table 2. Slope coefficient of trend analysis on study location based on RCLimDex

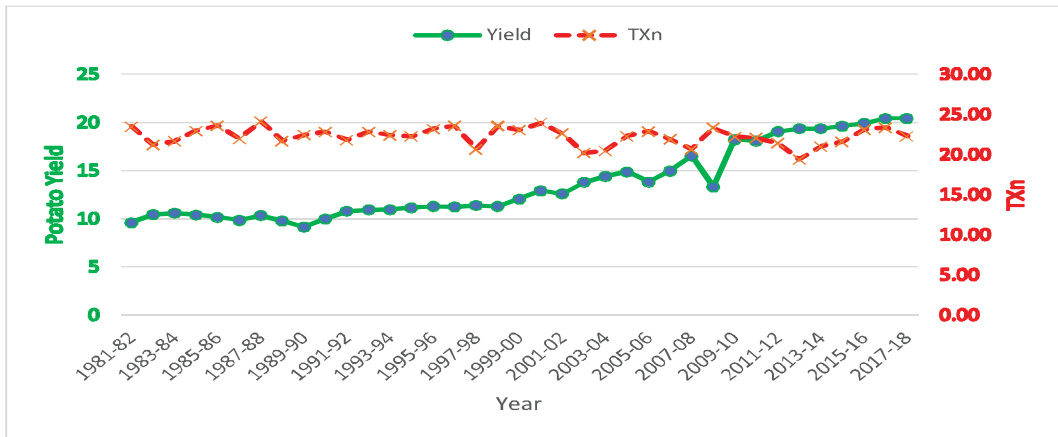
Station	TXx (°C)	TXn (°C)	TNx (°C)	TNn (°C)	RX1day (mm)
Bhola	0.013	-0.033	0.014 ⁺	-0.039**	0.074
Bogra	-0.023	-0.131***	0.011	-0.02	-1.055
Chandpur	0.052***	0.001	0.019 ⁺	-0.005	0.305
Dhaka	-0.019	-0.063 ⁺	0.017*	0.04 ⁺	0.033
Dinajpur	-0.014	-0.128***	0.017*	-0.035 ⁺	-0.046
Faridpur	0.002	-0.049	0.014	-0.04*	-0.226
Ishurdi	-0.034	-0.138***	-0.018	-0.022	0.409
Jashore	0.015	-0.035	0.012	-0.058**	-0.827
Madaripur	-0.022	-0.068 ⁺	0.01	-0.033*	-0.6
Mymensingh	0.011	-0.101***	0.023*	-0.026*	-0.401
Patuakhali	0.047***	-0.057 ⁺	0.004	-0.053***	1.119
Rajshahi	-0.023	-0.095**	0.016 ⁺	-0.031 ⁺	0.065
Rangpur	-0.024	-0.114***	0.012	-0.01	-0.614
Satkhira	-0.007	-0.07 ⁺	-0.029	-0.03	-0.372

0.1% '***', 1% '**', 5% '*', 10% '+'

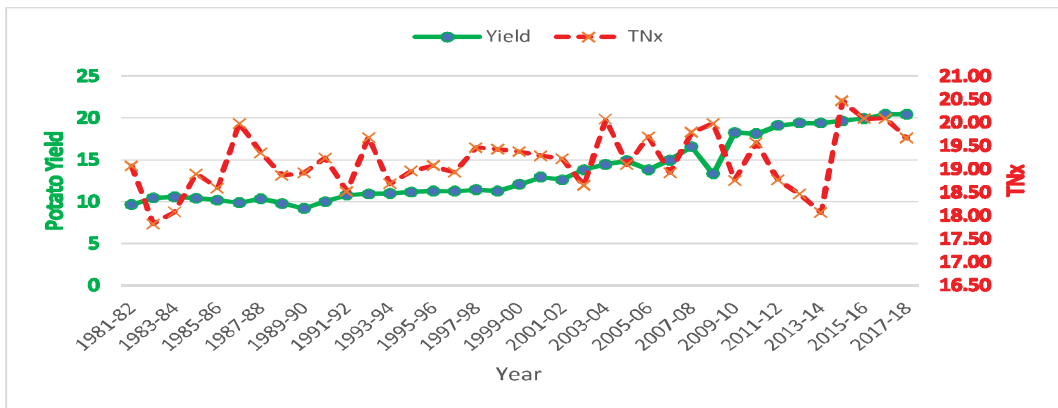
From Fig. 2, it can be said that the yield of potato follows increasing trend. Note that the aim of this study is not to predict the future yield of potato based on these extreme weather indicators rather to investigate the effect of these extreme weather indicators on potato yield.



(a)



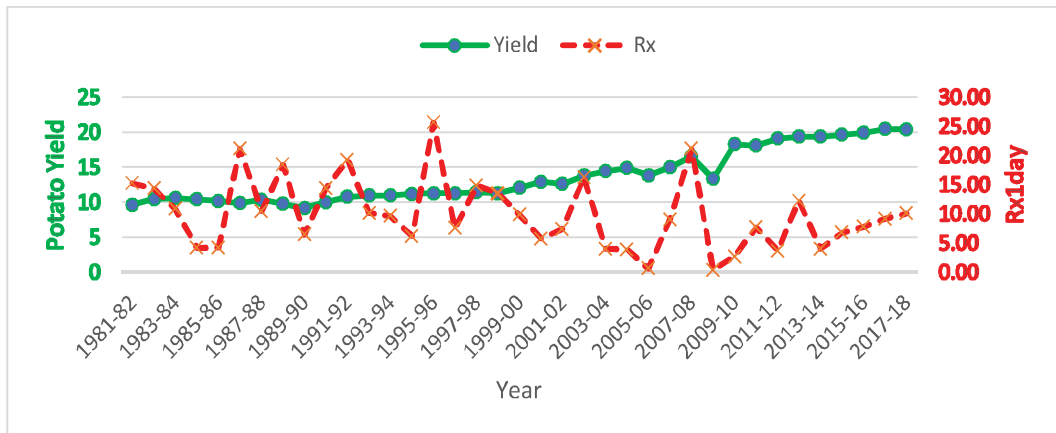
(b)



(c)



(d)



(e)

Fig. 2: Effects of (a) TXx (b) TXn (c) TNx (d) TNn and (e) RX1day on Potato yield

Mohammad Badrul Masud and Jannatul Ferdous (2011) used multiple linear regression to investigate the effects of extreme weather indicators on rice and wheat production. This study adopted the idea and used simple and multiple linear regression model to investigate the effects of extreme weather indicators on potato yield. The simple linear regression output is shown in Table 3.



Table 3. Simple linear regression output of weather extremes on potato yield

Weather variable	Intercept	Slope (se)	R-squared
TXx	-69.683 ⁺	2.744(1.179) *	0.134
TXn	37.4294**	-1.0689(0.5356) ⁺	0.1022
TNx	-18.7069	1.6849(0.9808) ⁺	0.07776
TNn	16.0719	-0.2282 (1.0116)	0.001452
RX1day	15.50266	-0.19074 (0.09889)	0.09608

5% ‘*’, 10% ‘+’, se=standard error

From regression output, monthly maximum value of daily maximum temperature and monthly maximum value of daily minimum temperature has a positive impact on potato yield which are significant (at 5% and 10% level respectively). And other three extreme indicators have negative impact. These positive factors are much more significant on potato yield than those negative factors. Factors having positive impacts on potato yield followed positive trend and the factors with negative impacts followed negative trend or does not follow any trend at all. Although the yield of potato is increasing due to high yielding variety and soil condition, climate extreme also has some positive impact on the increasing trend of potato yield.

The small R-squared value indicates that potato yield does not depend on these extremes separately. So let’s investigate the combine effects of these extreme indicators on potato yield by multiple linear regression analysis.

Table 4. Multiple linear regression output of weather extremes on potato yield

Weather variable	Coefficients (se)
Intercept	-39.70995 (33.2258)
TXx	2.32129(0.13538) ⁺
TXn	-1.63788 (0.52546) **
TNx	1.30482 (1.07984)
TNn	-0.34230 (1.03722)
RX1day	-0.19477 (0.08834) *

*0.1% ‘***’, 1% ‘**’, 5% ‘*’, 10% ‘+’, se=standard error



Multiple regression output indicates that monthly maximum value of daily maximum temperature and monthly maximum value of daily minimum temperature has a positive impact on potato yield and other three extreme indicators have negative impact. Monthly minimum value of daily maximum temp and monthly maximum 1-day precipitation has a significant effect on potato yield.

We further investigate whether the model suffers multicollinearity problem or not. The variance inflation factor (VIF) identifies correlation between independent variables and the strength of that correlation. VIFs start at 1 and have no upper limit. A value of 1 indicates that there is no correlation between this independent variable and any others. VIFs between 1 and 5 suggest that there is a moderate correlation, but it is not severe enough to warrant corrective measures. VIFs greater than 5 represent critical levels of multicollinearity where the coefficients are poorly estimated, and the p-values are questionable.

Table 5. VIF on individual independent variable

TXx	TXn	TNx	TNn	Rx
1.727385	1.343927	1.738353	1.632402	1.121685

Since the VIF on each independent variable lies between 1 and 5, which means there is a moderate correlation, but it is not severe enough to warrant corrective measures. Although the R-squared value increases a lot (0.4304), it still is not of a satisfactory level. This implies the known knowledge about the yield of any crop i.e.; yield of a crop depends not only on weather variable but also on soil fertility, irrigation management and other variables. So the continuation of this study will incorporate those variables in the future.

Conclusion

Extreme climate events have a great impact on the agriculture-based economy like Bangladesh. This study is conducted mainly to gain insight on the overall condition of extreme air temperature of suitable potato growing area in Bangladesh and the effects of some climate extreme indices on potato yield. For extreme air temperature of 14 suitable potato growing areas in Bangladesh, the monthly maximum value daily minimum temperature has continued to increase. While the monthly minimum value of both minimum and maximum temperature has continued to decrease. It is not possible to identify any specific trend for both monthly maximum value of daily maximum temperature. And for precipitation variable, monthly maximum 1-day precipitation also does not follow any particular pattern. Investigating the effects of these extreme indices, it



is found that the monthly maximum of daily maximum temperature and monthly maximum of daily minimum temperature has a significant positive impact on potato yield. And other three extreme indicators have negative effects. These positive factors are much more significant on potato yield than those negative factors. Positive factors follows positive trend and negative factors follows negative trend or does not follow any trend at all. Based on this study, it can be said that the yield of potato is increasing not only due to high yielding variety and soil condition but also climate extreme has some positive impact on the increasing trend of potato yield.

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SYNTHESIS OF CHIRAL POLYMERS BEARING QUININIUM MOIETY IN THE MAIN-CHAIN AND THEIR APPLICATIONS IN ASYMMETRIC EPOXIDATION OF *TRANS*-CHALCONE

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Abstract

A novel type of main-chain chiral ionic polymer has been synthesized from quinine dimer and disulfonic acid-disodium salt, using ion-exchange polymerization. The yields of the polymers were in the range 80~90%. The molecular weight (M_n) of the polymers were determined by Size-exclusion chromatography (SEC) and the values ranges from 5100 to 6600. These novel main-chain chiral polymers were employed as chiral polymeric organocatalysts in asymmetric epoxidation of *trans*-chalcone. Most of the polymeric organocatalysts showed good catalytic activity (up to 100% conversion and 84% ee) in asymmetric epoxidation of *trans*-chalcone.

Keywords: Chiral ionic polymers, Polymeric organocatalysts, Quinine dimer, Asymmetric epoxidation, *Trans*-chalcone.

Introduction

Organocatalyzed asymmetric epoxidation of *trans*-chalcone is one the major field of study in asymmetric synthesis. Cinchona alkaloid-derived quaternary ammonium salts, also called phase transfer catalyst (PTC) are widely used organocatalyst in asymmetric epoxidation of chalcone and its derivatives. The pioneering work was done by (Helder et al. 1976) using cinchona derived quaternary ammonium salts, under PTC condition to carry out asymmetric epoxidation of electron deficient olefins. Asymmetric epoxidation of α , β -unsaturated ketones using cinchona alkaloid-derived quaternary ammonium phase-transfer catalysts bearing an N-anthracenylmethyl function (Lygo et al. 1998; 1999; 2001) also carried out and high enantioselectivity and high conversion was achieved. Using charge-accelerated catalysis by a rigid quaternary ammonium salt (Corey et al. 1999), high enantioselectivity was obtained in asymmetric epoxidation of α , β -enones. There are some non-cinchona derived catalysts such as polyamino acids (Juliá et al. 1980), spiro ammonium salts (Oi et al. 2004), lanthanoid-binaphthol complexes (Shibasaki et al. 1997) and chiral crown ethers derived from D-glucose, D-galactose, and D-mannitol (Bako et al. 2004) have also been used in this kind of asymmetric epoxidation. Chiral octahedral complexes of Co (III) under phase transfer conditions was used for asymmetric epoxidation of chalcones (Larionov et al. 2015) and good yield and enantioselectivity was obtained. Hybrid amide-based Cinchona alkaloids was employed in asymmetric epoxidation with low catalyst loading and short reaction time (Majdecki et al. 2020). Recently, we have reported

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asymmetric epoxidation of *trans*-chalcone using main-chain chiral ionic polymer bearing cinchonidium moiety (Parvez et al. 2019).

Several researches have been carried out using low molecular weight cinchonidine and quinine derived quaternary ammonium salts but only few researches have been carried out utilizing main-chain chiral polymeric organocatalyst in the asymmetric epoxidation of chalcones. Quinine derived dimeric quaternary ammonium salts with the addition of surfactants (Jew et al. 2005) was quite effective in asymmetric epoxidation of chalcone with shorter reaction time. Polymer-supported cinchona derived phase transfer catalyst was reported by (Lv et al. 2006) in asymmetric epoxidation of chalcones. Traditional polymer-supported chiral catalysts contain flexible and sterically irregular polymer backbone, but main-chain chiral polymeric catalysts have rigid and sterically regular polymer backbone. The enantioselectivity of a monomeric catalyst can be maintained in a polymer catalyst by the use of a rigid and sterically regular polymer backbone. So, the main-chain chiral polymer bearing quininium unit should also show catalytic activity in asymmetric epoxidation of *trans*-chalcone. Moreover, the solubility of the main-chain chiral polymeric organocatalysts is lower than monomeric and dimeric organocatalysts. Thus, they can be easily separated from the reaction mixture and easing the complexity of column separation.

In this work, we have synthesized some main-chain chiral ionic polymers from quinine dimer (Parvez et al. 2012) and applied these polymers as polymeric organocatalyst in asymmetric epoxidation of *trans*-chalcone.

Experimental

General Methods

All reagents were purchased from Sigma-Aldrich, Wako Pure Chemical Industries, Ltd., or Tokyo Chemical Industry Co., Ltd. at the highest available purity and used as is unless noted otherwise. Disulfonic acid-disodium salt **4b** and **4c** prepared by the method reported by Parvez et al. 2012. DMF was distilled from calcium hydride before use. Reactions were monitored by thin-layer chromatography (TLC) using Merck precoated silica-gel plates (Merck 5554, 60F254). Column chromatography was performed with a silica-gel column (Wakogel C-200, 100–200 mesh). ¹H (300 MHz or 400 MHz) and ¹³C NMR (75 MHz or 100 MHz) spectra were measured on Mercury 300 or Jeol ECS 400 spectrometer. HPLC analyses were performed with a JASCO HPLC system comprising a three-line degasser DG-980-50, an HPLC pump PV-980, and a CO-965 column oven equipped with a chiral column (CHIRALPAC AD, Daicel). A UV detector (JASCO UV-975 for JASCO HPLC system) was used for peak detection. Optical rotations were recorded with a JASCO DIP-149 digital polarimeter, using a 10 cm thermostated microcell. Size exclusion chromatography (SEC) was obtained with Tosoh instrument with HLC 8020 UV (254 nm) or

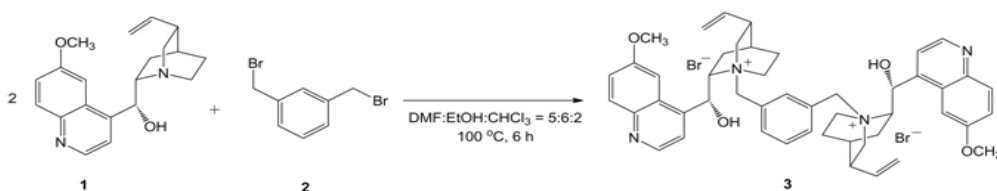
refractive index detection. DMF was used as a carrier solvent at a flow rate of 1.0 mL/min at 40 °C. Two polystyrene gel columns of bead size 10 m were used. A calibration curve was made to determine number-average molecular weight (M_n) and molecular weight distribution (M_w/M_n) values with polystyrene standards.

Synthesis of Dimer and Main-Chain Ionic Polymer

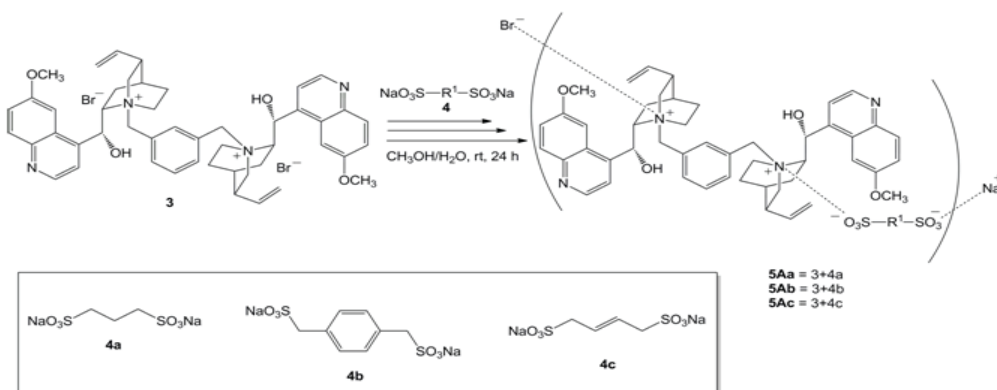
First of all, quinium dimer **3** was synthesized by the reaction between quinine **1** and dibromide **2** (Scheme 1) according to the reported procedure (Jew et al. 2005). Main-chain chiral polymeric organocatalysts **5A** (**a-c**) have been synthesized using ion-exchange polymerization (Scheme 2) (Itsuno et al., 2010; Parvez et al., 2012).

General Procedure for the Preparation of Main-Chain Chiral Ionic Polymer 5A(a-c)

A solution of quinine derived dimeric quaternary ammonium salt **3** (1 mmol) in 10 mL CH_3OH and a solution of disulfonic acid-disodium salt **4** (1 mmol) in 8 mL water were mixed together and stirred vigorously at room temperature for 24 hours. Then it was filtered and washed with water and hexane to obtain the resulting ionic polymer **5A(a-c)**. The yields of the products were in the range 80~90%.



Scheme 1 Synthesis of quinine dimer **3**



Scheme 2 Synthesis of main-chain chiral polymer from quinine dimer



Characterization of 5Aa

^{13}C NMR (d_6 -DMSO, 100 MHz) δ 157.48, 147.46, 143.94, 143.70, 138.73, 138.12, 135.18, 131.46, 129.65, 128.63, 125.44, 121.55, 120.37, 116.52, 101.99, 68.48, 63.65, 62.85, 59.07, 55.69, 50.70, 50.56, 36.98, 26.05, 24.15, 21.35, 20.47. IR (KBr) ν 3225, 2945, 1619, 1590, 1508, 1456, 1360, 1257, 1172, 1061, 913, 858. $[\alpha]_D^{25} = -1.90$ (c 1.0, DMSO). M_n (SEC) = 5100. $M_w/M_n = 1.09$.

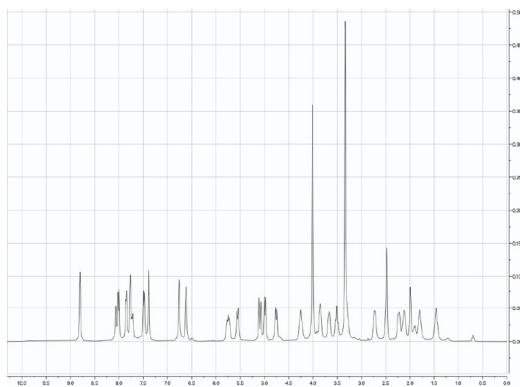


Fig. 1 ^1H NMR of 5Aa in d_6 -DMSO

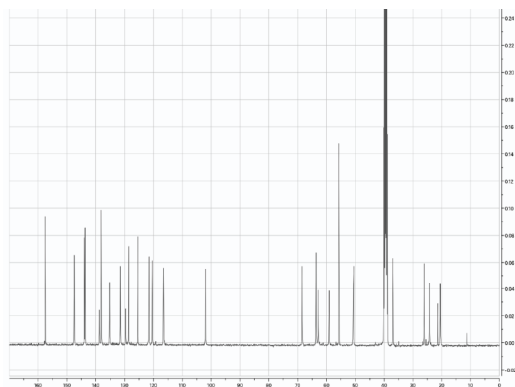


Fig. 2 ^{13}C NMR of 5Aa in d_6 -DMSO

Characterization of 5Ab

^{13}C NMR (d_6 -DMSO, 100 MHz) δ 158.01, 147.99, 144.49, 144.26, 139.29, 138.67, 135.68, 133.39, 131.99, 130.10, 129.94, 129.09, 126.02, 122.04, 120.88, 117.00, 102.57, 68.94, 64.23, 63.31, 59.60, 57.69, 56.23, 51.16, 37.45, 26.61, 24.66, 21.03. IR (KBr) ν 3221, 2945, 1619, 1590, 1509, 1457, 1361, 1259, 1174, 1061, 913, 857. $[\alpha]_D^{25} = -1.92$ (c 1.0, DMSO). M_n (SEC) = 5700. $M_w/M_n = 1.11$.

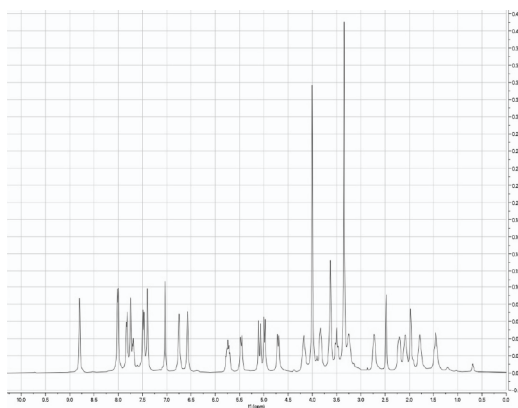


Fig. 3 ^1H NMR of 5Ab in d_6 -DMSO

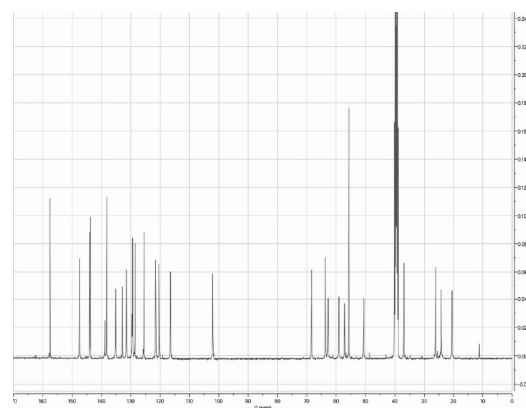


Fig. 4 ^{13}C NMR of 5Ab in d_6 -DMSO



Characterization of 5Ac

^{13}C NMR (d_6 -DMSO, 100 MHz) δ 157.49, 147.37, 143.92, 143.59, 138.70, 138.12, 135.15, 131.37, 129.62, 128.59, 125.43, 121.60, 120.36, 116.48, 102.01, 68.40, 63.67, 62.82, 59.09, 55.74, 50.68, 36.96, 26.02, 24.12, 20.5. IR (KBr) ν 3219.58, 2941.88, 1619.91, 1590.02, 1508.06, 1456.96, 1361.50, 1259.29, 1173.47, 1059.69, 922.22, 858.17. $[\alpha]_D^{25} = -1.73$ (c 1.0, DMSO). M_n (SEC) = 6600. $M_w/M_n = 1.17$.

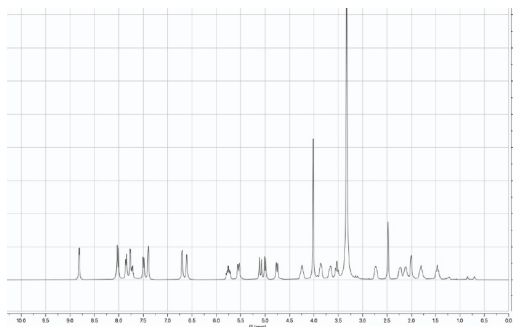


Fig. 5 ^1H NMR of 5Ac in d_6 -DMSO

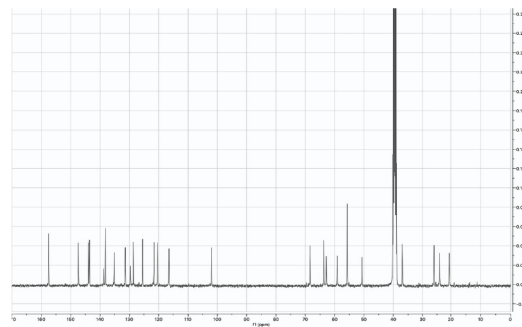


Fig. 6 ^{13}C NMR of 5Ac in d_6 -DMSO

General Procedure for Asymmetric Epoxidation of *Trans*-Chalcone

Aqueous hydrogen peroxide (30%, 0.27 mL; 2.4 mmol) and 50% aqueous KOH (0.027 mL, 0.24 mmol) were added to a mixture of chalcone **6** (50 mg, 0.24 mmol), catalyst **5Aa** (5 mol%) and Triton-X 100 (5 mol%) in Bu_2O (0.8 mL), and the reaction mixture was stirred vigorously at room temperature until the starting material had been consumed. The resulting suspension was diluted with ether (10 mL), washed with water (2×5 mL), dried over MgSO_4 , filtered, and concentrated in vacuo to get the desired product **7** as a white solid. The enantioselectivity was determined by chiral HPLC analysis (DAICEL CHIRALPAC AD), hexane/ethanol=90:10, flow rate=1.0 mL min^{-1} , 23 $^\circ\text{C}$, λ =254 nm; retention times: 16.6 min (minor), 24.0 min (major). The absolute configuration was determined by comparison of the HPLC retention time with reported data (Lygo et al. 1998).

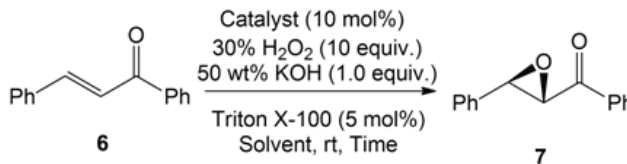
Results and Discussion

Application of Main-Chain Chiral Polymers

We have applied novel type of main-chain chiral ionic polymer **5Aa**, **5Ab** and **5Ac** bearing quininium moiety as polymeric organocatalysts in asymmetric epoxidation of *trans*-chalcone (Scheme 3) and the results are summarized in Table 1. Polymeric organocatalyst **5Aa** and **5Ab** both showed 100% conversion and 63% ee and 36% ee respectively (entry 1 and 2). Changing the solvent from $^i\text{Pr}_2\text{O}$ to Bu_2O , the reaction completed within 3 hours and enantioselectivity increased to 84% in case of **5Aa** (entry 3). **5Ab** and **5Ac** also showed good catalytic activity when Bu_2O was used as solvent (entry 4 and 5). When the reaction was carried out at 0 $^\circ\text{C}$, the reaction



was not completed even after 16 hours and enantioselectivity also decreased (entry 6 and 7).



Reducing the amount of catalyst from 5 mol% to 2.5 mol%, enantioselectivity drastically decreased to 6% ee and 5% ee in case of **5Aa** and **5Ab** respectively (entry 8 and 9). When the reaction was carried out in CPME, only 24% conversion and 16% ee was obtained using catalyst **5Aa** (entry 10). In 1,4 dioxane racemic product was obtained, although the conversion was 100% (entry 11). When the amount of 50 wt% KOH increased to 3.0 equiv. from 1.0 equiv. 71% ee was obtained (entry 12). Increasing the amount of oxidant (30% H₂O₂) to 30.0 equiv. from 10.0 equiv. racemic product was obtained (entry 14). Changing the surfactant to “Span 20” (1 mol%) from Triton X-100 (5 mol%), 18% ee and 14% ee was obtained in case of **5Aa** and **5Ab** respectively (15 and 16).

Table 1. Asymmetric epoxidation of *trans*-chalcone using polymeric organocatalysts **5Aa**, **5Ab** and **5Ac**

Entry	Catalyst	Solvent	Time (h)	Conv. (%) ^a	Ee (%) ^b
1	5Aa	^t Pr ₂ O	15	100	63
2	5Ab	^t Pr ₂ O	15	100	36
3	5Aa	Bu ₂ O	3	100	84
4	5Ab	Bu ₂ O	6	100	52
5	5Ac	Bu ₂ O	16	100	69
6 ^c	5Aa	Bu ₂ O	16	42	71
7 ^c	5Ab	Bu ₂ O	16	53	53
8 ^d	5Aa	Bu ₂ O	16	100	6
9 ^d	5Ab	Bu ₂ O	16	100	5
10	5Aa	CPME	16	24	16
11	5Aa	1, 4dioxane	3	100	Racemic
12 ^e	5Aa	Bu ₂ O	5	100	71
14 ^f	5Aa	Bu ₂ O	12	100	Racemic
15 ^g	5Aa	^t Pr ₂ O	8	99	18
16 ^g	5Ab	^t Pr ₂ O	8	100	14

^aDetermined by ¹H NMR. ^bDetermined by HPLC (CHIRALPAC AD column). ^b(α S, β R) major product. ^cCarried out at 0 °C. ^d2.5 mol% catalyst was used. ^e3 equiv. of KOH was used. ^f30 equiv. of 30% H₂O₂ was used. ^gSpan 20 (1 mol%) was used as surfactant.



The highest yield 100% and 84% ee was obtained using polymeric organocatalyst **5Aa** (entry 3) bearing quininium moiety in the main-chain. These values are quite higher than using monomeric catalyst bearing quininium salt 84% yield, 55% ee (Helder et al. 1976). Whereas, using dimeric catalyst bearing quininium moiety showed 90% yield and 92% ee when applied in asymmetric epoxidation of trans-chalcone. Although the plausible reaction mechanism using monomeric and dimeric quininium salt was proposed by Helder et al. in 1976 and Jew et al. in 2005 respectively, the actual mechanism of main-chain chiral ionic polymer bearing quininium moiety is still unclear when applied in asymmetric epoxidation of chalcone.

Conclusion

Main-chain chiral ionic polymers bearing quininium moiety have been synthesized from dimeric quaternary ammonium salt of quinine and disulfonic-acid disodium salt, using ion-exchange polymerization. These main-chain chiral ionic polymers were effective in asymmetric epoxidation of trans-chalcone. The reaction is susceptible to change in solvent system, amount of catalyst, amount of base, amount of oxidant and types of surfactants used. Using catalyst **5Aa**, up to 84% enantioselectivity (ee) and 100% conversion of trans-chalcone was obtained. To obtain, higher conversion and enantioselectivity, selection of catalyst and optimization of the reaction condition is very important.

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NUMERICAL ANALYSIS OF OPTIMIZATION OF THE COST AND ESTIMATION OF EFFICIENCY OF THE CHARGES OF A COMMERCIAL ENTERPRISE

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Abstract

This research aims to inspect the process of minimization of cost and estimation of efficiency of the charges using a ramble, which is based on the use of vehicles of duality. The base of this work is to analyze the cost as well as scrutiny in the condition of efficiency of the charges and optimization of volumes of the production. The economic raising over of the task is brought, the algorithm of decision and its programmatic realization are worked out.

Keywords: Cost Optimization, Efficiency of the Charges, Commercial Enterprise, Profitability, Algorithm.

Introduction

Evaluation of the actual efficiency of the given development phase of the market and enterprise itself shall be based on the development of the market share of the company in the market where it operates. A high and increasing market share of the company may indicate that an effective cost and effective management model is being used. Moreover, it is indisputable that both the enterprise and the market environment are changing constantly. On one hand, it means that the past efficiency of the model will not guarantee successful business in the future, on the other hand, it points out the significant benefits and advantage of those cost and effectiveness models which take into account constant changes in the enterprise and market conditions as much as possible.

An enterprise acting without clearly defined, rational, adequate, implemented, and constantly developed cost and effectiveness models may of course be imagined. It can only be said of such an enterprise that is having a development strategy as well as elementary tools necessary for effective operation on the global market with competition. The necessity to have such a system in place is especially crucial when an enterprise operating in the market of developed technology plans to multiply its share by taking over the shares of much stronger competitors. In the case of companies trying to operate in the business of new, dynamically developing technologies working without implementing an efficient system of cost and efficiency management, an attempt at competitiveness on the global market is ruined to fail. Majorities of companies hold discussions on cost and cost reduction frequently and extensively. Employees are allocated to constant accounting and control of the cost. However, the scope of such accounting and controlling is suited mostly to the requirements of tax regulations,

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financial reporting and financial control regulations. However, it seems that the main purpose is a precise registration of cost. From time to time also cost reduction actions are initiated. Therefore, employees of most of the companies are convinced that their company has some sort of cost management system in place. Regretfully, in many cases, these are illusions based on misconceptions. Registration and controlling as well as periodical cost reduction actions may hardly be considered as "clearly defined, rational, adequate, implemented and constantly developed cost and effectiveness management model". The requirements concerning quality management systems have been standardized and described in detail in series standards, thus existing in the collective consciousness as a set of defined and established ideas, however, the requirements and expectations towards the cost and effective management system probably have not yet been similarly codified by series standards. Therefore, the presentation of the main features of the proposed concept is given bellow.

Methodology

A productive unit cost is a basic factor that determines the size of gross revenue. If a productive unit cost increases, then at other equal terms, a gross profit margin necessarily will diminish due to this factor on an analogical sum. The less productive prime price, the greater the gross revenue, and vice versa. It is good evidence from the formula of calculation of gross profit margin:

$$GP = NP - CP \quad (1)$$

Where GP– Gross profit;

NP– Net profit;

CP– Production cost of products sold.

Other types of charges in the field of the operating room, financial and investment activity, from emergency events, and also an income tax is diminished general financial result of the economic activity of an enterprise. The charges of enterprise from payment of dividends diminish a net income (Abryutina MS and Grachev AV, 1998) and (Andreychykov AV. and Andreychykova O., 2000). Coverage of losses of enterprise diminishes its property asset. The objects of analysis of charges of an enterprise are next indexes:

- productive made unit, rendered services, and produced works cost on the whole and after the items of expenses of enterprise and him structural subdivisions;
- realized unit and other assets cost;
- administrative charges;
- charges are on a sale;
- charges are from an operating-room, financial, investment activity, emergency events, income tax, payments of dividends, coverage of losses;



- charges are on 1 unit of net profit;
- operating charges are after the elements of charges;
- separate elements and items of expenses;
- correlation.

Taking into account it, the primary purpose of economic analysis in the field of charges of design of optimal between's by a consumer cost (by a net profit) from the object of charges and charges on his forming. This aim can be attained in the next terms:

- * the consumer cost (net profit) of the object of charges increases, and charges diminish on his creation;
- * the consumer cost (net profit) of the object of charges increases, and charges do not change on his creation;
- * the consumer cost (net profit) of the object of charges increases at greater rates, than charges are on his creation;
- * the consumer cost (net profit) of the object of charges does not change, and charges diminish on his creation;
- * consumer cost (net profit) of the object of charges diminishes fewer rates than charges are on his creation.

The economic analysis of charges of enterprise concerning present backlogs for providing of the above-mentioned terms is begun with description by the changes of the productive prime price of a unit of products and charges on the next indexes. Level of planned (expected) change of prime price of a unit of products (Bakanov M. I. and Sheremet AD. 2002):

$$PR = PC/CB \times 100 \quad (2)$$

where, PR-the level of expected changes in the cost,
PC –planned (expected) unit costs,
CB -unit costs for the previous (base) period.

Absolut echange in unit cost estimates for planned (or soles expensive plan will be produced in the reporting period compared to last):

$$ABS = PC - CB \quad (3)$$

The expected size of the economy (additional) of charges as a result of the change of unit cost:

$$Eo = (CC - CB) \times OP \quad (4)$$

where, OP - planned production of goods volume in natural expression.

Level of dynamics of the actual cost of a unit of products:

$$Pdc = Cu/CB \times 100 \quad (5)$$

where, Pdc -the prime price of a unit of products of the period covered.



Absolute change of prime price of a unit of products in a period covered as compared to the past:

$$ABS = C_u - C_B \quad (6)$$

Size of the actual economy of additional charges as a result of a change of unit cost in dynamics:

$$E_f = (C_C - C_B) \times O_u \quad (7)$$

Where, E_f – current production of goods volume in natural expression.

Level of fulfilling the plan for the prime prices of a unit of products:

$$P_{fc} = C_u / C_p \times 100 \quad (8)$$

Absolute change of prime price of a unit of products in comparing to the plan:

$$A_{bf} = C_u - C_p \quad (9)$$

Size of the actual economy of additional charges in comparing to the plan:

$$E_f = (C_C - C_p) \times O_u \quad (10)$$

Comparing the size of the actual economy of charges from expected (planned) a size, expect the size of the planned economy of charges:

$$E_{or} = E_f - E_o \quad (11)$$

Between the considered indexes there is dependence:

$$P_{dc} = P_{oc} \times P_{fc} \quad (12)$$

The presence of excess economy of charges can be related to two factors: firstly, with a deviation of the actual production volume from foreseen according to plan secondly, with a deviation of the actual level of prime price of a unit of products from planned. Excess economy got due to every factor determined size upon the next settlement (Basovskyy E. L., 2001):

a) due to the deviation of the actual production volume from planned:

$$E_1 = (C_p - C_b) \times (O_u - O_p) \quad (13)$$

b) due to the deviation of the actual level of prime price from planned:

$$E_2 = (C_u - C_p) \times O_u \quad (14)$$

The actual economy of charges as compared to a past (by a base) period:

$$E_{or} = E_1 + E_2 \quad (15)$$



Analytical researches of influence of factors on the rejection of fact sheets about charges on the production of goods and unit cost in comparison to the planned or past (by a base) indexes it maybe to carry out utilizing reception of chain substitutions.

To the erected indexes of productive charges that allow analyzing their level and dynamics belong:

- productive made (realized) unit (works, services) cost;
- a level of productive charges is on a 1 euro of net profit.

For the analysis of change of made (realized) unit cost as compared to a plan or base (by the past) period the aggregate index of unit cost can be used:

$$I = \frac{\sum O_u \times C_u}{\sum O_u \times C_m} \quad (16)$$

where, I- actual productive charges on the made products (works, services) in a period covered;

$O_u \times C_b$ -productive charges are on making in a period covered of products (works, services), calculated going out the prime price of a unit of products of every kind according to plan or in (to the past) a base period.

A difference between an index and denominator shows by itself the actual sum of the economy (overruns), got as a result of the change of unit cost as compared to planned calculations or with a base (by the past) period (Mas-Collel A. et al., 1995) and (KantranovychL., 1999). The change of productive charges depends not only on internal but also from external for the enterprise of factors, namely from a price change on raw material, materials, tariffs on energy and services. Therefore, the analysis of the activity of enterprise interest presents the calculation of the index of productive charges comparable with a base period term. This index will show the change of productive charges only under the act of internal for enterprise factors:

$$I = \frac{\sum O_u \times C_u \pm \Delta}{\sum O_u \times C_B} \quad (17)$$

In the numerator of index brought in to the amount of reduction of prices or rising in the price of elements of material charges (costs of the users are in the production of raw material, materials, fuel, energy, services).

The index of charges on 1 unit of net profit is calculated as an attitude of productive charges of realized unit (commodities, works and services) cost toward the net profit got an enterprise.

$$P = \frac{\sum O_p \times C}{\sum O_p \times U} \quad (18)$$



where, P - a level of productive charges is on 1 unit of net profit,

O_p – volume of the realized products (commodities, works, services);

C – productive prime price of a unit of the realized products (commodities, works, services);

U – cost of a unit of the realized products (commodities, works, services).

This index is determined, firstly, in exact accordance with his name as a sum of productive charges necessary for a receipt of the enterprise of 1 unit. Net profit; secondly, as a relative size that characterizes the structure of net profit. The index of level of productive charges on 1 unit of net profit can be calculated after all types of the realized products (commodities, works, services), and also on an enterprise on the whole.

Comparing the actual and planned (base level of productive charges on 1 unit of net profit, calculate the index of productive charges on 1 unit of net profit in the costs of corresponding periods :

$$I_B = P_3/P_M = \frac{\sum O_u \times C_u}{\sum O_u \times U_o} / \frac{\sum O_M \times C_M}{\sum O_M \times U_M} \quad (19)$$

$$\Delta_B = P_u - P_M \quad (20)$$

Change of productive charges on 1 unit of net profit on an enterprise, on the whole, it can take place under the act of three factors:

- prices on the realized products;
- productive prime price of a unit of products of every kind;
- to the volume and assortment of the realized products.

Influence of every factor on the level of productive charges on 1 unit of net profit it is possible to calculate after the next calculations:

- change of volume and assortment of the realized products

$$I_a = \frac{\sum O_3 \times C_M}{\sum O_3 \times U_M} / \frac{\sum O_M \times C_M}{\sum O_M \times U_M} \quad (21)$$

$$\Delta_a = \frac{\sum O_u \times C_M}{\sum O_u \times U_M} - \frac{\sum O_M \times C_M}{\sum O_M \times U_M} \quad (22)$$

- change of productive realized unit cost

$$I_c = \frac{\sum O_u \times C_M}{\sum O_u \times U_M} / \frac{\sum O_u \times C_M}{\sum O_u \times U_M} \quad (23)$$



$$\Delta c = \frac{\sum O_u \times C_3}{\sum O_u \times U_M} - \frac{\sum O_u \times C_M}{\sum O_u \times U_M} \quad (24)$$

– a price change is on the realized products

$$I_p = \frac{\sum O_u \times C_u}{\sum O_u \times U_o} / \frac{\sum O_u \times C_u}{\sum O_u \times U_m} \quad (25)$$

$$\Delta p = \frac{\sum O_u \times C_u}{\sum O_u \times U_o} - \frac{\sum O_u \times C_u}{\sum O_u \times U_m} \quad (26)$$

Intercommunication between indexes that characterize the influence of separate factors, following:

$$I_B = I_a \times I_c \times I_p \quad (27)$$

$$\Delta B = \Delta a + \Delta c + \Delta p \quad (28)$$

Production costs as one of the factors affecting gross profit. The value of gross profits affect the price of the sold products (works, services, products) (a direct relationship rising prices increase gross profit and vice versa); production cost of goods (works, services, products) (inverse relationship rising costs reduce gross profit (increases the loss) and vice versa) natural volume of products (works, services, products) (an increase of profit production increases the amount of gross profit and vice versa, and the increase of sales of unprofitable products increases the gross loss and vice versa) and the range of products (services, works, goods) (increase by densities of viable (more profitable) products, reducing unprofitable (more unprofitable) increases the gross profit (loss decreases) and vice versa). The value of gross profit from sales of the specific type of products (works, services, and products) is influenced by three factors: cost, production cost and natural turnover (Yastremska OI. and Gryshchenko OG., 1993). To determine the impact of price changes of products to change the value of gross profit compared to therevenue of a fiscal year with the one that would be obtained by keeping the prices of last year:

- to identify the impact on gross profit level change should compare the cost of production cost, subject to specified reporting year of sales and production unit cost of last year, with production cost reporting year;
- to determine the impact of the natural volume of sales to change the size of gross income, you should calculate the index of physical output. Change in gross profit is directly proportional to the change of the output;
- the fact that the range of products sold in the reporting year has changed, and changed the amount of gross income.



The main task of studying the economic costs of elements is to determine the value of the cost of living past work and relations between them. Since the classification of expenses by economic elements reflects expenses associated with manufacturing production, it is called the estimated cost of production. With help summarize the costs for enterprises regardless of the nomenclature of economic activity. Determining the structure of expenditures on economic elements makes it possible to determine the role of various elements in the total costs, to identify further reserves to decline due to changes in the ratio between the reified and live work, reveal the influence on the cost of productivity.

Depending on the cost structure emit language materials, funds and labor-intensive business entities. The material belongs to entities that transform raw materials (high proportion of material inputs) (Ponomarenko AI. and Ponomarenko VA., 1995). Consuming owned business entities, where costs of living and working under a very large share of high wages and deductions for social events. Formation costs for elements of economic analysis have prevented the production unit cost, especially if made two or more kinds of products because each item costs, although homogeneous by economic nature, but diverse from the ratio of production costs to specific business objects activity. For detection of internal planning and cost reduction of reserves necessary to know not only the total costs of the enterprise for a certain element of economic and cost and size depending on their place of origin and the specific form of productive use, to know how much is spent on main and auxiliary production, management. This task group is responsible for cost accounting articles. The essence of this classification is that all expenses are grouped based on their common industrial purposes. The enterprises of various economic activities using different in their composition range order cost items, due to the peculiarities of their production costs (Perestyuk NA. and Brown VM., 2004). The major ones include the expenditures that have the largest share in total industrial production costs and other costs. The nature of costs can be grouped into three main groups. In the first group –the cost of energy in the production process work items (raw materials, basic materials, semi-Cropped and components, manufacturing, fuel and energy, etc.). The second - Labor. The third - the costs associated with the use of fixed assets. According to this cost, analysis can be conducted in terms of basic economic cost elements, revealing: (1) the ratio of productivity and wages, (2) inventory cost savings, which leads to increased material and reduction of inventory costs in total costs, (3) management of fixed assets, which tends not only to improve capital productivity but also to reduce the share of depreciation in total costs. Expenditures on inventory-related manufacturing unit can be considered as the sum of the products spent on materials production unit (unit costs) and expenses (price) per unit of spent material. Note that production costs per unit of material including their purchasing price and freight harvesting costs. When analyzing the dynamics of the cost of the article "Raw" expects its unit cost index and price index. Index of unit costs of raw materials reflects the impact of



cost changes on the value of the actual costs of raw materials per unit of output and price index reflects the impact of price changes. These indices are calculated by the following formulas:

$$I_{p.B.} = \frac{K_u \times UM}{KM \times UM} \quad (29)$$

$$I_{price} = \frac{K_u \times C_m}{K_u \times C_s} \quad (30)$$

where, $I_{p.B.}$ - charges of raw material, materials and other productive supplies on the unit of products accordingly in the past and current periods in natural expression;
 C_m, C_s - cost of a unit of raw material, materials and other productive supplies accordingly in the past and current periods.

Except for material charges on the size of prime price have a certain influence of expense on the remuneration of labor (Takayama A., 1994) and (Varian H.R., 1992). The sum of charges on the remuneration of labor depends on the amount of spending labor on the unit of products and the middle salary for the working time unit. Influence of them can be defined using such indexes:

$$I_T = \frac{T_u \times OM}{TM \times OM} \quad (31)$$

$$I_s = \frac{T_s \times O_s}{T_s \times OM} \quad (32)$$

The first index removes the influence of the change of labor intensiveness (to labor productivity), the second influence of the change of the middle salary. Except for material and labor charges a considerable place informing of the level of unit cost is occupied by charges that are related to the rational use of the fixed assets. Participating in the fixed assets informing of unit cost is expressed in the form of depreciation decrees. The sum of depreciation depends on the average cost of the fixed assets that are used in the process of making products and the middle rate of depreciation. The influence of these factors can be defined using such indexes:

$$I_B = \frac{B_s \times HM}{BM \times HM} \quad (33)$$

$$I_H = \frac{B_s \times H_s}{B_s \times HM} \quad (34)$$



The first index removes the influence of the cost of the fixed assets to the number of depreciation, the second influence the change of the rate of depreciation.

The decline of the prime price of the unit of products and charges on 1 unit of products is arrived at by such measures:

- increase of volume of mine-out products;
- reduction of charges as a result of the introduction of organizationally-technical measures;
- removal of unproductive charges and unjustified overruns after elements and calculation items of expenses.

The economic model of forming of charges and intercommunication between permanent, variable charges and volumes of mine-out can be expressed by equalization:

$$OP = PC + VC \times VE \quad (35)$$

where, OP – operating charges of an enterprise (after the centers of forming of the productive unit, works, services cost, administrative and on a sale);

PC – permanent charges (administrative, on a sale);

VC – variable charges are on the unit of products in natural (to money) expression; VE

– volumes of economic activity.

The increase of production of products assists the decline of the prime price of a unit of products due to the economy of permanent charges:

$$Co = \frac{OP + PC \times VE}{VE} = \frac{OP}{VE} + \frac{OP \times VE}{O\Gamma} = \frac{OP}{VE} + PC \quad (36)$$

where, Co – prime price of a unit of products is.

Reduction of charges due to the realization of organizationally-technical measures is arrived at: From the material cost-cutting:

$$Em = (Ho - Hs) \times Av \times Ac \quad (37)$$

where, Em- norm of charges of materials on a unit of products in natural (to money) expression by the introduction of organizationally-technical measures and after introduction;

Av – actual volume of the made products (works, services); Ac – actual cost of a unit of materials;

And, from the reduction of charges on the remuneration of labor:

$$Eo = (To - Ts) \times TC \times Av \quad (38)$$

where, Eo– labor intensiveness of production of a unit of products by introduction of organizationally-technical measures and after introduction, by hours;



TC – total cost tariff rate,
Av – actual volume of the made products (works, services);
– due to more effective use of productive equipment :

$$Es=(A_o-as) \times Av \quad (39)$$

Where, Es -the sum of depreciation of equipment on a unit of products by the introduction and after introduction;

Separately in the process of analysis investigate charges on maintenances of production and his management that is formed after the article of the productive prime price (Ponomarenko O.I., 2000). It is necessary to take into account the complex character of forming of these charges, association in their composition of different after connection with a production of charges, the feature of their plugging volume in the prime price of separate types of products. The article is consists of separate elements that stipulate the necessity of reflection of these charges on the independent articles of calculation. For the estimation of efficiency of the forming of charges, there is a certain system of economic indicators on an enterprise. The constituent of economic analysis of charges;

$$GR = VR \times VC + PC \quad (40)$$

where, GR - general charges of enterprise from operating activity after the current period (month, quarter, year);

VR – a volume of realization (to the sale) of objects of entrepreneurial activity is after an assortment in natural expression;

VC – variable charges are on a unit of products (works, services);

PC – permanent charges after the current period (month, quarter, half-year, 9 months, year).

$$VC = VR \times PC \quad (41)$$

where, VC– variable charges after the current period (month, quarter, half-year, 9 months, year);

$$PC = AC + SC \quad (42)$$

where, PC – permanent charges after the current (month, quarter, half-year, 9 months, year);

AC – administrative charges after the current period (month, quarter, half-year, 9 months, year);

SC – charges on a sale after the current period (month, quarter, half-year, 9 months, year);

$$NP = AD \times U \quad (43)$$



where, NP – net profit (profit yield) from the sale of products (works, services);
U – unit (works, services) costs.

$$VR = VC + PC \quad (44)$$

where, VR – variable charges after the current period (month, quarter, half-year, 9 months, year).

An analysis of correlation of expense of is a net profit an income is based on such pre-conditions:

- production and realization (to the sale) of products (works, services) volume after the current period gather;
- charges can be divided into variables and permanent. On the indexes of financial accounting realized unit (works, services) cost taking into account all of the total charges of it is variable charges, and permanent – it is administrative charges and charges on a sale;
- variable charges are proportional to the volume of entrepreneurial activity, and the permanent depends only on the period;
- price on products (works, services) has a certain stable character.

In the process of analysis such indexes are calculated and analyzed:

- marginal income (loss);
- marginal profit ratio;
- equilibrium volume of operating (productive) activity (break-even point);
- strength of operating activity security;
- volume of operating activity (production volume) that provides having special purpose profitability;
- operating leverage (operating dependence), that gives an opportunity operatively to analyze the dependence of income on the dynamics of the volume of products and structure of charges (Wijaard J. Beyond, 1990).

At an analysis, an important value has an index of marginal income and its relative size marginal profit ratio. Marginal income, that is sometimes named coverage, or payment in an income, calculated on a formula:

$$Mi = Np - Vc \quad (45)$$

where, Mi –the size of marginal income is for a certain period, Vc – variable charges are for this period. Thus, a marginal income equals permanent charges and operating profit, to the income from the sale of products:

$$Op = Pc + P \quad (46)$$

where, Op – operating profit,

Accordingly, an operating profit, or simply income, is a difference:



$$P = I - Op \tag{47}$$

A between by a marginal income and volume of net profit it comfortably to analyze using the relative index of marginal profit ratio:

$$Mpr = Op/Np \tag{48}$$

where, Mpr - a marginal profit ratio is (IvanovaN., 2002).

Operating activity concerning the production (to the sale) of goods, grant of services, implementation of works is considered balanced, when a net profit is from the sale of these products (works, services), thus profit yield, equals the combined charges. This volume of products is yet named a break-even point, as on a chart in a point that answers his size, the functions of charges and net proceed (to the profit) intersect. Marked production volume a break-even of point will delimit the spheres of unprofitable (area 1) and profitable (area 2) production (to the sale).

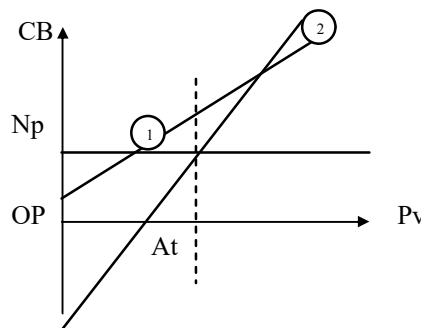


Figure 1: Cost behavior (CB), profit yield (NP) and break-even (At) point

At a break-even point a profit yield equals the combined charges:

$$Q \times Up = Fc \times Vc + Up \tag{49}$$

$$Q = \frac{Fc}{Up - Vc} \tag{50}$$

In a numerator by it formulas permanent charges, in the denominator of marginal income on the unit of products. For the leading out of the formula of calculation of break-even production volume monetary will take advantage of the formula:

$$Q = Fc / (Up - Vc) \tag{51}$$



$$Q \times U_p = F_c / [(U_p - V_c) / U_p] \quad (52)$$

As (a net profit provides that break-even activity), and it is a marginal profit

$$M_{pr} = F_c / V_r \quad (53)$$

It is possible to show out this formula and on basis nevertheless correlations. In a break-even point:

$$T_c = V_c + F_c \quad (54)$$

where, T_c – variable charges on the break-even volume of products (to the sale),
Expressed dependence of variable charges on a production (to the sale) volume, taking advantage of for this purpose coefficient to the break-even point:

$$M_{pr} = (N_p - F_c) / N_p \quad (55)$$

$$F_c = N_p - V_c \times M_{pr} \quad (56)$$

In a break-even point:

$$N_{pr} = F_c - V_c \times M_p + O_p \quad (57)$$

From here:

$$M_{pr} = M_p / O_p \quad (58)$$

At a break-even point, permanent charges are covered by a marginal income. During the analysis of the dependence of income from operating activity two questions turn out:
– what volume of realization provides the having a special purpose income of enterprise;
– like the size of income reacts to the change of volume of realization.

Having a special purpose an income that an enterprise would like to get in a certain period coming from the strategic tasks is named in this case. Therefore there is a question, how many are needed to sell to the products at certain prices and level of charges, to provide the marked income. Such volume of products is calculated on a formula:

$$O_u = \frac{P_u + M_u}{U_p - F_u} \quad (59)$$

or

$$O_u = M_p \frac{P_u}{U_p - F_u} \quad (60)$$

In the case of the cost measuring of the volume of products :



$$R = \frac{PB + P}{P.r} \quad (61)$$

or

$$R = R_0 + \frac{I}{P.r.} \quad (62)$$

Where, R –the volume of products, that must be realized, is, to provide a having a special purpose income accordingly in natural and money expression;

Sp – having a special purpose income

Operating leverage characterizes the increase of income on the unit of increase of volume of realization of products (commodity, works, services), that is:

$$OP = \Delta I / \Delta R \quad (63)$$

where, OP-operating leverage;

ΔI – change of income;

ΔR – change of volume of realization.

Application of operating leverage for the design of financial results from realization allows not only defining the change of income as compared to his size in a base period but also estimating factors that influence this change. The certain possible dynamics of prices and natural volume of realization provides an operating profit, necessity margin to the enterprise. Knowing it, an enterprise within the limits of present possibilities can indexes price and natural volume of realization changes, approaching the terms of demand on the products to the desired result.

Numerical Analysis

For the numerical analysis, we consider the necessary information for the years 2009 and 2010 of a company. The most important indexes that characterize technical and economic position of enterprise are indexes of efficiency. For these aims of predictions a number of indexes, that characterizes both the state of basic and circulating money for financial and economic position of enterprise on the whole. The indexes of efficiency of the fixed assets are given in Table 1.

Table 1. Indexes of the use of capital assets

Name of index	2009	2010	Changes, %
Assets ratio	1.22	1.85	+51.6
Fund Capacity	0.81	0.54	-33.3
Capital-labor ratio of thousand per person	77.44	69.59	-10.1
Coefficient of physical wear	10%	21.4%	+11.4



Except the indexes of efficiency, it is important to analyze the efficiency of the use of turnover means in Table 2.

Table 2. Efficiency of the use of turnover means

Name of index	2009	2010	Changes, %
Coefficient of rotation	1.12	0.95	-14.3
Duration of one turnover, days	321	379	+21
Profitability of turnover means, %	55	76	+21

In the process of feasibility analysis, it is important to analyze the indexes that characterize motion of personnel on an enterprise. Indexes over, that characterize motion of labor force on an enterprise, are brought in the Table 3.

Table 3. Indexes of motion of labor force

Name of index	2009	2010	Changes, %
Coefficient of current of personnel	13.6	3.6	-10
Turnover of labor force is on an acceptance, %	22.7	28.6	+5.9
Turnover of labor force is on liberation, %	13.6	3.6	-10

As a result of the conducted calculations it is possible to draw conclusion that, on the draught of the year 2010 composition of workers of enterprise composition of enterprise became in anymore degrees permanent, than percent of exempt workers grew in the previous year. Calculation of indexes of liquidity of given in the Table 4.

Table 4. Calculation of indexes of liquidity

Index	2009	2010
The coefficient of coverage is general	0.88	1.27
Rapid liquidity ratio	0.56	0.77
Absolute liquidity ratio	0.16	0.2

The coefficient of coverage general represents, in how many onetime circulating assets exceed current duties. If circulating assets exceed current duties on a size, that is an index equals 1, an enterprise can look over as more or less solvency. The next important group of indexes is a group of financial firmness (independences). The level of the financial risk related to the structure of sourcing of capital appears in the process of analysis of financial firmness, and accordingly, and feet of financial stability of enterprise. Calculation values over of indexes are brought in Table 5.



Table 5. Calculation of indexes of financial firmness

Index	2009	2010
Coefficient of concentration of property asset, %	53.3	59.4
Debt ratio	0.85	0.81
Coefficient of self-finance	1.15	1.08
Coefficient of financial of elasticity	0.55	0.49
Coefficient of correlation of mobile and immobilized assets	0.89	0.91

The coefficient of concentration of property asset characterizes the fate of proprietors of enterprise in the lump sum of facilities, advancing in his activity. Normal the value of index of is considered 50% – 60%.

Table 6. Calculation of indexes of business activity

Indexes	2009	2010	Changes,%
Rotations of assets, turnover	0.52	0.57	+9.6
Rotations of inconvertible assets, turnover	1	1.4	+40
Rotations of own capital, turnover	1.22	1.15	-5.7
Rotation of account receivable, turnover /days	2.75/130	2.42/149	-12/19
Rotation of productive supplies turnover /is days	3.14/115	2.4/150	-23.6/35
Rotation of account payable, turnover /days	0.98/365	1.22/295	24.5/70
Operating cycle, days	245	299	54
Financial cycle, days	-122	4	126

In this case risk of reduced to the minimum: sold the half of the property formed due to a property asset, an enterprise can liquidate promissory duties, even if the second half will be for that to reasons. Calculation values of index are within the limits of 53. 3% – 59.4% testifies that on a draught in 2009-2010 financial position was proof. Increase of coefficient of rotation of inconvertible assets it can be attained as due to in relation to not high specific gravity of inconvertible assets due to their advanced-technology. A subzero coefficient testifies or about the insufficient volume of sale, or about the too high level of contributions to these types of assets. Rotation of inconvertible assets of enterprise on



draught analyzable periods considerably grew on 40%, which is the consequence of increase of size of profit yield from realization of products on the draught in 2010.

The rotation of property asset of characterizes the various aspects of activity: in terms of money he determines the lack of the personal funds; from financial – speed of turnover of the inlaid property asset; from economic activity of monetary resources a shareholder risks that. The expected values of index testify that activity of monetary resources that belong to the shareholders is high enough, but on a draught analyze what to the period this activity insignificantly goes down a index in 2010 grew short comparatively with 2009 on 5.7%. The rotation of account receivable of represents efficiency of credit policy of firm and shows, how many turns for a year carried out the facilities inlaid in calculations. This coefficient characterizes ability to get paying for the products realized in credit. An index can be expected in days, representing the period of debtor debt liquidation. The next important group of indexes is a group of indexes of profitability that is used for description of profitability and effectiveness of activity of enterprises. A calculation over of indexes of profitability is brought in Table 7.

Table 7. Calculation of indexes of profitability

Index	2009	2010	Changes, %
Profitability of all capital, %	6	7	+1
Profitability of sale, %	12	12	0
Profitability of property asset, %	14.4	15.5	+1.1
Profitability of capital assets, %	13	20	7

Profitability of all capital of is summarizing and characterizes a net income that is brought by every euro inlaid in assets. This index, in essence, allows answering the question of what profits are got as a result of the use of all assets that is owned by an enterprise. The results of calculations testify that the income got on a 1 uah inlaid in assets, sharply grew short an enterprise in 2010 was profitable and cost effective. Such tendency of increase was observed on a draught 2009-2010. Profitability of sale of testifies to effectiveness of basic activity of enterprise and characterizes what fate of net income in a profit yield from realization. This index allows defining, as far as a price on products answers interests of enterprise, as an income is mortgaged exactly on the stage of forming of price. The index of profitability of sale also sharply grew short on the draught of analyzing period.

Conclusion

This research article intends a method that describes the optimal plan of production, which is determined on a maximum of profit yield from realization and minimum charges. Defined the optimal plan of producing products with a maximum profit yield from realization and found such prices on the types of raw material, that charges were



were minimized. And also explained zero values in an optimal plan and defined, as a profit yield and plan of producing of products will change at the increase of supplies of raw material. The theoretical aspects of management charges are analyzed and a comparative description over of classification of charges is brought. Thus, it is possible to conclude, that minimization of charges is the major index of efficiency of the economic activity of an expensive enterprise.

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SYNTHESIS AND PHYSICO-CHEMICAL CHARACTERIZATION OF OMEPRAZOLE COMPLEXES OF Co(II), Ni(II) AND Cu(II)

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Abstract

Omeprazole is a proton pump inhibitor (PPI) that is used for various types of acid-peptic disorders. It is a weak base and it has a strong tendency to form metal complexes. In this paper, we report several omeprazole complexes of transition metal ions like Co(II), Ni(II), and Cu(II). These metal complexes were characterized by various physico-chemical methods including solubility, melting point, metal contents estimation, FT-IR and UV spectral analysis, magnetic measurement and thermogravimetric analysis. Omeprazole behaves as bidentate O, N donor. It forms coordinate bond through C-N⁻ and S=O groups. The metal content analysis of the complexes confine to their stoichiometry [Co(omep)₂].2H₂O, [Co(omep)₂(H₂O)₂].2H₂O, [Ni(omep)₂(H₂O)₂], and [Cu(omep)₂(H₂O)₂].2H₂O. [Co(omep)₂].2H₂O possesses high spin tetrahedral geometry while the other complexes [Co(omep)₂(H₂O)₂].2H₂O, [Ni(omep)₂(H₂O)₂], [Cu(omep)₂(H₂O)₂].2H₂O are high spin octahedral.

Keywords: Omeprazole, Infrared spectrum, Thermogram, Magnetic susceptibility.

Introduction

Omeprazole (omepH) was the first PPI introduced in market, followed by pantoprazole, lansoprazole, esomeprazole and rabeprazole (Strand, Kim and Peura, 2017). PPIs inhibit the gastric H⁺, K⁺-ATPase by covalent bonding at cysteines near the ion pathway (Shin and Kim, 2013). They are lipophilic weak bases composed of two moieties, a substituted pyridine with a primary pK_a value of about 4.0 and a benzimidazole with a second pK_a value of about 1.0 (Shin and Sachs, 2008). In stomach gastric acid PPIs are converted to sulfenic acids or sulfenamides that react covalently with the H⁺/K⁺-ATPase enzyme resulting in irreversible inhibition of acid secretion by the proton pump in the acidic environment (Shin and Sachs, 2006). Since in our blood serum, micromolar levels of loosely bound metal ions, e.g. Cu(II), Co(II), Zn(II) etc. (Lippard and Berg, 1994) are present, it is likely that these metal ions will interact with the PPI molecules under in-vivo conditions. This is expected, since heterocyclic nitrogens of the PPI bases carry lone electron pairs, they are good ligands for alkali/alkaline earth and transition metals cations

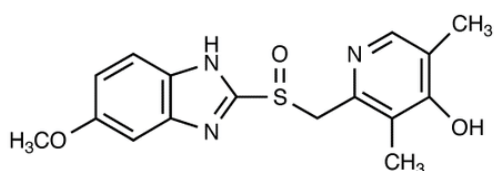
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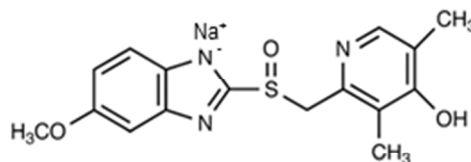


(Cotton, Wilkinson and Murillo, 1999). Also the interaction of metal ions with prodrug molecules and the possible effect on their conformation and biological activity are important especially in the design of slow release and long acting drugs (Ajibola, 1990).

Considering the importance of the complexes of omeprazole with metals, it is worthy to synthesize and structural studies of these complexes. Omeprazole ($C_{17}H_{19}N_3O_3S$, triclinic, $P\bar{1}$, $a = 10.686(5)$, $b = 10.608(7)$, $c = 9.666(6)$ Å, $\alpha = 119.75(5)$, $\beta = 112.02(5)$, $\gamma = 68.33(4)^\circ$, $Z = 2$) (Ohishi *et al.*, 1989) is a lipophilic weak base and insoluble in water while sodium salt of omeprazole is freely soluble in water and methanol (Bosch *et al.*, 2007).



Omeprazole



Sodium salt of omeprazole

Omeprazole (omepH) has three donor sites (two tertiary N atoms in pyridine and benzimidazole ring and one O atom in sulfinyl group) while sodium salt of the weak base (omepNa) has four donor sites (two tertiary N atoms in pyridine and benzimidazole ring, one secondary anionic N^- in benzimidazole ring and one O atom in sulfinyl group). The anionic N^- is formed in solution when Na^+ leaves the molecule. In alkaline medium, both omepH and omepNa provide the anionic secondary nitrogen, N^- and O atom of sulfinyl group ($S=O$) that have high electron density and are capable of forming coordinate bonds with transition and non-transition metal ions. Literature survey indicates that omeprazole commonly acts as a bidentate ligand, coordinating in chelating mode through benzimidazole ring N atom and oxygen atom of sulfoxide ($S=O$) group. Complexes can have tetrahedral and octahedral geometries (Mohamed *et al.* 2009, Malik *et al.* 2010, Verma *et al.* 2011, Verma *et al.* 2012, Ahmad *et al.* 2017).

Experimental

Chemicals: Omeprazole (omepH) was provided from SK+F Pharmaceutical Ltd., Bangladesh. Cobalt(II) chloride hexahydrate, nickel(II) chloride hexahydrate, copper(II) sulphate pentahydrate, nitric acid, sodium hydroxide and organic solvents etc. used in all synthetic and analytical work were analar grade, procured either from Aldrich (U.S.A.), E. Merck (Germany) or E. Merck (India).



Methods and Equipments: The melting temperatures of the prepared complexes were recorded on a SMP11 electrothermal melting point apparatus, Shimadzu, Japan. The metal contents of the complexes were determined complexometrically using EDTA as the titrating agent (Vogel, 1978). Fourier transform infrared spectra (FT-IR) were recorded on an infrared spectrometer of model IR-470 (Shimadzu, Japan) in the range of 400 - 4000 cm^{-1} using KBr pellets. The UV-visible spectra of the complexes were obtained using UV-Visible spectrophotometer, Model UV- 160A (Shimadzu, Japan), using the wavelength range of 200 - 600 nm and water as the reference solvent. Magnetic susceptibility of the complexes was determined by the SHERWOOD SCIENTIFIC Magnetic Susceptibility Balance (M.S.B.) of model Magway MSB Mk1, Cambridge, England. The quasi-static thermal analysis (QSTG) was carried out in a CARBOLITE calibrated muffle furnace of the type CWF 11/5. The thermogravimetric analysis was carried out with TGA-50 thermogravimetric analyzer (Shimadzu, Japan), while the differential scanning calorimetric analysis of the complexes was carried out with DSC-60 analyzer (Shimadzu, Japan).

Synthesis: In the present study, the chosen PPI is omeprazole and the metal ions are Co(II), Ni(II) and Cu(II). Ligand, omeprazole that was collected from SK+F Pharmaceutical Ltd., Bangladesh is an off-white powder, which melts at about 155 - 157°C with decomposition. Due to poor solubility of omeprazole in water, its solution was made in methanol; while the metal salt solution was made in water during synthetic work. The synthetic procedures of metal complexes of omeprazole that are adopted in the present study are detailed below:

(i) $[Co(omep)_2] \cdot 2H_2O$

1.0743 g (3.11 mmol) omeprazole was taken in a beaker and dissolved with 70 mL methanol. 0.3687 g (1.55 mmol) $CoCl_2 \cdot 6H_2O$ was taken in another beaker and dissolved with 20 mL distilled water. Two solutions were mixed together with constant stirring. To it, 0.41 M Na_2CO_3 solution was added drop by drop with stirring until the pH of the solution raised to 9.80. Light pink precipitate was started to appear instantly. The resulting solution was kept at room temperature for complete precipitation. After a day, the precipitate was filtered, washed with distilled water and dried in air. The complex is stable in air. Yield, % = 85.5 (with respect to cobalt content). Melting point, °C: 192-195 (d). Cobalt(II) content, % = 9.18 (7.52).



FT-IR (cm^{-1}): 450(m), 500(w), 520(w), 590(w), 633(m), 720(w), 800(m), 846(m), 1000(s), 1033(m), 1075(m), 1152(s), 1199(s), 1270(s), 1302(m), 1361(m), 1411(s), 1480(s), 1571(s), 1613(m), 2827(m), 2945(w), 2994(m), 3050(w), 3530(s, br), 3520(w).

(ii) $[\text{Co}(\text{omep})_2(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$

1.0742 g (3.11 mmol) omeprazole was taken and dissolved with 70 mL methanol in a beaker. 0.3672 g (1.54 mmol) $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ was taken and dissolved with 20 mL distilled water in another beaker. Two solutions were mixed together with stirring. 0.41 M Na_2CO_3 solution was added to the mixture dropwise with constant stirring until the pH of the solution raised to 9.50. At this pH, light purple coloured precipitate was started to appear. The resulting solution was kept at room temperature for complete precipitation. After a day, the precipitate was filtered, washed with distilled water and dried in air. The complex is stable at ambient condition. Yield, % = 89.0 (with respect to cobalt content). Melting point, $^\circ\text{C}$: 192-195 (d). Cobalt(II) content, % = 8.11 (7.19).

FT-IR (cm^{-1}): 400(w), 460(w), 510(w), 640(m), 700(w), 770(w), 840(w), 850(w), 992(m), 1040(w), 1070(m), 1120(w), 1150(s), 1199(s), 1230(w), 1271(m), 1300(w), 1350(w), 1410(m), 1480(m), 1570(m), 1612(m), 2840(m), 2950(s), 3000(w), 3400(s, br).

(iii) $[\text{Ni}(\text{omep})_2(\text{H}_2\text{O})_2]$

1.0753 g (3.11 mmol) omeprazole was taken in a beaker and dissolved with 70 mL methanol. 0.3942 g (1.42 mmol) $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ was taken in another beaker and dissolved with 10 mL distilled water. The solutions were mixed together with stirring. To it, 0.41 M Na_2CO_3 solution was added drop by drop with constant stirring until the pH of the solution raised to 9.10. A light green precipitate was started to appear. The solution was then kept at room temperature for complete precipitation. After a day, the precipitate was filtered, washed with distilled water and dried in air. The complex is stable in air. Yield, % = 81.7 (with respect to nickel content). Melting point, $^\circ\text{C}$: 225-227 (d). Nickel(II) content, % = 9.15 (7.49).

FT-IR (cm^{-1}): 455(m), 530(w), 600(w), 634(m), 680(w), 837(w), 979(s, br), 1075(w), 1157(s), 1200(s), 1272(s), 1304(w), 1359(m), 1412(m), 1488(s), 1568(m), 1612(m), 1708(w), 2830(m), 2941(m), 2996(m), 3370(m,br).



The synthesized complexes are powdery solids of different colors for different metal ions. They are non-hygroscopic, non-deliquescent and stable at room temperature. They do not melt but decompose at higher temperatures. They are soluble in methanol and hot ethanol but sparingly soluble in water. Inorganic qualitative analysis such as silver nitrate test and barium chloride test (Vogel, 1953) suggests the absence of Cl^- and SO_4^{2-} ions in the complexes. Empirical formulation of the complexes was done on the basis of their measured metal contents.

FT-IR Spectral Analysis: Some important FT-IR peaks of omeprazole and its metal complexes are given in Table 1. Assignments of peaks are done on the basis of standard literature (Nakamoto, 1976; Bellamy, 1956). Standard abbreviations (s = strong, m = medium, w = weak, br = broad) are used to describe the absorption peaks. Absorption peaks shown by the complexes in the region $450\text{-}640\text{ cm}^{-1}$ are due to M-O and M-N^+ stretching vibrations. In complexes, the stretching frequency of characteristic sulfoxide group, $\nu(\text{S=O})$ is weak-to-medium intensity appeared at ca. 1074 cm^{-1} , while that of omeprazole at 1076 cm^{-1} with strong intensity. It implies that the absorption peak originated from $\nu(\text{S=O})$ are weaken and shifted slightly to lower frequency region in complexes. This downward shifting can be explained on the basis of its participation in coordination with metal ions through O atom. Stretching of $>\text{C-N}^+$ in benzimidazole ring appear at $1410\text{-}1415\text{ cm}^{-1}$ in the complexes, while that of omeprazole is at 1461 cm^{-1} . Shifting of this frequency to the lower wave number as compared to the free ligand is indicative of participation of this group with the metal ions. The tertiary amine group ($>\text{C=N-}$) stretches at $1568\text{-}1571\text{ cm}^{-1}$ and its position is at 1585 cm^{-1} observed in free ligand. All complexes also show a broad band of medium intensity at about $3300\text{-}3600\text{ cm}^{-1}$ due to (O-H) bond stretching of H_2O molecule. This broadened (O-H) stretching absorption suggests that the complexes have either coordinated and/or H-bonded crystalline water molecules.

Table 1. A comparison of different vibrational frequencies of the complexes.

Complexes	$\nu(\text{M-O})$ cm^{-1}	$\nu(\text{M-N}^+)$ cm^{-1}	$\nu(\text{S=O})$ cm^{-1}	$\nu(\text{C-N}^+)$ cm^{-1}	$\nu(\text{C=N-})$ cm^{-1}	$\nu(\text{C=C})$ cm^{-1}	$\nu(\text{O-H})$ cm^{-1}
omepH	-	-	1076(s)	1461(s)	1585(m)	1630(s)	-
$[\text{Co}(\text{omep})_2] \cdot 2\text{H}_2\text{O}$	450(m)	633(m)	1075(m)	1411(s)	1571(s)	1613(m)	3520(w)
$[\text{Co}(\text{omep})_2(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$	460(w)	640(m)	1070(m)	1410(m)	1570(m)	1612(m)	3400(s,br)
$[\text{Ni}(\text{omep})_2(\text{H}_2\text{O})_2]$	455(m)	634(m)	1075(w)	1412(m)	1568(m)	1612(m)	3370(m,br)
$[\text{Cu}(\text{omep})_2(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$	450(w)	637(m)	1074(m)	1415(m)	1568(s)	1614(s)	3392(m,br)



UV Spectral Analysis: The electronic spectra of omeprazole show two absorption bands at 219 and 301 nm (Table 2). The former is assigned to $\pi \rightarrow \pi^*$ electronic transitions of C=C bonds and the later arises possibly due to $n \rightarrow \pi^*$ electronic transition of C=N bonds of the hetero aromatic ring present within the ligand, omeprazole. However, the complexes display a broad band around 295 nm may assigned as a combination of $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions. The red shift of $\pi \rightarrow \pi^*$ transition in their spectra is attributed to the effects of the ligation of the omeprazole to the metal ions. Though Co(II), Ni(II) and Cu(II) complexes are coloured but they do not show any noticeable band in the visible region of their spectra possibly due to their low solubility in water.

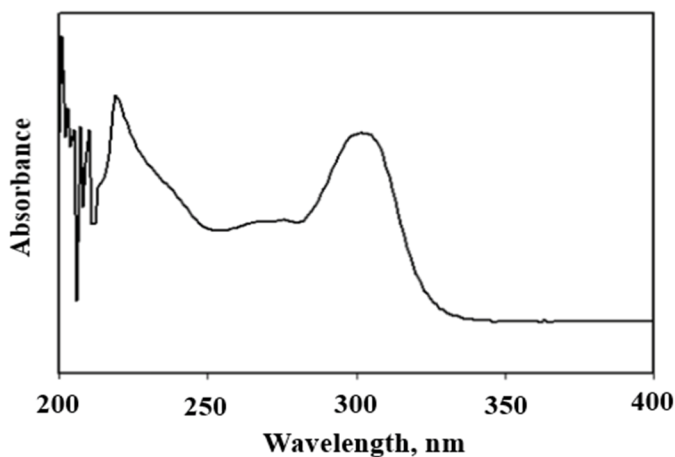


Fig. 1: UV spectrum of omeprazole

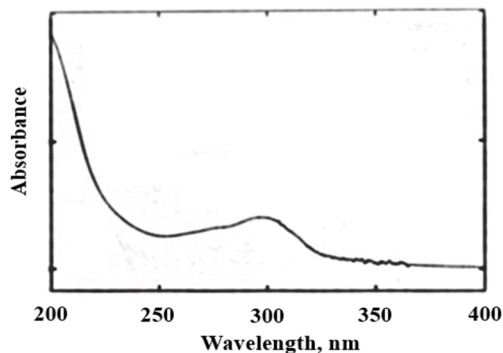


Fig. 2: UV spectrum of $[\text{Co}(\text{omep})_2] \cdot 2\text{H}_2\text{O}$

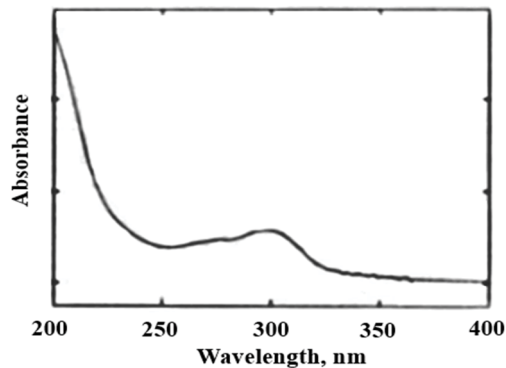
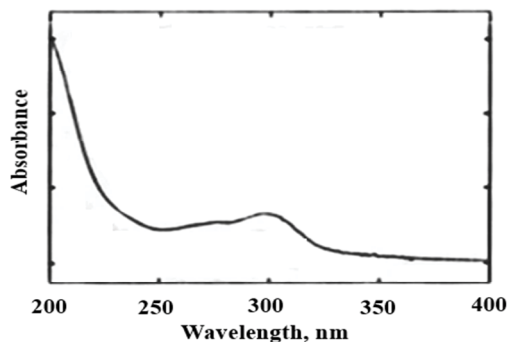
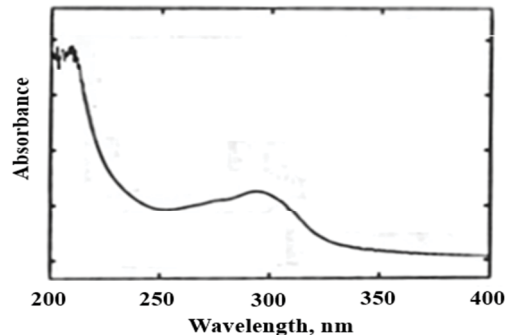


Fig. 3: UV spectrum of $[\text{Co}(\text{omep})_2(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$


 Fig. 4: UV spectrum of $[\text{Ni}(\text{omep})_2(\text{H}_2\text{O})_2]$

 Fig. 5: UV spectrum of $[\text{Cu}(\text{omep})_2(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$
Table 2. Electronic spectral data of the complexes

Complexes	λ , nm
Omeprazole (omepH)	219, 301
$[\text{Co}(\text{omep})_2] \cdot 2\text{H}_2\text{O}$	297
$[\text{Co}(\text{omep})_2(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$	297
$[\text{Ni}(\text{omep})_2(\text{H}_2\text{O})_2]$	297
$[\text{Cu}(\text{omep})_2(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$	215, 294

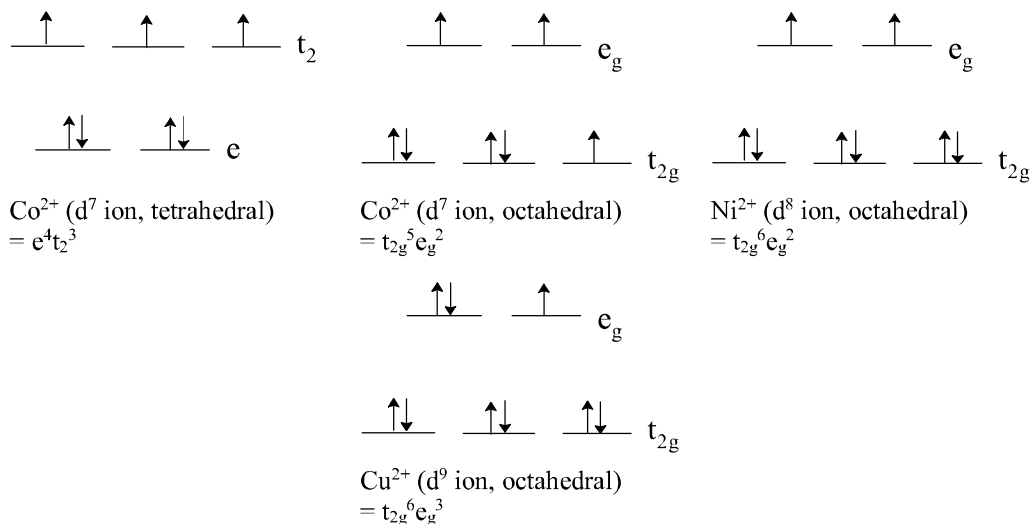
Magnetic Measurements: The magnetic susceptibilities of the prepared complexes were measured and the results are shown in Table 3. $[\text{Co}(\text{omep})_2] \cdot 2\text{H}_2\text{O}$, $[\text{Co}(\text{omep})_2(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$, $[\text{Ni}(\text{omep})_2(\text{H}_2\text{O})_2]$ and $[\text{Cu}(\text{omep})_2(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$ complexes are paramagnetic with effective spin only magnetic moment (μ_{eff}) of 4.40, 5.55, 2.91 and 1.57 BM corresponding to three, three, two and one unpaired electrons respectively. These experimental μ_{eff} values support the proposed geometry of the complexes i.e., tetrahedral geometry for $[\text{Co}(\text{omep})_2] \cdot 2\text{H}_2\text{O}$ complex and octahedral for $[\text{Co}(\text{omep})_2(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$, $[\text{Ni}(\text{omep})_2(\text{H}_2\text{O})_2]$ and $[\text{Cu}(\text{omep})_2(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$ complexes (Carlin and Duyneveldt, 1977).

Table 3. The magnetic susceptibility values of the complexes

Complexes	C_{Bal}	l , cm	m , mg	R	R_0	χ_{g} , C.G.S. unit	T , K	μ_{eff} , BM
$[\text{Co}(\text{omep})_2] \cdot 2\text{H}_2\text{O}$	0.8622	2.2	0.0806	388	-36	9.978×10^{-6}	299	4.40
$[\text{Co}(\text{omep})_2(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$	0.8678	2.0	0.0842	697	-39	1.517×10^{-5}	299	5.55
$[\text{Ni}(\text{omep})_2(\text{H}_2\text{O})_2]$	0.8622	2.3	0.0646	104	-37	4.328×10^{-6}	299	2.91
$[\text{Cu}(\text{omep})_2(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$	0.8591	2.2	0.0583	0.00	-37	1.200×10^{-6}	299	1.57



All are high spin complexes. Larger ligands with multiple bonding sites like omep⁻ and ligands with donor atom containing more than one free electron pair like water are weak field ligands, produce small splitting and favor high spin complexes (Haider, 1975). The d electron configurations for the high spin tetrahedral [Co(omep)₂].2H₂O, and high spin octahedral [Co(omep)₂(H₂O)₂].2H₂O, [Ni(omep)₂(H₂O)₂] and [Cu(omep)₂(H₂O)₂].2H₂O complexes are as follows:



Thermal Analysis: All complexes were studied by quasi-static thermogravimetric (QSTG) analysis. The QSTG thermograms of the investigated complexes are plotted in Fig. 6.

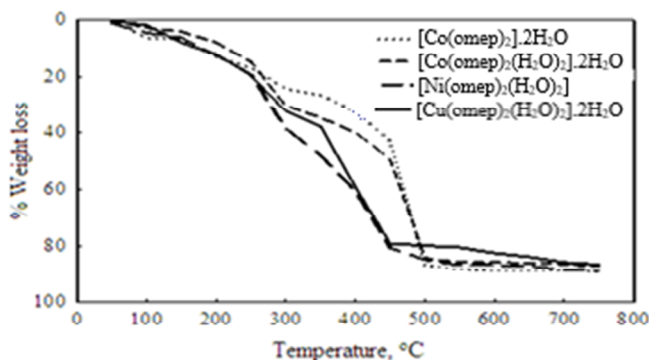
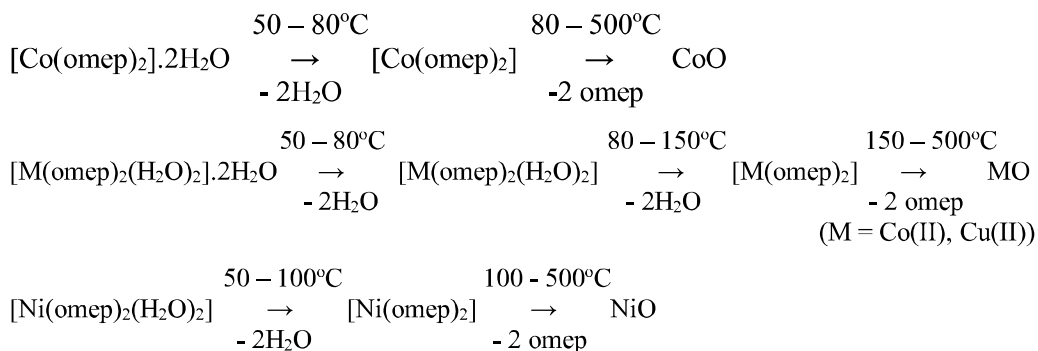


Fig. 6: Quasi-static thermograms of the complexes.

All four complexes start losing weight at relatively low temperature possibly due to the loss of water of hydration and/or coordinated water. The TG curves are essentially

continuous, which indicate that elimination of water molecules followed immediately by decomposition of organic moiety of the complex molecules. This is obvious since they have no melting temperature. Within the temperature range of 500-550°C, the complexes are converted to their corresponding stable metal oxides. The end products are black irrespective of the metal ion present. The metal contents calculated from the end product are consistent with the formulae of the complexes. The possible way of the thermal decompositions of studied complexes are as follows:



Very identical thermal behaviors of the complexes are observed in the dynamic thermogravimetric analysis (TGA).

The differential scanning calorimetric (DSC) analysis of $[\text{Co}(\text{omep})_2(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$, $[\text{Ni}(\text{omep})_2(\text{H}_2\text{O})_2]$, and $[\text{Cu}(\text{omep})_2(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$ complexes at temperature up to 400°C was also carried out. Table 4 and Fig. 7 summarize the results obtained.

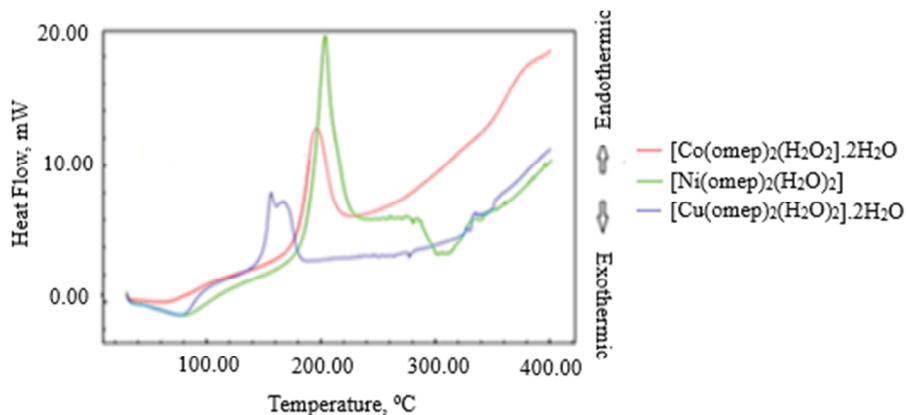


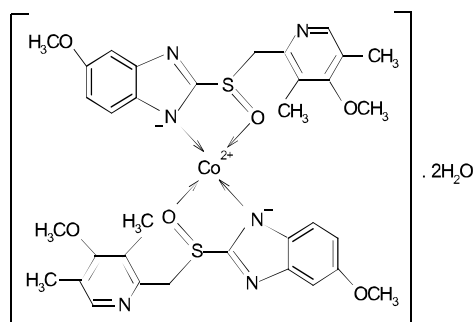
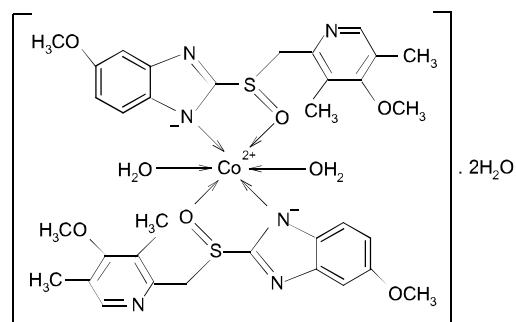
Fig. 7: DSC curves of complexes

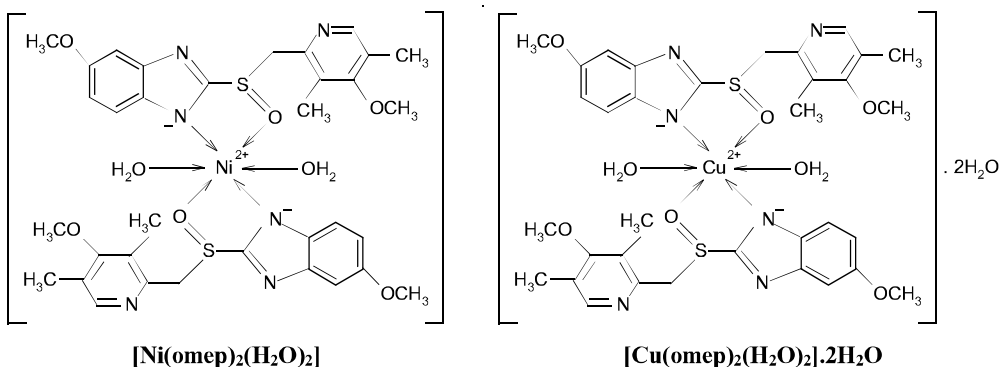

Table 4: DSC results of complexes

Complexes	Temperature, °C	ΔH , mW	Chemical change	Nature of decomposition
[Co(omep) ₂ (H ₂ O) ₂].2H ₂ O	196.18	+ 12	- 2H ₂ O	Endothermic
[Ni(omep) ₂ (H ₂ O) ₂]	203.99	+ 14.5	- 2H ₂ O	Endothermic
	300.57	-1.2	- Part of omep	Exothermic
[Cu(omep) ₂ (H ₂ O) ₂].2H ₂ O	156.57	+ 7.2	- 2H ₂ O	Endothermic
	167.37	+ 6.5	- 2H ₂ O	Endothermic

Conclusion

Several metal complexes of omeprazole were synthesized and characterized. They are powdery solids of different colors, non-hygroscopic, non-deliquescent and stable at room temperature. All complexes have incongruent melting temperature. They are soluble in methanol but sparingly soluble in water. The chemical structures of all synthesized complexes were deduced with the help of studied physical, spectroscopic and thermal methods. Physical data and metal content analysis of these complexes were in good agreement with the proposed formulae. [Co(omep)₂].2H₂O possesses high spin tetrahedral geometry while the others are high spin octahedral around the central metal ion because both omep⁻ and H₂O are weak field ligands (Haider, 1975). The proposed structural formulae of the studied complexes are:


[Co(omep)₂].2H₂O

[Co(omep)₂(H₂O)₂].2H₂O



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COMPARISON OF TOP AND WAVY BOTTOM LID-DRIVEN CAVITY WALLS MOVING DIRECTED TOWARDS AND OPPOSITELY IN THE PRESENCE OF MIXED CONVECTION

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Abstract

This paper investigates the transport of flow and heat on both sided lid-driven square cavity where wavy bottom walls are directed towards and opposite directions. In this cavity, the top wall is movable and deals with a constant velocity. The wavy bottom wall is sustained lower temperature compared to the top wall. The perpendicular walls are insulated and assumed to no slip. The bottom wavy surface is also maintained no slip condition. Here, two types of boundary conditions have been examined. In first case the top and bottom walls move with uniform velocity in the same direction towards right side and while the top and bottom walls move in opposite direction in other cases. In this paper, mathematical formulation for this physical problems are presented in the form of governing equations. The Galerkin weighted residual method of finite element formulation using COMSOL Multiphysics is applied to solve the non-dimensional lid-driven cavity equations. The graphical representation for streamlines, isotherms and Nusselt number for Grashof number (Gr), Reynolds number (Re), number of undulations (n) and wavy surface amplitude (A) are investigated. The results show that heat transfer rate is enhanced in the opposite directed movements in horizontal walls. The comparison of present study with some previous published papers is shown in both graphical and tabular forms.

Keywords: Lid-driven square cavity, Galerkin weighted residual method, Mixed convection, Wavy Bottom wall, Grashof number, Reynolds number, Richardson number.

Introduction

The transportation of flow and heat functioning with mixed convection in a lid-driven enclosure is found curious for researchers for its numerous applications. The presentation of such type of enclosure with moving horizontal and vertical walls has been attracted more attention for many years due to the increasing importance in natural, engineering and industrial sector. Such fields include lubrication technologies, electronic cooling, food processing, drying technologies, thermal-hydraulics of nuclear reactors, solar system and dynamics of solar waves etc. Combination of magneto hydrodynamics forced and natural convective cavity flow filled with electrically conducting fluid is significant in many industrial reservoirs, reactors and cooling applications. Here, we mention some previous works which have been studied for this paper. (Kumar, 2000) showed a detail interpretation of flow behavior and heat transfer in a porous vertical wavy area. It has been described that

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the surface temperature was very sensitive to the drifts in the surface undulations, phase of the wavy surface and the number of considered waves. Also, (Adjlout et al., 2002) have investigated free or natural convection in an inclined cavity where the wall is heated and undulated i.e. contains smooth wave-like behavior. The results present that the heated wall undulation effects on flow and heat transfer and also the local Nusselt numbers decrease gradually with the comparison of heat transfer rate in square enclosure. (Moskin and Poochinapan, 2010) have studied the finite difference method over the N-S equations for two dimensional flow. (Das and Mahmud, 2003) have analyzed natural convection in a cavity having horizontal wavy walls and adiabatic perpendicular walls. (Botella and Peyret, 1998) have studied a finite difference method named Chebyshev collocation method for the solution of cavity flow. Here, the asymptotic expansion of the solution of Navier Stokes equations is solved by subtraction method where velocity is discontinuous. Also, the study shows the accurate spectral solutions for the cavity flow has been generated with maximum grid mesh 160 (polynomial degree) and for the Reynolds numbers is less than 9,000. The study reveals that the numerical solutions perform a periodic behavior across this Reynolds numbers. Moreover, (Iwatsu et. al., 1993) and (Khanafer and Chamkha, 1999) investigated the detailed mixed convection effect in a driven cavity with porous medium. (Saha, G., 2010) presented magneto hydrodynamics convection in a sinusoidal corrugated field with discrete isoflux heating. (S. Arun and A. Satheesh, 2015) analyzed the flow behaviour of lid-driven cavity using two dimensional nine directional lattice model (D2Q9). (Pal et al., 2018) applied finite difference method to explore the low Reynolds numbers in a double lid driven cavity. Actually, numerous applications to the lid-driven square cavity has been examined where the cavity has different shapes i.e. one sided, double sided, three or four sided, rectangular, triangular, L-shaped, Γ -shaped etc. and also different characteristics too. (Kamel et al., 2020) investigated finite difference method in three-sided lid-driven cavity for two-dimensional time-dependent Newtonian fluid flow. (Huang et al., 2020) showed Lattice Boltzmann method in a lid-driven cavity with internal two-dimensional circular obstacles where Reynolds numbers ranging from 100 to 5000. Also, very recently (S. Aljabair et al., 2021) observed mixed convection in a sinusoidal lid-driven arc cavity with sinusoidal variation of temperature using nano fluid and (Fazuruddin et al., 2021) analyzed the flow characteristics for various values of Reynolds number in a double lid-driven square cavity with partial slip conditions by vorticity-Stream function approach. Currently, the wavy lid-driven cavity is considered as an effective heat transfer mechanism in engineering and scientific applications. In the area of industrial sector i.e. thermal engineering and many other facilities of modern technological life, this model can be used frequently. So, it is necessary to figure out the variation in fluid flow and heat transfer due to the physical changes with different boundary conditions. The objective of the present study is to examine the comparison of heat and energy transportation in a moving top and bottom lid-driven square cavity while bottom wall is considered as wavy. In this paper, the flow attributes in a cavity has been studied where the top and bottom walls moves in same and opposite



direction. To describe the flow behavior, the pertinent parameters are analyzed graphically and numerically. The heat transfer rate is also compared with some respective previously published papers in tabular form.

Mathematical Modeling and Boundary Conditions

In this problem formulation, the bottom wall is considered as wavy. The top wall is kept at a uniform hot temperature (T_h) while the bottom wall is maintained at cold temperature (T_c). Under all circumstances $T_h > T_c$ condition is maintained. The left and right vertical walls are adiabatic and the horizontal walls are considered as lid-driven. The configuration under consideration is shown schematically in Figure 1. Both bottom and top walls are moving in the same direction from left to right in case I. Also, the top wall is moving from left to right while the bottom wall is moving in the opposite direction from right to left in the other case. The constant velocity (U_0) remains in the horizontal moving walls and having a gravitational force is in perpendicular direction to the movable bottom wall. The side length of the cavity is considered as H and all walls of the cavity have no-slip condition except horizontal walls.

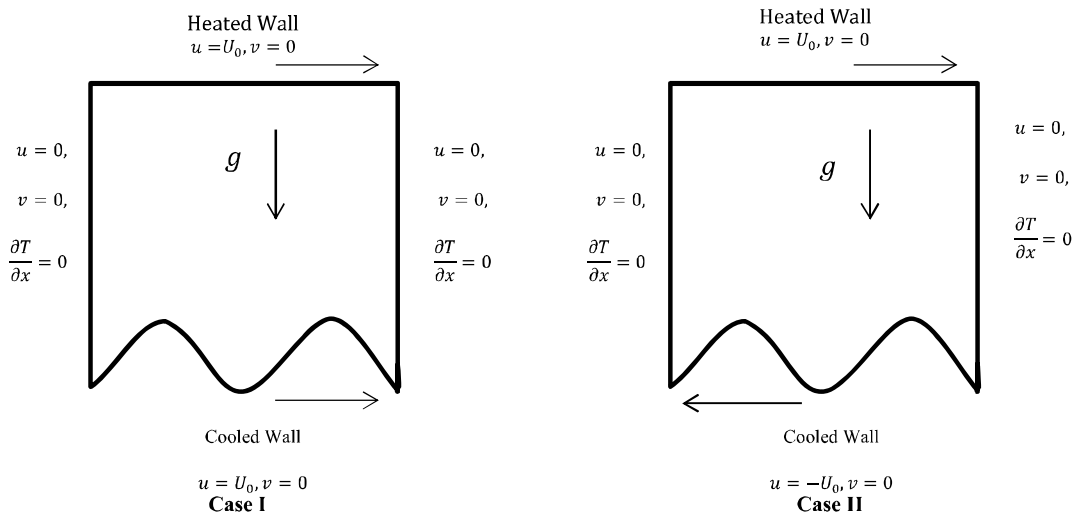


Figure 1: Computation Domain and boundary conditions

The fluid flow is considered as two dimensional. The property of viscosity is maintained and also treated as incompressible. The transportation of flow and heat distribution in the cavity are described by the Navier–Stokes equations. The buoyancy-driven flow is caused by a temperature and density difference in the flow field. For such type of flows, a body force term needs is included to the momentum equations in gravity direction to find out



the effect of local density differences. For temperature-driven flows, the Boussinesq approximation is often employed as $g(\rho - \rho_c) = g\beta(T - T_c)$, Where g is the acceleration due to gravity. While the viscous dissipation term is discarded, the following continuity, momentum and energy equation with Boussinesq approximation forms,

$$\frac{\partial u}{\partial x} + \frac{\partial v}{\partial y} = 0 \tag{1}$$

$$u \frac{\partial u}{\partial x} + v \frac{\partial u}{\partial y} = -\frac{1}{\rho} \frac{\partial p}{\partial x} + \nu \left(\frac{\partial^2 u}{\partial x^2} + \frac{\partial^2 u}{\partial y^2} \right) \tag{2}$$

$$u \frac{\partial v}{\partial x} + v \frac{\partial v}{\partial y} = -\frac{1}{\rho} \frac{\partial p}{\partial y} + \nu \left(\frac{\partial^2 v}{\partial x^2} + \frac{\partial^2 v}{\partial y^2} \right) + g\beta(T - T_c) \tag{3}$$

$$u \frac{\partial T}{\partial x} + v \frac{\partial T}{\partial y} = \frac{k}{\rho C_p} \left(\frac{\partial^2 T}{\partial x^2} + \frac{\partial^2 T}{\partial y^2} \right) \tag{4}$$

With boundary conditions, for **Case I and Case II:**

$$\begin{aligned} u = U_0, v = 0, T = T_h & \quad \text{for } 0 \leq x \leq H, y = H \text{ (top wall)} \\ u = 0, v = 0, \frac{\partial T}{\partial x} = 0 & \quad \text{for } x = 0, 0 \leq y \leq H \text{ (left wall)} \\ u = 0, v = 0, \frac{\partial T}{\partial x} = 0 & \quad \text{for } x = H, 0 \leq y \leq H \text{ (right wall)} \end{aligned} \tag{5}$$

$$u = U_0 \text{ or } -U_0, v = 0, T = T_c \quad \text{for } 0 \leq x \leq H, y = A[H - \cos(2n\pi x)] \text{ (bottom wall)}$$

The non-dimensional technique is to totally or partly removal of physical variables or quantities by a suitable substitution of variables. The transformed non-dimensional terms appeared in governing equations of motion by reducing the number of variables acting in the system. That’s why the mathematical technique is described easily and it reduces the number of times to solve the equation numerically. Here, using the following non-dimensional variables:

$$X = \frac{x}{H}, Y = \frac{y}{H}, U = \frac{u}{U_0}, V = \frac{v}{U_0}, P = \frac{p}{\rho U_0^2}, \theta = \frac{T - T_c}{T_h - T_c} \tag{6}$$

Therefore, we obtain the non-dimensional form of the equations as follows:

$$\frac{\partial U}{\partial X} + \frac{\partial V}{\partial Y} = 0 \tag{7}$$



$$U \frac{\partial U}{\partial X} + V \frac{\partial U}{\partial Y} = -\frac{\partial P}{\partial X} + \frac{1}{Re} \left(\frac{\partial^2 U}{\partial X^2} + \frac{\partial^2 U}{\partial Y^2} \right) \quad (8)$$

$$U \frac{\partial V}{\partial X} + V \frac{\partial V}{\partial Y} = -\frac{\partial P}{\partial Y} + \frac{1}{Re} \left(\frac{\partial^2 V}{\partial X^2} + \frac{\partial^2 V}{\partial Y^2} \right) + \frac{Gr}{Re^2} \theta \quad (9)$$

$$U \frac{\partial \theta}{\partial X} + V \frac{\partial \theta}{\partial Y} = \frac{1}{RePr} \left(\frac{\partial^2 \theta}{\partial X^2} + \frac{\partial^2 \theta}{\partial Y^2} \right) \quad (10)$$

The dimensionless boundary conditions become, for **Case I and Case II**:

$$U = 1, V = 0, \theta = 1 \quad \text{for } 0 \leq X \leq 1, Y = 1 \text{ (top wall)}$$

$$U = V = 0, \theta = 0 \quad \text{for } X = 0, 0 \leq Y \leq 1 \text{ (left wall)} \quad (11)$$

$$U = V = 0, \theta = 0 \quad \text{for } X = 1, 0 \leq Y \leq 1 \text{ (right wall)}$$

$$U = 1 \text{ or } -1, V = 0, \theta = 0 \quad \text{for } 0 \leq X \leq 1, Y = A[1 - \cos(2n\pi X)] \text{ (bottom wall)}$$

The non-dimensional commanding or governing parameters such as the Reynolds number Re , Grashof number Gr , Richardson number Ri , Prandtl number Pr are defined as $Re = \frac{U_0 H}{\nu}$, $Gr = \frac{g\beta\Delta TH^3}{\nu^2}$, $Ri = \frac{Gr}{Re^2}$ and $Pr = \frac{\nu}{\alpha}$, where, $\alpha = \frac{k}{\rho c_p}$ be the thermal diffusivity.

The wavy shape of the bottom wall is structured to obey the type $Y = A[1 - \cos(2n\pi X)]$, where n is the undulation number and A is the dimensionless wavy surface amplitude. At the walls, heat transfer rate or local Nusselt number (Nu_l), $Nu_l = \frac{hH}{k} = \left(-\frac{\partial\theta}{\partial n}\right)H$, where, h is the heat transfer coefficient, n is the normal direction on the surface (a negative sign refers to the heat transfer from the hot wall to the fluid). The

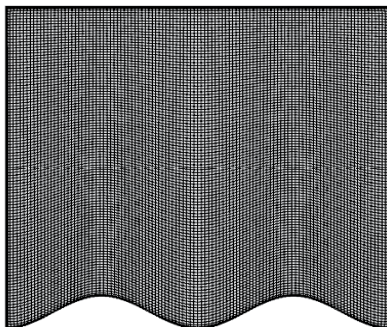
dimensionless normal temperature gradient can be written as $\frac{\partial\theta}{\partial n} = \frac{1}{H} \sqrt{\left(\frac{\partial\theta}{\partial X}\right)^2 + \left(\frac{\partial\theta}{\partial Y}\right)^2}$. The average nusselt number is, $\overline{Nu} = \frac{1}{l} \int_0^L Nuds$, where L is the total chord length of the wavy structure and l is the length of the coordinate along the wall.

Numerical Scheme

We have used the Galerkin weighted residual method for numerical scheme which is a very well-known finite element method also known as spectral method. In this procedure, the dimensionality scale is reduced so that the solution of the flow problem is quickly achieved. This weighted residual method gives the idea that a solution of the flow problem can be assumed analytically or also characterized as piecewisean alytically. The non-



linear partial differential has been transformed into ordinary differential equations. Then, solve the partial differential equations by setting the unknown results into a form of basis functions, accompanied by unknown coefficients or parameters, which is called the shape or trial solutions. The boundary and initial conditions both are must satisfied by the trial solutions. State the weighted residual to the value equal to zero and solve the equations to get the required solution. Construct successive approximations and detect the error terms. Finally, step out the convergence of the problem which can be made as the number of basis functions rises (Reddy and Gartling, 2010). In this paper, the respective solution domain is divided into a group of non-overlapping regions, is known as elements. In this domain, the governing nonlinear partial differential equations are converted into a system of integral equations. Then the numerical results can easily solve by the respective method. The Gauss's quadrature method is used to solve the integrating terms of these equations which forms a set of non-linear algebraic equations. These equations are then modified by imposing boundary equations which are transferred into algebraic equations by Newton-Raphson iteration technique (Saha et al., 2013). Then the linear equations are solved by Triangular Factorization method. It should be noted that, this method creates symmetric positive definite coefficient matrix if the differential operator is self-adjoint. It also requires less computational effort compared to the other methods such as least square method, subdomain collocation method etc. The numerical simulations are done using the COMSOL Multiphysics commercial solver. The working fluid is air. The Prandtl number equals to 0.712, other fluid physical properties are Density (ρ) is 1.00 kgm^{-3} and viscosity (μ) is $1,00 \times 10^{-2} \text{ kgm}^{-1}\text{s}^{-1}$. Mesh system used here is a mapped mesh and the size of the mesh is considered to be normal. 110×110 meshes are utilized for the flow computation, mesh is arranged as to be denser near the wall in order to resolve boundary layer flow with a vertical temperature gradient and time-independent study was executed. In this case the maximum element size considered to be 0.045 and the minimum element size 0.02 also the maximum element growth rate considered here 1.15. The resolution of curvature considered here 0.3. In this case, the number of degrees of freedom solved for 52804. Mesh system for 110×110 is given below. Here $A = 0,05, n = 2$



Mesh statistics

Minimum element quality	0.1128
Average element quality	0.667
Quadrilateral elements	12100
Edge elements	440
Vertex elements	4

Results and Discussion

The results are represented for numerical values of Gr, Re, A and n in graphical format. For all the cases, Prandtl number is treated here 0.712, the number of undulations are $n = 0, 1, 2$ and 3 and their amplitude is $A = 0.05$.

Case I: Wall movements in the same direction

Streamlines and Isotherms

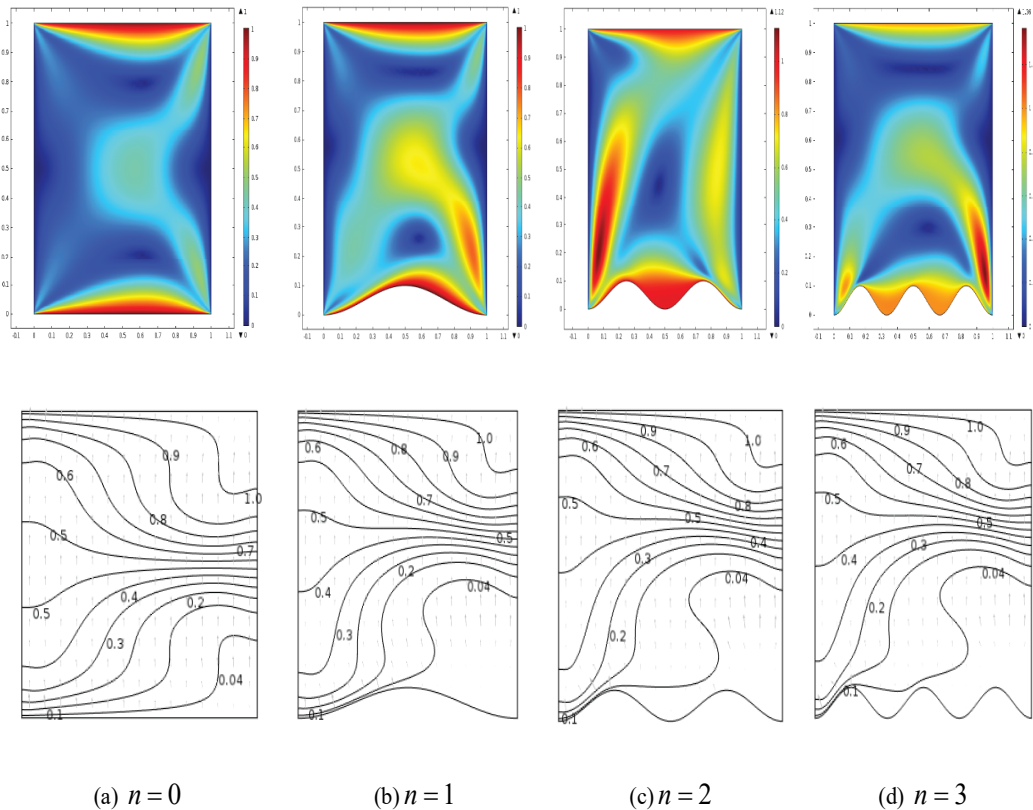


Figure 2: Streamlines and Isotherms obtained at $Re = Gr = 10^2$

Figure-2 shows the stream lines and isotherms for different undulations. The values are treated as $Re = 10^2$ and $Gr = 10^2$, so $Ri = 0.01$. When $Ri = 0.01$ is low, in Figure-2(a), forced convection is powerful through the flow field and controls over the natural convection. The double cellular (circular shaped) counter rotating vortices with two secondary cells at the top and bottom walls in all considered value of n . This happens due to the gradual reduction of natural convection and the fluid motion occurs from the

automatic moving lid of the horizontal walls. It is found from the results that each velocity profile makes an essential vortex. For $n = 0$, both streamline and isotherm contours are symmetrical along the horizontal centerline. Also, a clear increase in the isotherms near right of the horizontal centerline which specify that a strong significant effect of the temperature gradient in this specific region and decrease in left of the horizontal centerline can be detected as shown in Figure-2. It is seen that with the increasing the number of undulations, the right sided vortex grows faster and gathered isotherms near right of the horizontal centerline shifting upwards. $Gr = 10^4$ have approximately same results as $Gr = 10^2$ for streamlines and isotherms. Then we forward to case $Gr = 10^6$.

Figure-3 illustrates the streamlines and isotherms for various undulations and for $Re = 10^2$ and $Gr = 10^6$, $Ri = 100$. The decreasing behavior of cavity flow is shown from the above graphs with the increase of Gr . The higher values of Gr enhances the buoyancy effect of the flow field and free or natural convection occurs in the flow cavity grows slightly. When Richardson number becomes greater than unity, then the flow buoyancy

Streamlines and Isotherms

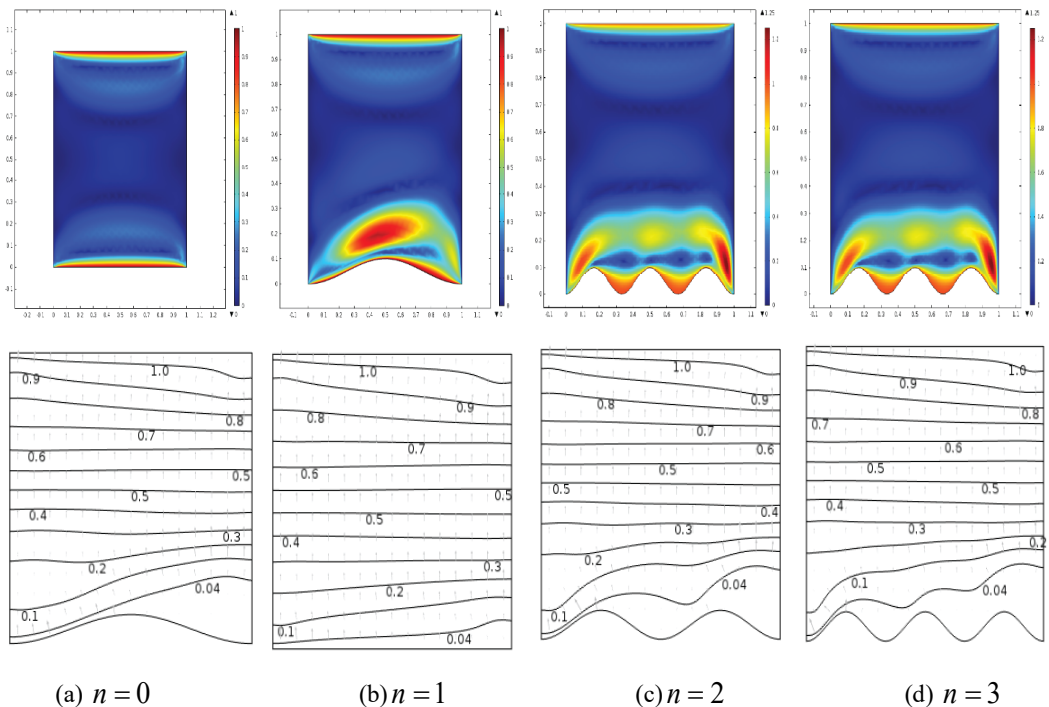


Figure 3: Streamlines and Isotherms obtained at $Re = 10^2$, $Gr = 10^6$



effect exceeds the enforcement of moving wall as shown in Figure-3. From the top wall, less energy is transmitted into the whole cavity and simultaneously, the conductive heat transportation plays a significant role in energy transfer. Therefore, the impact of the automatic lid driven walls go through the neighborhood of the interior section. From Figure-3(a), when streamlines and isotherms contour are symmetrical along the horizontal centerline, then the flow field of the whole cavity is subdivided into four primary vortices. It appears from Figure 3(c) and 3(d) that, different undulations must govern the streamlines arrangement in the surrounding area of the wavy surface by partitioning into two, three secondary vortices. The isothermal region enlarges to keep the most powerful natural convection effect throughout the whole cavity field. With the increasing number of undulations, isotherms close to right corner of the bottom wall shifts upwards directly. Inside the cavity, buoyancy force expands the flow rate and viscous effect is increasing by the bottom wall. The cavity flow around lower boundary area is separated at the highest point of wavy bottom area depending on various numbers of undulations. As the buoyancy effect grows powerful and exceeds the effect of moving wall, then heat transfer is mostly conductive in the cavity except the neighborhood area of top and bottom walls.

Case II: Walls movements in opposite direction

Streamlines and Isotherms

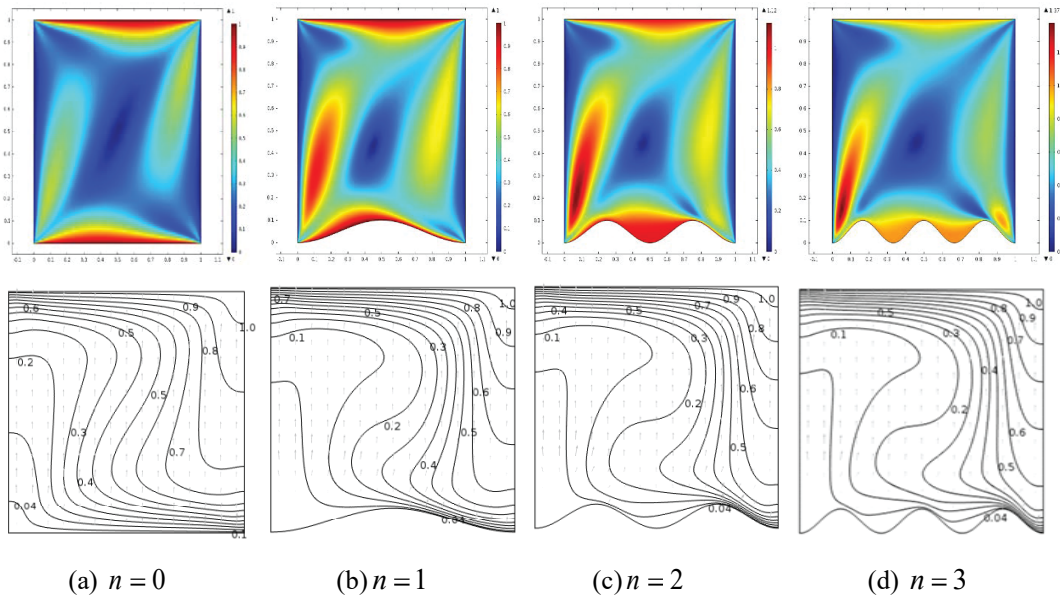


Figure 4: Streamlines and Isotherms obtained at $Re = Gr = 10^2$



Figure-4 illustrates the stream function and isotherm contours for various undulations. Here value of $Ri = 0.01$. Figure-4 shows that the forced convection is dominant over the cavity and generates the recirculation flow from the motion of the lids. A single clockwise circulation vortex is constructed from the streamlines of the flow field. The streamlines near to top left and lower right corners, generating some perturbations due to intrusion or friction of fluid flow to the horizontal walls for considered value of n . The isotherms are gathered also the upper left and lower right corner regions as such as streamline's arrangement. These congregated isotherms are lying like parallel kind for $n = 0$. Also, a clear increase in the isotherms is shown near the upper left and lower right corners. It indicates that the powerful temperature gradients are active in this region and decrease in the lower left corners can be detected as shown in Figure. This occurs due to the moving behavior of fluid. For the number of undulations $n = 1, 2$ and 3 the isotherm patterns are approximately same except in the neighbourhood of the bottom wall.

Streamlines and Isotherms

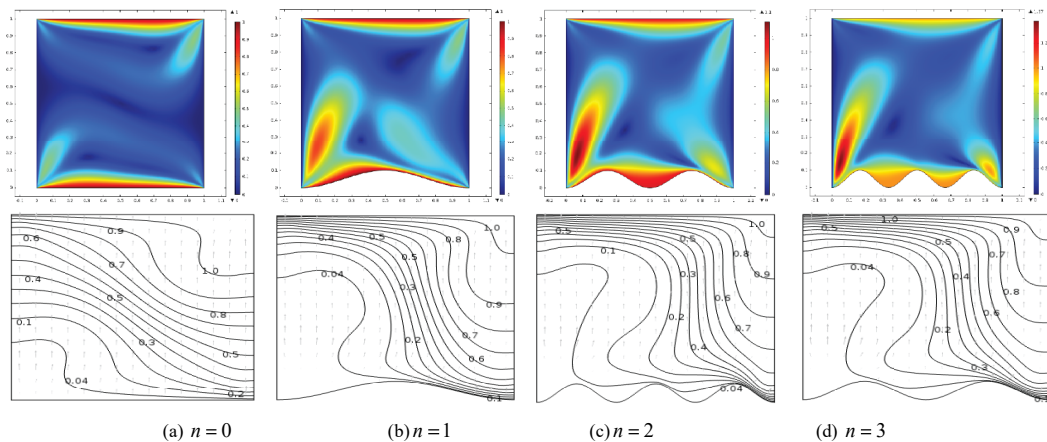


Figure 5: Streamlines and Isotherms obtained at $Re = 10^2$, $Gr = 10^4$

Figure-5 illustrates the stream function and isotherm contours for various undulations and for $Re = 10^2$ and $Gr = 10^4$, $Ri = 1$. For both streamlines and isotherms, there is slighter dominant effect of the moving lids. When $n = 0$ i.e. wavy surface is not happening at the bottom wall, the single primary vortex divide into two primary vortexes and forms a shape looks hour glass at the mid vertical plane. From Figure 5(b)-(d) analyzes that the undulation numbers where two vortexes merge together because of the opposite walls movement and makes a single primary vortex, the center of the vortex moved towards left. This phenomenon are different from the previous cases. When forced and natural convections are related to close ($Ri = 1$), a slight change of the isothermal lines behavior can be seen. It is noted that with the increasing number of undulations, the isothermal lines are close to left vertical wall is shifting upwards gradually.



Figure-6 illustrates the streamlines and isotherms for various undulations and for $Re = 10^2$ and $Gr = 10^6$. With the increase of Gr , the parametric effects due to driven cavity decreases. From the previous case to present, it is seen that if Gr increases, the buoyancy behavior of flow becomes stronger inside the cavity and gradually the free convection increases. Here, the Richardson number, $Ri = 100$.

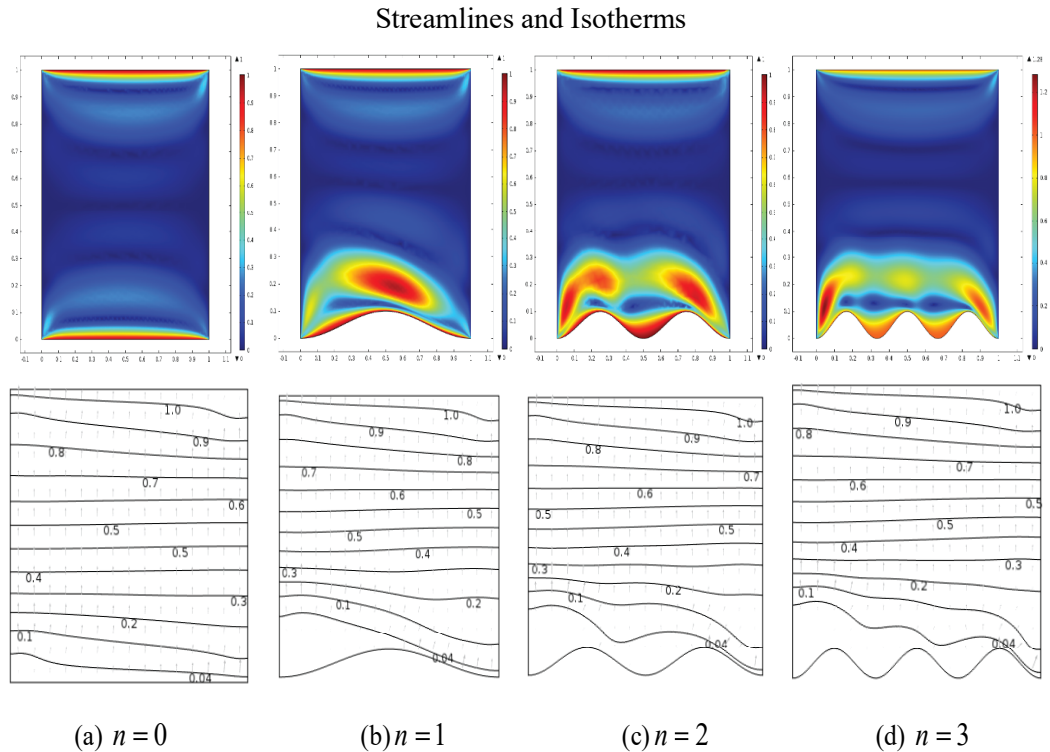


Figure 6: Streamlines and Isotherms obtained at $Re = 10^2$, $Gr = 10^6$

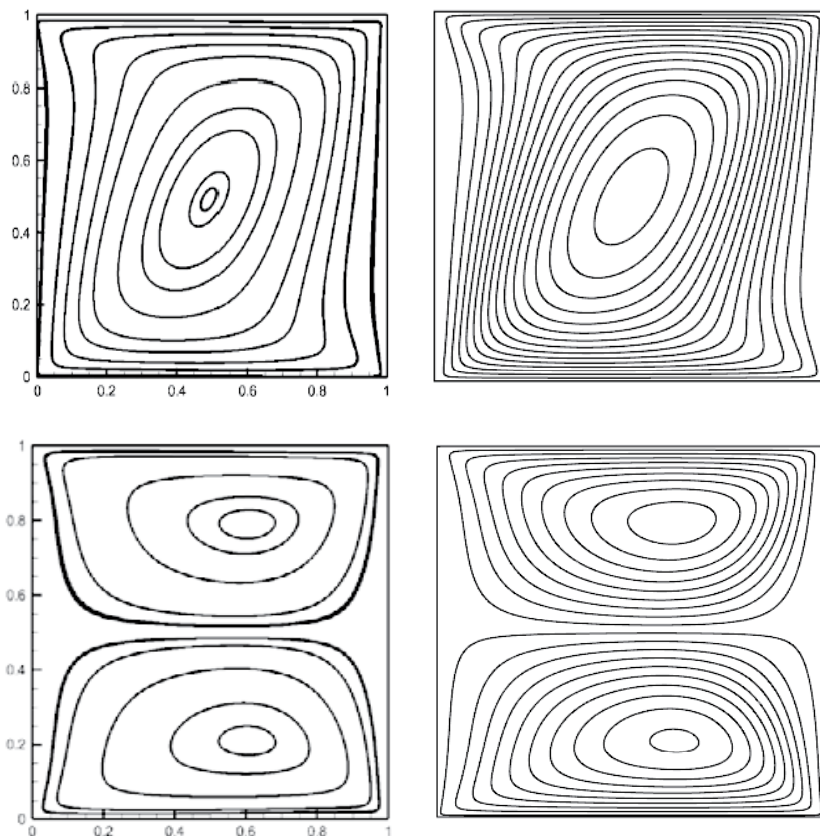
In case of the Richardson number becomes greater than 1, due to buoyancy effect outweighs the result of the moving wall. On the move of the top wall, less energy is transmitted away into the cavity and the conduction procedure has become stronger in the cavity. Therefore, the impact of moving lids cannot go far from the interior area. In Figure-6 (a) it is shown that the streamlines contour is symmetrical along the horizontal centerline and the flow field is subdivided into four primary vortices. From Figure-6 (c)-(d), it is clear that the undulation numbers make changes the streamlines gradually in the neighbourhood of the wavy bottom surface by partitioning into two, three secondary vortices respectively. Also for $n = 3$, each velocity vector forms separate primary



vortexes and also forms shapes like hour glass at the midway of the square cavity. The isothermal zone enlarges to occupy almost the cavity length because of powerful natural convective effect. With the increasing number of undulations, in the left corner position of the bottom wall, the isothermal lines slightly shift upwards.

Comparison

Now, the comparison is to be set graphically with the boundary conditions by making $n = 0$, $U = 0.1$ at both horizontal walls for case - I and $U = -0.1$ at bottom wall for case-II. The results are compared with (Arun S. and Satheesh A., 2015), which gives good agreement followed by each investigation.



(a) wall moving in the same direction (b) wall moving in the opposite direction

Figure 7: Comparison of stream lines between present study (right) and (Arun S. and Satheesh A., 2015) (left)



Table 1: Comparison of computed average Nusselt number with previously published researches.

Re	$Gr = 10^2$					
	Present Study	(Saha et al., 2013)	(Khanafer and Chamkha, 1999)	(Iwatsu et al., 1993)	(Waheed, 2009)	(Pal et al., 2018)
100	2.02	2.01	2.01	1.94	2.03	2.05
400	4.01	3.97	3.91	3.84	4.02	3.83
1000	6.44	6.28	6.33	6.33	6.48	6.15

Table 2: Average Nusselt number \overline{Nu} for various undulation at the upper wall:

Case I : Re	$Gr = 1e^4, A = 0.05, n = 0, 1, 2, 3$			
10	1.01247	1.08786	1.09665	1.10387
100	1.84886	2.3425	2.44235	2.47371
1000	7.67053	9.61045	10.53193	10.8121

Case II : Re	$Gr = 1e^4, A = 0.05, n = 0, 1, 2, 3$			
10	1.01154	1.0889	1.09774	1.10524
100	1.99767	4.70699	5.39151	5.60475
1000	15.16492	22.38919	23.05466	23.66641

The average Nusselt number comparison has been displayed in tabular form for different ranges of Re . The boundary conditions is presented for $n = 0$ and $U = 0$ at the lower wavy wall. The wonderful agreement is observed between the previous paper and the present study in Table 1. Table 2 shows average Nusselt number at the upper wall for various undulations.



Conclusion

Two different cases are observed by the movement of horizontal walls. The following findings may be summarized:

i) For lower values of Gr , only primary vortexes is found. For small values of Gr , with increasing n , there is a formation of secondary vortexes. For higher Gr , there is a formation of secondary minor vortexes. The quantity and size of the vortexes changes with increase of n . It is evident that when Re and Pr are fixed, then increasing with Gr the strength of circulation increases. The isotherms are extended along the horizontal linecauses to the expansion of circulation strength.

ii) For lower values of Richardson number, prominent rotating vortices are formed in the streamline and temperature fields. The increasing value of Richardson number obstructs flow and thermal distributions which happens to the increasing of imposed vertical temperature gradient. When Richardson number is higher or being one, some specific primary vortices are observed in streamline contour over the flow field. In this case, heat transfer procedure seems to be conduction except near the moving walls of the cavity. When the horizontal walls move in the same direction, rate of heat transfer becomes reduced compared to the other case. This is especially discernable for $Ri \leq 1$.

iii) The average Nusselt number (\overline{Nu}) decreases with increasing Richardson number and also increases with the increasing number of amplitude of the waves. While employing three undulations, average Nusselt number is at supreme position at low Richardson number, when horizontal wall moves in opposite direction.

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A COMPARATIVE STUDY AMONG PERTURBATION METHOD, TAYLOR SERIES METHOD, ADOMIAN DECOMPOSITION METHOD, FOR SOLVING AIRY'S DIFFERENTIAL EQUATION

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Abstract

This paper examines how the perturbation method for differential equation compares with the Taylor series and Adomian decomposition method. The comparison is shown in a table and graphically. It has been found that the perturbation series approximation performed better than the Taylor series solution and Adomian series solution. Also, the numerical solution and two-term perturbation series approximation are in good agreement.

Keywords: Perturbation method, Taylor series method, Adomian decomposition method, Airy's differential equation, Exact solution

Introduction

Many methods have been proposed and used to solve various types of differential equations accurately. However, numerous works are carried out for solving initial value problem (IVP) numerically using the perturbation method (Nayfeh A. 1973, Smith D. R. 1985, Hinch E. J. 1991, Kevorkian J. and Cole J.D. 1989, Kato T. 1980), Taylor series method (Corliss G. F. and Chang Y. F. 1982, Corliss G. F. and Kirlinger G. 1992, Pryce J. D. 1998, Kevorkian J. 1987), Adomian decomposition method (ADM) (Adomian G. 1992), Variational iteration method (VIM) (He J. H. 2007), and Runge-Kutta method (Islam M. A. 2005) to quickly obtain high precision. In (Wazwaz A.M. 2007), the author made a comparison of Homotopy perturbation method (HPM) and variational iteration method (VIM) for homogenous and nonhomogeneous advection problems. (Saha B. K., Mohiuddin A. M. and Parua S. 2017) analyzed a comparative study of HPM and other conventional methods for solving Fredholm integro-differential equation. In their studies, they found that Homotopy perturbation method is comparatively a very powerful mathematical tool than other conventional numerical methods for solving Fredholm integro-differential equation. Also, in (Ogunrinde, R. B., Fadugba, S. E. and Okunlola, J. T. 2012) author studied some numerical methods for solving initial value problems in ordinary differential equations.

This paper represents a comparative study between perturbation method and the conventional methods, namely the Taylor series method and Adomian decomposition method (ADM) for solving Airy's differential equations. From these methods, Perturbation theory (Nayfeh A. 1973, Smith D. R. 1985, Hinch E. J. 1991, Kevorkian J. and Cole J.D.

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1989, Kato T. 1980) is an extensive collection of iterative techniques involving a small parameter for obtaining the approximate solution. These methods are potent, and sometimes it is recommended to temporarily introduce the parameter in complex problems without small parameters. Most importantly, the actual problem is determined by setting $\varepsilon = 1$. The explicitly artificial variation to a perturbation problem may be the only way to make betterment (Bender C. M., Orszag S. A. 1999). The thematic approach of perturbation theory is to construe a complicated problem into an infinite number of comparatively easy ones. However, perturbation theory is most efficient when the first few steps elicit the essential features of the solution and the remaining ones give slight corrections (Bender C. M., Orszag S. A. 1999). This paper only focuses on a brief discussion of the perturbation method as detailed information can be found in (Nayfeh A. 1973, Smith D. R. 1985, Hinch E. J. 1991, Kevorkian J. and Cole J.D. 1989, Kato T. 1980) in any related works. For the self-sufficiency of this study, the Taylor series solution (Corliss G. F. and Chang Y. F. 1982, Corliss G. F. and Kirlinger G. 1992, Pryce J. D. 1998, Kevorkian J. 1987) and the ADM (Adomian G. 1992) are recalled for comparison.

Numerical Methods

Brief theory of Perturbation method

Perturbation theory includes a mathematical method used to find approximate solutions to related and simpler problems starting from the exact solutions. A critical feature of this technique is an intermediate step that breaks the problem into "solvable" and "perturbation" parts (Hinch E. J. 1991). If the problem cannot be solved precisely, we use the perturbation method to solve it. In the perturbation method, we use a small parameter to the mathematical description of the exactly solvable problem.

Perturbation theory leads to an expression for the desired solution in a formal power series in some "small" parameter known as a perturbation series that quantifies the deviation from the exactly solvable problem (Kevorkian J. and Cole J. D. 1989). The leading term in this power series is the solution of a completely solvable problem. On the contrary, other terms describe the deviation of the solution due to deviation from the original problem. Formally, we have for the approximation to the complete solution u , a series in the small parameter, as shown below:

$$u = u_0 + \varepsilon u_1 + \varepsilon^2 u_2 + \dots \dots \dots \quad (1)$$

Here, u_0 is a known solution to the exactly solvable initial value problem, and u_1, u_2, \dots represents the higher-order terms that can be found iteratively through some system procedures (Kevorkian J. and Cole J. D. 1989). These higher order terms in the series gradually get smaller for small ε . An approximate solution is obtained by truncating the series, usually by keeping only the first two terms, the initial solution and the "first-order" perturbation correction can be expressed as

$$u \approx u_0 + \varepsilon u_1 . \quad (2)$$



However, we cannot find the exact solution in closed form in perturbation methods. Considering an initial value problem (IVP),

$$z'' = f(x)z, \quad z(0) = z'(0) = 1 \tag{3}$$

where $f(x)$ is continuous. Eq. (3) has no closed-form solution. But, for a very special option of $f(x)$, which can be solved by perturbation method. Firstly, initiating the ε in the unperturbed problem so that the problem is solvable:

$$z'' = \varepsilon f(x)z, \quad z(0) = z'(0) = 1, \tag{4}$$

Secondly, assuming a perturbation expansion for $y(x)$ of the form,

$$z(x) = \sum_{n=0}^{\infty} \varepsilon^n z_n(x), \tag{5}$$

where, $z_0(0) = z'_0(0) = 1$, and $z_n(0) = z'_n(0) = 0$, ($n \geq 1$)

The term $z'' = 0$ is zeroth order problem which is obtained by setting $\varepsilon = 0$. And the solution that satisfies the initial conditions is $z_0(x) = 1 + x$. The $n - th$ order problem ($n \geq 1$) is obtained by substituting Eq. (5) into Eq. (4) and setting $i - th$ coefficient of ε^n ($n \geq 1$) equal to 0.

The result is

$$z''_n = f(x)z_{n-1}, \quad z_n(0) = z'_n(0) = 0 \tag{6}$$

Here, perturbation theory has replaced the differential equation Eq. (3) with a non-homogeneous differential equation Eq. (6). Generally speaking, as long as the solution of the related homogeneous equation is known, any non-homogeneous equation can be solved conventionally by the variation of parameter method (He J. H. 2007). However, the homogenous equation is precisely unperturbed. Thus, it is clear why the unperturbed equation can be solvable.

$$z_n = \int_0^x \int_0^r f(s)z_{n-1} dr ds, \quad n \geq 1 \tag{7}$$

Aiming to calculate successive terms in the perturbation series, Eq. (7) provides a simple iterative procedure

$$z(x) = 1 + x + \varepsilon \int_0^x dt \int_0^r (1 + s)f(s)ds + \varepsilon^2 \int_0^x dt \int_0^r f(s)ds \int_0^s dv \int_0^v (1 + u)f(u)du + \dots \tag{8}$$



Thirdly, calculating sum of the series. It can be shown that the absolute value of the N-th term of the series is bounded by $\varepsilon^N x^{2N} k^N (1 + |x|)/(2N)!$ for larger N. On the other hand, where k is an upper bound for $|f(r)|$ in the interval $0 \leq |r| \leq |x|$, so the series Eq. (8) is convergent for all x. Moreover, it is concluded that if $x^2 k$ is small, then the perturbation series will quickly convergent for $\varepsilon=1$. And the original problem can be accurately solved by only taking a few terms.

Brief theory of Taylor series method

Considering the one-dimensional initial value problem (IVP),

$$z' = f(x, z); \quad z(x_0) = z_0 \dots \dots \dots \tag{9}$$

The function f is composed of two variables say x and z, and x_0 & z_0 represent point on the solution curve.

Assuming that all the higher-order partial derivatives of z at the initial point x_0 exists, then according to the Taylor series (Corliss G. F. and Kirlinger G. 1992, Pryce J. D. 1998, Bender C. M., Orszag S. A. 1999, Kevorkian J. 1987) the value of z at any neighboring point x+h can be written as,

$$z(x_0 + h) = z(x_0) + h z'(x_0) + \frac{h^2}{2!} z''(x_0) + \frac{h^3}{3!} z'''(x_0) + \dots \dots \dots \tag{10}$$

Where the superscript “ ’ ” represents the derivatives with respect to x. Since, (x_0, z_0) is known, z' at x_0 can be obtained by evaluating $f(x_0, z_0)$.

Similarly, the higher order derivatives of z at $x = x_0$ can also be computed by using the following relation

$$\begin{aligned} z' &= f(x, z), \\ z'' &= f_x + f_z z', \\ z''' &= f_{xx} + 2f_{xz} z' + f_{zz} z'^2 + f_z z'' \\ &\dots \text{ and so on} \end{aligned}$$

Therefore,

$$\begin{aligned} z(x_0 + h) &= z(x_0) + hf + \frac{h^2(f_x + f_z z')}{2!} + \frac{h^3(f_{xx} + 2f_{xz} z' + f_{zz} z'^2 + f_z z'')}{3!} \\ &+ 0(h^4) \end{aligned}$$

Which is equivalent to

$$\begin{aligned} z(x) &= z(x_0 + x - x_0) \\ &= z_0 + (x - x_0)z'(x_0) + \frac{(x - x_0)^2 z''(x_0)}{2!} + \frac{(x - x_0)^3 z'''(x_0)}{3!} \\ &+ \frac{(x - x_0)^4 z^{(iv)}(x_0)}{4!} + \dots \dots \end{aligned}$$



Therefore, the value of z can be found by adding the above infinite series at any neighboring point $x_0 + h$. However, in any actual calculation, the summation has to be terminated after the p^{th} derivative term. The approximated formula is called the Taylor series approximation to z order of p . And, the error is order of $p + 1$. The same procedure can repeatedly apply to obtain z at the other points of x in the interval $[x_0, z_0]$ in a marching process.

Brief theory of the Adomian decomposition method

The Adomian decomposition method (ADM) is a well-known systematic procedure for solving linear or nonlinear and stochastic operator equations, including ordinary differential & partial differential equations (PDE's), integral & integro-differential equations, etc (Adomian G. 1992, He J. H. 2007). Adomian decomposition method allows solving the non-linear initial value problem (IVP) without nonphysical restrictive assumptions required by linear perturbation. In addition, the Adomian decomposition method does not require the use of Green's function, which complicates this analysis and calculation because Green's function is not easy to determine in most cases.

The main ADM principle of general non-linear equations has the following form,

$$Lu + Ru + Nu = g. \tag{11}$$

Invers operator L , with $L^{-1}(\cdot) = \int_0^x (\cdot) dx$, Eq. (11) can be expressed as,

$$u = L^{-1}(g) - L^{-1}(Ru) - L^{-1}(Nu). \tag{12}$$

The solution of Eq. (12) by ADM can also be written as the following infinite series,

$$u = \sum_{n=0}^{\infty} u_n \tag{13}$$

The term $Nu = \tau(u)$ is decomposed as nonlinear operator:

$$Nu = \sum_{n=0}^{\infty} A_n. \tag{14}$$

Where, A_n are Adomian polynomials, that can be defined as,

$$A_n = \frac{1}{n!} \frac{d^n}{d\mu^n} \tau \left[\sum_{i=0}^{\infty} \mu^i y_i \right]_{\mu=0} \quad n = 1, 2, 3, \dots \tag{15}$$

Using Eqs. (13) & (14) in Eq. (12) we have

$$u = \sum_{n=0}^{\infty} u_n = 0 - L^{-1}(R(u = \sum_{n=0}^{\infty} u_n)) - L^{-1} \left(\sum_{n=0}^{\infty} A_n \right), \tag{16}$$

Therefore, it can be written as

$$u_0 = \varphi + L^{-1},$$

$$u_1 = L^{-1}(R(u_0)) - L^{-1}(A_0),$$



$$\begin{aligned}
 u_2 &= L^{-1}(R(u_1)) - L^{-1}(A_1), \\
 &\vdots \\
 u_n &= L^{-1}R(u_{n-1}) - L^{-1}(A_{n-1}),
 \end{aligned}$$

Where,

$$\begin{aligned}
 A_0 &= \tau(u_0) = u_0^p, \\
 A_1 &= u_1 \tau'(u_0) = pu_0^{p-1}, \\
 A_2 &= u_1 \tau'(u_0) + \frac{1}{2} u_1' \tau''(u_0) = pu_0^{p-1}u_2 + \frac{p(p-1)}{2} u_1^2,
 \end{aligned}$$

Where, p is the exponent of the nonlinear term.

Airy's equation

The Airy function is named after the British astronomer and physicist George Biddell Airy (1801-1892), who found it in his early study of optics in physics (Airy, 1838). Harold Jeffrey has introduced the notation of Airy's equation, which is $Ai(x)$.

Airy's function

The Airy function of the first kind can be expressed by the improper Riemann integral for the actual value of x

$$Ai(x) = \frac{1}{\pi} \int_0^\infty \cos\left(\frac{t^3}{3} + xt\right) dt = \frac{1}{\pi} \lim_{b \rightarrow \infty} \int_0^b \cos\left(\frac{t^3}{3} + xt\right) dt. \tag{17}$$

Airy's Differential equation

The first kind of Airy function $Ai(x)$ is named after the British astronomer George Biddell Airy (1801–92). The function $Ai(x)$ and $Bi(x)$ represent the Airy functions of the second kind and sometimes also called the Bairy functions, are linearly independent solutions to the differential equation $\frac{d^2y}{dx^2} - ty = 0$ known as the Airy equation.

Example of Airy's Differential Equation

Considering the Airy's equation

$$y'' - ty = 0; \quad y(0) = y'(0) = 1 \tag{18}$$

And to find its solution by Perturbation method, Taylor series method and Adomian decomposition method for showing a comparison among those solutions.

The exact solution

The accurate solution of the differential Eq. (18) becomes,

$$\begin{aligned}
 y(t) &= \frac{1}{6} \left(-33^{\frac{1}{3}} AiryAi(t) Gamma\left(\frac{1}{3}\right) + 3^{\frac{5}{6}} AiryBi(t) Gamma\left(\frac{1}{3}\right)\right) \\
 &\quad + 33^{\frac{2}{3}} AiryAi(t) Gamma\left(\frac{2}{3}\right) + 33^{\frac{1}{6}} AiryBi(t) Gamma\left(\frac{2}{3}\right)
 \end{aligned}$$



The perturbation solution

Now aiming to find an approximate solution of the problem Eq. (18), using the perturbation method. Firstly, introducing a small parameter ε so that the unperturbed problem is solvable

$$y''(t) = \varepsilon ty; \quad y(0) = y'(0) = 1 \tag{19}$$

Assuming that the solution has the form of a perturbation series,

$$y(t) = \sum_{n=0}^{\infty} \varepsilon^n y_n(t) \tag{20}$$

Hence

$$y''(t) = \sum_{n=0}^{\infty} \varepsilon^n y''_n(t) \tag{21}$$

Now with the use of Eq. (20) and Eq. (21) in Eq. (19) gives,

$$\begin{aligned} \sum_{n=0}^{\infty} \varepsilon^n y''_n(t) &= \varepsilon t \sum_{n=0}^{\infty} \varepsilon^n y_n(t) \\ \text{or, } y''_0 + \varepsilon y''_1 + \varepsilon^2 y''_2 + \dots + \varepsilon^n y''_n + \dots &= \varepsilon t y_0 + \varepsilon^2 t y_1 + \varepsilon^2 t y_1 + \dots + \varepsilon^n t y_{n-1} + \dots \end{aligned} \tag{22}$$

Which gives a series of differential equation as follows

$$y''_0 = 0, \quad y_0(0) = 1, \quad y'_0(0) = 1. \tag{23}$$

$$y''_n = t y_{n-1}, \quad y_n(0) = 0, \quad y'_n(0) = 0, \quad n \geq 1. \tag{24}$$

Solving Eq. (23),

$$y_0 = 1 + t,$$

In case for $n=1$ the problem

$$y''_1 = t y_0, \quad y_1(0) = 0, \quad y'_1(0) = 0$$

has the solution as follows

$$y_1 = \frac{t^3}{6} + \frac{t^4}{12},$$

For $n = 2$

$$y''_2 = t y_1, \quad y_2(0) = 0, \quad y'_2(0) = 0,$$

The solution becomes

$$y_2 = \frac{t^6}{180} + \frac{t^7}{504},$$

Again for $n=3$

$$y''_3 = t y_2, \quad y_3(0) = 0, \quad y'_3(0) = 0,$$

Whose solution is

$$y_3 = \frac{t^9}{12960} + \frac{t^{10}}{45360},$$



Continuing in this way

$$y_4 = \frac{t^{12}}{1710720} + \frac{t^{13}}{7076160} ,$$

$$y_5 = \frac{t^{15}}{359251200} + \frac{t^{16}}{1.07 \times 10^{10}} ,$$

Thus the perturbation series is

$$y(t) = y_0 + \varepsilon y_1 + \varepsilon^2 y_2 + \varepsilon^3 y_3 + \varepsilon^4 y_4 + \varepsilon^5 y_5 + \dots \dots \dots$$

When $\varepsilon = 1$, the required solution becomes as follows

$$y(t) = 1 + t + \frac{t^3}{6} + \frac{t^4}{12} + \frac{t^6}{180} + \frac{t^7}{504} + \frac{t^9}{12960} + \frac{t^{10}}{45360} + \frac{t^{12}}{1710720} + \frac{t^{13}}{7076160} + \frac{t^{15}}{359251200} + \frac{t^{16}}{1.07 \times 10^{10}} + o(t^{17})$$

The Taylor series solution

The solution procedure of the Eq. (18) is given below. However, differentiating the Eq. (18) successively,

$$\begin{aligned} y'''(t) &= y(t) + ty'(t), \\ y^{(iv)}(t) &= 2y'(t) + ty''(t), \\ y^{(v)}(t) &= 3y''(t) + ty'''(t), \\ y^{(vi)}(t) &= 4y'''(t) + ty^{(iv)}(t), \\ y^{(vii)}(t) &= 5y^{(iv)}(t) + ty^{(v)}(t), \\ y^{(viii)}(t) &= 6y^{(v)}(t) + ty^{(vi)}(t), \\ y^{(ix)}(t) &= 7y^{(vi)}(t) + ty^{(vii)}(t), \\ y^{(x)}(t) &= 8y^{(vii)}(t) + ty^{(viii)}(t), \\ y^{(xi)}(t) &= 9y^{(viii)}(t) + ty^{(ix)}(t), \\ y^{(xii)}(t) &= 10y^{(ix)}(t) + ty^{(x)}(t), \\ y^{(xiii)}(t) &= 11y^{(x)}(t) + ty^{(xi)}(t), \\ y^{(xiv)}(t) &= 12y^{(xi)}(t) + ty^{(xii)}(t), \\ y^{(xv)}(t) &= 13y^{(xii)}(t) + ty^{(xiii)}(t), \end{aligned}$$

Putting $x = 0$ in each of the derivatives,

$$\begin{aligned} y''(0) &= 0, \\ y'''(0) &= 1, \\ y^{(iv)}(0) &= 2, \\ y^{(v)}(0) &= 0, \\ y^{(vi)}(0) &= 4, \\ y^{(vii)}(0) &= 10, \\ y^{(viii)}(0) &= 0, \\ y^{(ix)}(0) &= 24, \end{aligned}$$



$$\begin{aligned}
 y^{(x)}(0) &= 80, \\
 y^{(xi)}(0) &= 0, \\
 y^{(xii)}(0) &= 240, \\
 y^{(xiii)}(0) &= 880, \\
 y^{(xiv)}(0) &= 0, \\
 y^{(xv)}(0) &= 3120,
 \end{aligned}$$

Using these values, finally get the Taylor series expansion of $y(t)$ as follows

$$\begin{aligned}
 y(t) = 1 + t + \frac{t^3}{6} + \frac{t^4}{12} + \frac{t^6}{180} + \frac{t^7}{504} + \frac{t^9}{15120} + \frac{t^{10}}{45360} + \frac{t^{12}}{1995840} \\
 + \frac{t^{13}}{7076160} + \frac{t^{15}}{41926400} + \frac{t^{16}}{1698278400} + 0(t^{17}).
 \end{aligned}$$

Adomian decomposition method

The Eq.(18) can be written in the form

$$Ly - Ry = 0.$$

With $L = \frac{d^2}{dt^2}$, $R=t, L^{-1}(\cdot) = \int_0^t \int_0^t (\cdot) dt dt$. Then operating with L^{-1}

$$y(t) = y(0) + ty'(0) + L^{-1}Ry,$$

$$y_0 = 1 + t,$$

$$y_1 = L^{-1}Ry_0 = L^{-1}t(1 + t) = \int_0^t \int_0^t (1 + t^2) dt dt = \frac{t^3}{6} + \frac{t^4}{12},$$

In the similar manner,

$$y_2 = L^{-1}Ry_1 = \frac{t^6}{180} + \frac{t^7}{504},$$

$$y_3 = L^{-1}Ry_2 = \frac{t^9}{12960} + \frac{t^{10}}{45360},$$

$$y_4 = L^{-1}Ry_3 = \frac{t^{12}}{1710720} + \frac{t^{13}}{7076160},$$

$$y_5 = L^{-1}Ry_4 = \frac{t^{15}}{359251200} + \frac{t^{16}}{1698278400},$$

Using these values finally get the Adomian decomposition series for $y(t)$ as follows

$$y(t) = \sum_{i=0}^{\infty} y_i$$

$$y(t) = y_0 + y_1 + y_2 + y_3 + y_4 + y_5 + \dots \dots \dots$$

$$\begin{aligned}
 y(t) = 1 + t + \frac{t^3}{6} + \frac{t^4}{12} + \frac{t^6}{180} + \frac{t^7}{504} + \frac{t^9}{12960} + \frac{t^{10}}{45360} + \frac{t^{12}}{1710720} + \frac{t^{13}}{7076160} + \frac{t^{15}}{359251200} + \\
 \frac{t^{16}}{1698278400} + o(t^{17})
 \end{aligned}$$



Results and Discussion

Fig. 4 shows, the exact solution and Taylor series approximation of zeroth, 12th, and 15th order for the Eq. (18). It can be seen in Fig.4 that for the increment of the order of Taylor series approximation the result gets closer to the exact solution. Same trends can also be seen in Fig. 2 & Fig. 3 for the successive Perturbation and Adomain Decomposition series approximations respectively. However, the comparative study of the solutions of the Perturbation series, Taylor series, and Adomian Decomposition method to the exact solution for the Eq. (18) is shown in Fig.4. Figure 4 shows, the exact solution and perturbation series approximation with $\varepsilon = 1$ for the Eq. (18) are very good agreement. Moreover, a comparative study among the Perturbation series, Taylor series, and Adomian Decomposition method is established as shown in Table 1. Therefore, it can be concluded that the solution of Perturbation method converges much better than Taylor series and Adomian Decomposition method for solving initial value problem of the ordinary differential equations.

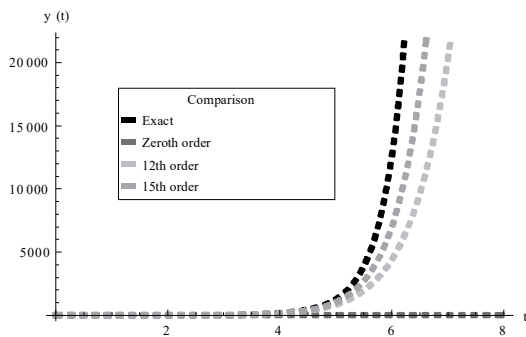


Figure 1. The successive Taylor series approximations of the Eq. (18).

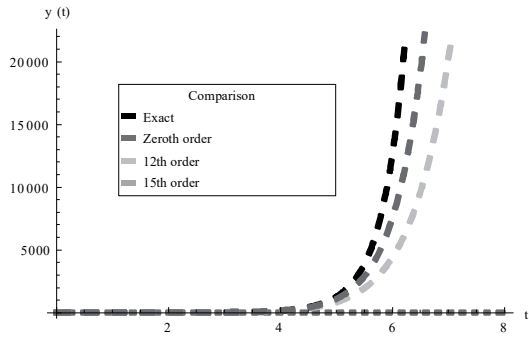


Figure 2. The successive Perturbation approximations of the Eq. (18).

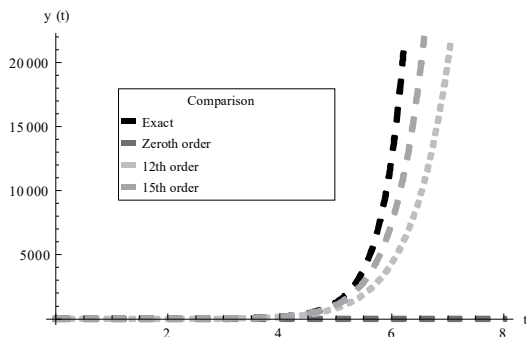


Figure 3. The successive Adomian Decomposition series approximations of the Eq. (18).

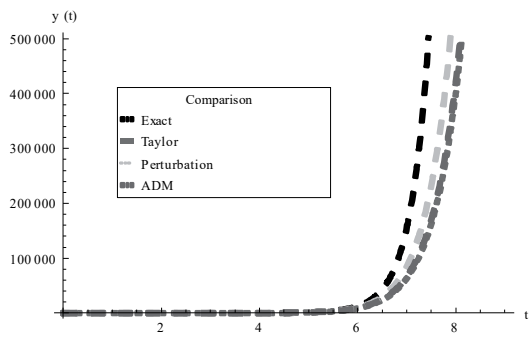


Figure 4. A comparison of Perturbation series, Taylor and Adomian Decomposition series approximations to the solution of the Eq. (18).

**Table 1:** Comparative result of the solution of Perturbation series, Taylor series and Adomian Decomposition method with error estimation.

t	Exact	Taylor	Perturbation	ADM	Error of Taylor's solution	Error of Perturbation solution	Error of ADM's solution
0	1	1	1	1	0	0	0
0.5	1.52614	1.52614	1.52614	1.52614	2.15496E-8	9.93042E-10	2.22045E-16
1	2.25764	2.25763	2.25764	2.25764	0.00001111	1.01688E-6	1.08447E-11
1.5	3.5859	3.58546	3.58596	3.5859	0.00043478	0.000058637	1.73974E-8
2	6.34196	6.33595	6.343	6.34195	0.00600216	0.00104079	3.34924E-6
2.5	12.4914	12.4438	12.501	12.4912	0.0475991	0.00965427	0.000202251
3	27.067	26.794	27.1253	27.0611	0.272935	0.0583887	0.0058858
3.5	63.7448	62.4323	63.9892	63.6409	1.3125	0.244396	0.103923
4	161.695	155.699	162.233	160.416	5.99654	0.537454	1.27896
4.5	438.894	410.283	436.593	426.88	28.6111	2.30108	12.0137
5	1268.52	1122.69	1228.32	1176.75	145.831	40.2077	91.7791

Conclusion

This paper conducted a comparative discussion of Airy's equation by Perturbation method, Taylor series solution and Adomian decomposition method. The proximate result shows perturbation method has better overall performance than other for finding the numerical solution of differential equations.

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THE EVOLVING ROLE OF FUNCTIONALISED PYROGLUTAMATES IN DRUG DISCOVERY

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Abstract

The pyroglutamate moiety is found to be important for exerting biological functions. This review paper has explored the widespread application of pyroglutamate and its derivatives in drug discovery.

Keywords: Pyroglutamate, Pyrrolidines, Pyroglutaminol, Drug Discovery, Michael Addition, Natural Product.

Introduction

Pyroglutamate **1**, also known as pyrrolidone carboxylate or 5-oxoproline, is a cyclised derivative of glutamic acid **2**. It derives from prolinatate **3** (Fig. 1).

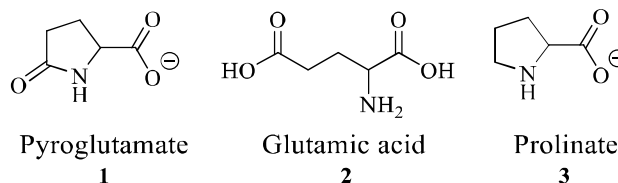


Fig. 1: Structures of pyroglutamate, glutamic acid and prolinatate

Pyroglutamate has been an important part of the synthesis of several important heteroatom-containing compounds, as well as other drug precursors. This work aims to study the use of pyroglutamates in various synthetic protocols of drug discovery process.

Pyroglutamate as One of the Building Blocks for Drug Discovery

Proline chimeras **4**, that is mono-substituted prolines bearing a substituent on the pyrrolidine ring, have been synthesised as useful tools (Chalmers et al. 1995; Mollica et al. 2012; Mollica et al. 2012; Paradisi et al. 2003) in drug discovery (Fig. 2, Mollica et al. 2014), since they represent side-chain modifications of naturally occurring amino acids in

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which restriction of the conformational freedom for χ^1 and χ^2 can change the bio-activity of peptides which contain them. It has been demonstrated that a proline chimera can modify the folding of a peptides by inducing features like β -turns in the peptide backbone without changing recognition behaviour (Chalmers et al. 1995).

Substituted pyroglutamic acids exhibit similar structural features to proline chimeras (Fig. 3, Mollica et al. 2014) and may be inserted into a bio-active peptide backbone, resulting in the modification of secondary structure and leading to improvement of interactions with the biological target (Paradisi et al. 2003).

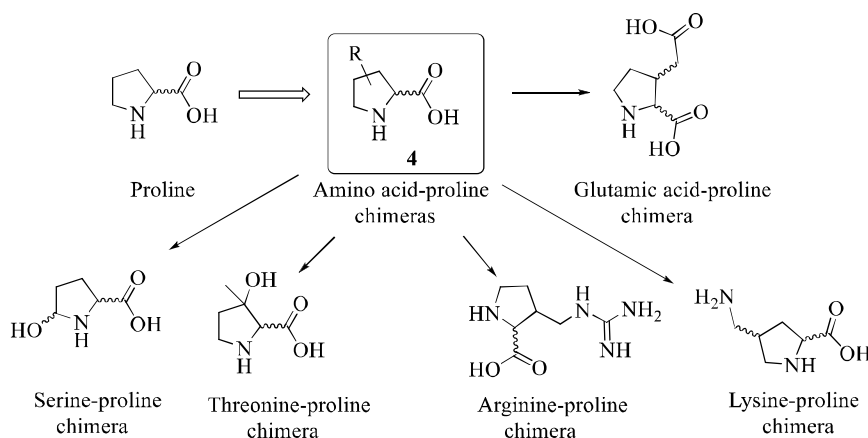


Fig. 2: Representative amino acid-proline chimeras

For example, Tsai et al. (Tsai et al. 2010) reported the use of 4-substituted pyroglutamate derivatives in the design and SAR studies of Fibroblast Activation Protein (FAP) inhibitors.

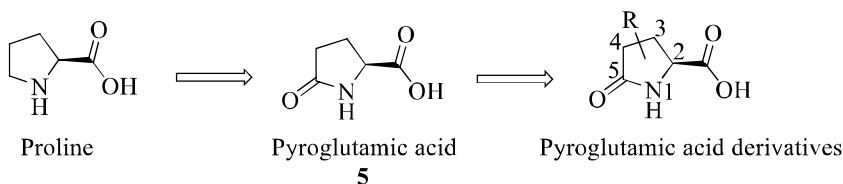


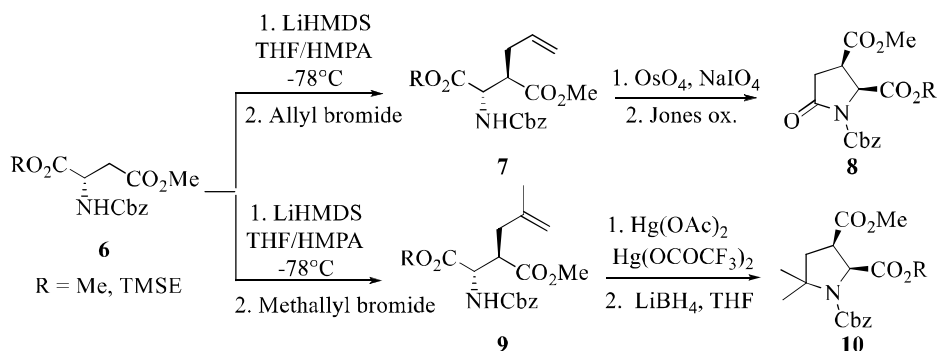
Fig. 3: Schematic representation of pyroglutamic acid structure and its derivatives

For this reason, the synthesis of pyroglutamic acid derivatives has attracted significant levels of interest, and some of the more important approaches are outlined below.



Synthesis of 3-Substituted Pyrrolutamic Acid Derivatives

3-Substituted Pyrrolidines and Pyrrolidinones by Hanessian

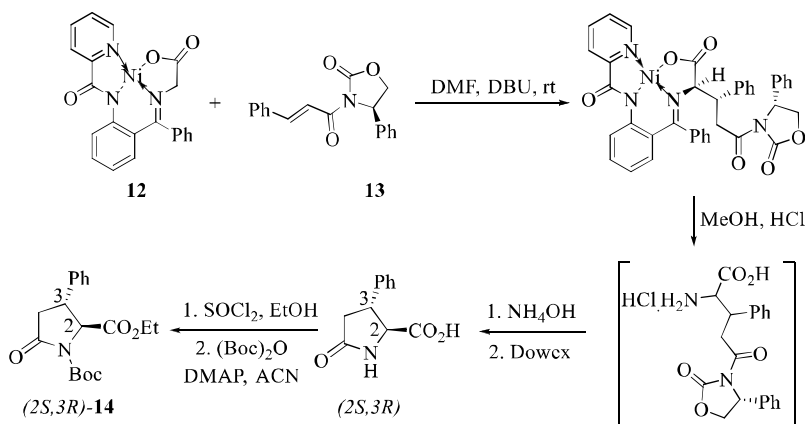


Scheme 1: Synthesis of 2,3-*cis*-substituted pyrrolidines and pyrrolidinones

Hanessian and Margarita (Hanessian et al. 1998) reported the synthesis of 3-substituted pyrrolidines and pyrrolidinones by modifying the γ -unsaturated side-chain of allylated amino acid derivatives (Scheme 1). Pyrrolidinone **8** was prepared from the ester **6** by dihydroxylation and oxidation. Alternatively, cyclisation of **9** using Hg(OAc)₂ and demercuration of the resulting product yielded 5,5-dimethyl-pyrrolidine diester **10** (Cardillo et al. 1990).

3-Phenylpyroglutamate via Asymmetric Michael Addition Reaction

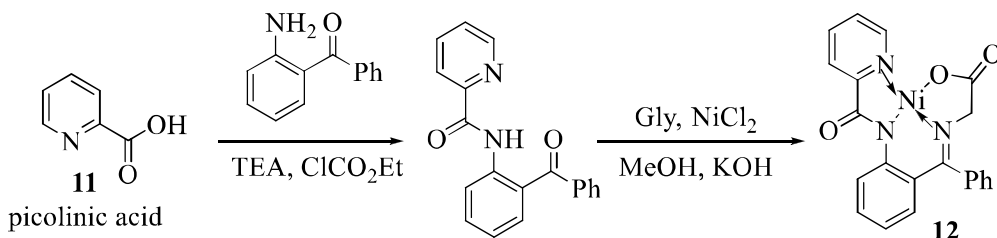
A useful synthetic procedure in the synthesis of pyroglutamates was reported by Soloshonok (Soloshonok et al. 2004), which involves the reaction between the glycine Ni(II) complex **12** and oxazolidinone-2-one **13** to yield enantiomerically pure 3-substituted pyroglutamate **14** (Scheme 2).



Scheme 2: Michael Addition methodology for the synthesis of 3-phenylpyroglutamate



Nickel complex **12** was easily prepared from the picolinic acid **11** as reported by Ueki (Scheme 3, Ueki et al. 2003).



Scheme 3: Preparation of Ni complex **12**

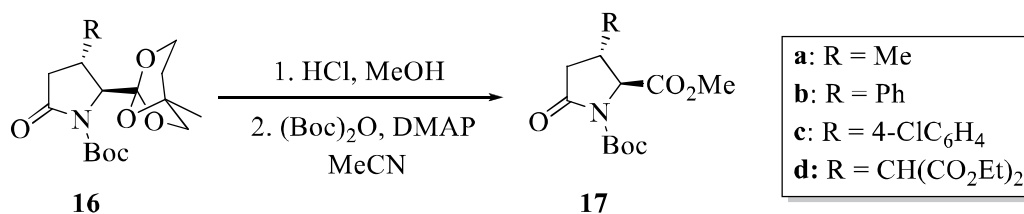
Michael Addition to Unsaturated Orthopyroglutamate Derivative

The conjugated double bond in the 3,4-didehydro derivative of pyroglutamate facilitates nucleophilic attack at the 3-position. Oba described the stereoselective introduction of substituents at the 3-position of pyroglutamate derivatives via Michael addition to 2,7,8-trioxabicyclo [3.2.1] octane **15** (ABO ester) (Table 1, Oba et al. 2009).

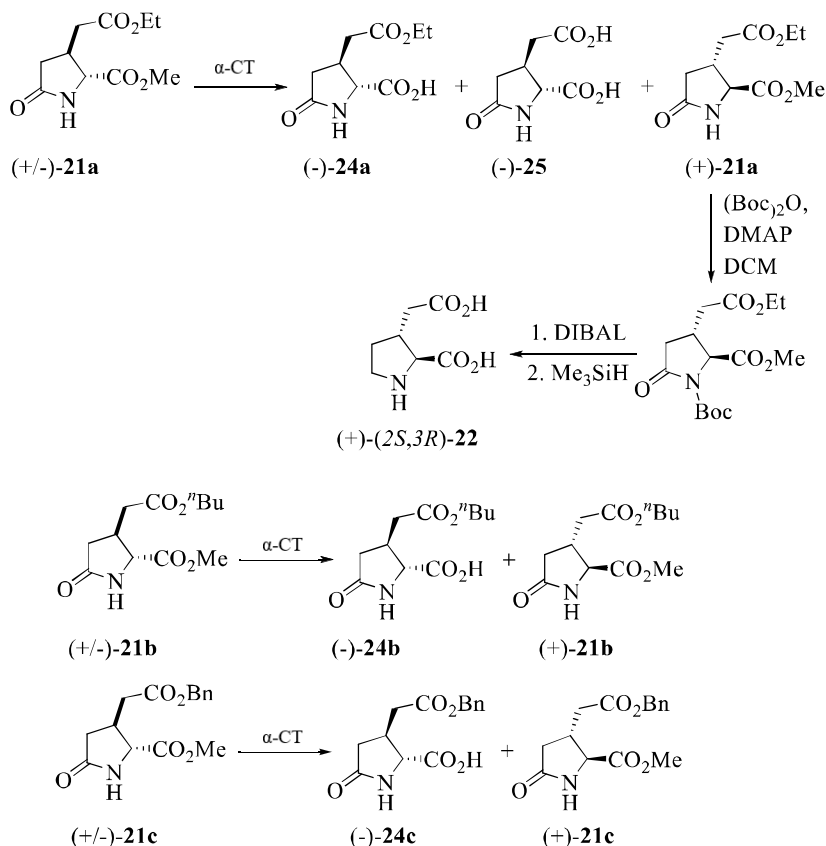
Table 1: Michael addition to unsaturated orthopyroglutamate **15**

	SL	Reagent	R	Product
	1	Me ₂ CuLi	Me	16a
	2	Ph ₂ CuMgBr	Ph	16b
	3	(4-ClC ₆ H ₄) ₂ CuMgBr	4-ClC ₆ H ₄	16c
	4	NaCH(CO ₂ Et) ₂	CH(CO ₂ Et) ₂	16d

The ABO ester **16a-d** was converted to the methyl ester by HCl-promoted methanolysis followed by the reprotection of the amido group with a Boc group, yielding pyroglutamate derivatives **17a-d** in good yields (Scheme 4, Oba et al. 2009).



Scheme 4: Synthesis of 3-substituted pyroglutamates



Scheme 6: Enzymatic hydrolysis and conversion to pyroglutamate derivative

As the *trans*- and *cis*- diastereomers were not separable by FCC, each mixture was subjected to enzymatic resolution with the most selective hydrolytic enzyme being alpha-chymotrypsin (α -CT) (Table 2, Felluga et al. 2012).

Table 2: Key results of the hydrolysis of mixtures of **21a-c** and **23a-c** with α -CT.

Substrate (relative ratio)	E	Ca. 20% Conversion		Ca. 80% Conversion	
		Time	Acid [ee %], (yield)	Time	Unreacted Ester [ee %], (yield)
21a + 23a (9:1)	nd	10 min	(-)- 25 [65] (16)	30 min	(+)- 21a [>99] (16)
21b + 23b (9:1)	10	2 h	(-)- 24b [72] (15)	8 h	(+)- 21b [>99] (16)
21c	5	8 h	(-)- 24c [61] (21)	36 h	(+)- 21c [95] (22)

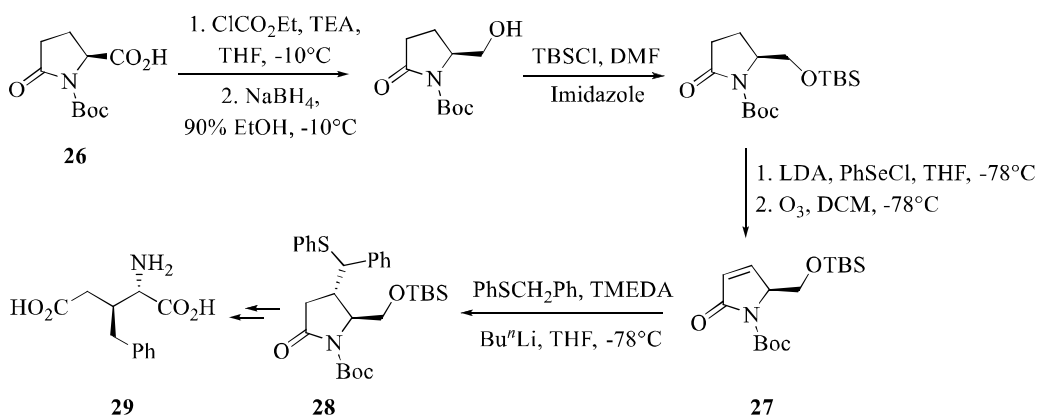
nd = not determined



Application of 3-Substituted Pyroglutamates and Pyroglutaminols

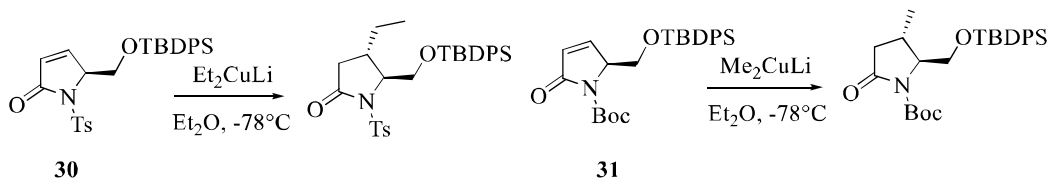
Pyroglutamate and its derivatives are widely used in asymmetric synthesis because of their easy modification and functionalisation at ring positions as well as side-chains. Some examples of the application of pyroglutamate derivatives are the synthesis of kainic acid derivatives, carbapenems, neurotransmitter, PKC modulators, antihypertensive and gastroprotective substances and antibiotics.

Yanagida (Yanagida et al. 1989; Yanagida et al. 1996) reported the synthesis of an acyclic analogue of the kainoids to examine their neuroexcitatory activity. Michael addition of lithiated benzyl phenyl thioether to the α , β -unsaturated lactam **27** gave adduct **28**, which was transformed to (2*S*,3*S*)-3-benzylglutamic acid **26**, an acyclic analogue of kainoids, after several steps (Scheme 7). The lactam **27** was prepared from *N*-Boc-L-pyroglutamic acid **29** by a literature procedure (Ohfuné et al. 1982).



Scheme 7: Synthesis of (2*S*,3*S*)-3-benzylglutamic acid **29**, an acyclic analogue of kainoids

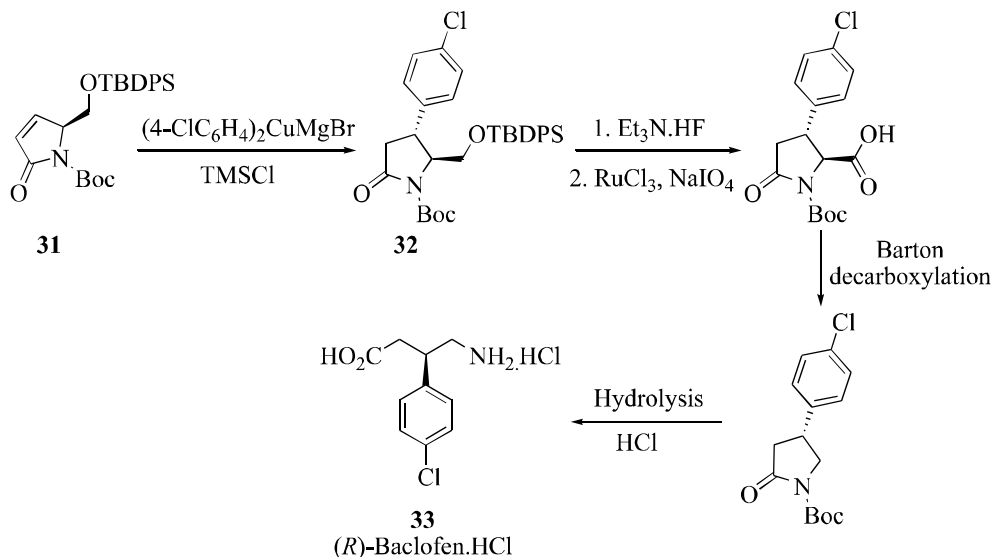
The γ -lactam nucleus can be synthesised diastereoselectively via the Michael addition of lithium diethylcuprate to the *O*-silylated *N*-tosyl-didehydropyroglutaminol **30** (Somfai et al. 1991). A similar transformation was reported by Woo for *N*-Boc compound **31** (Scheme 8, Somfai et al. 1991; Woo et al. 1991).



Scheme 8: Transformation of didehydropyroglutaminols

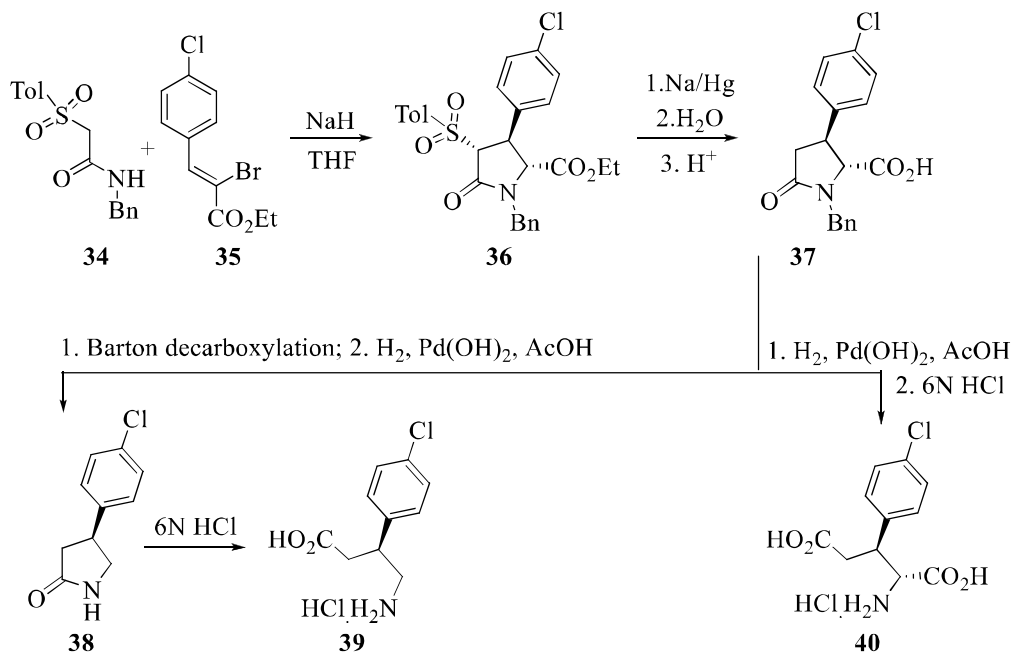


The same strategy has been used for the preparation of (*R*)-baclofen, a derivative of the inhibitory neurotransmitter GABA. The synthesis started with a Michael addition using excess arylcuprate and trimethylsilyl chloride to yield lactam **32**. Oxidation and Barton decarboxylation transformed the compound **32** into a γ -lactam, which was then hydrolysed to desired compound, (*R*)-baclofen **33** (Scheme 9, Herdeis et al. 1992).



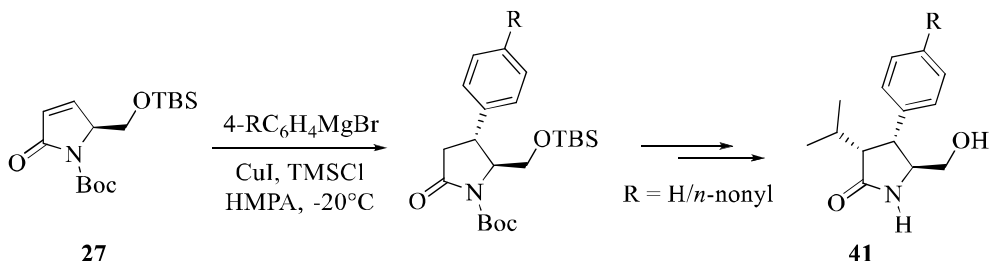
Scheme 9: Synthesis of (*R*)-baclofen via 3-arylpyroglutamic acid

Baclofen was found to be a selective and therapeutically useful GABA_B agonist (Kerr et al. 1992; Berthelot et al. 1991; Kerr et al. 1993). Chlorphleg is a glutamic acid analogue having selective enhancement on the excitatory and depolarizing action of L-HCA on the neuron of amphibian and mammalian central nervous system (Davies et al. 1985; Zeise et al. 1988; Ito et al. 1991). Chang and co-workers (Chang et al. 2003) reported the use of a 3-arylpyroglutamic acid for the synthesis of baclofen and chlorphleg (Scheme 10). The stereo- and regioselective [3+2] annulation reaction of α -sulfonylacetamide **34** with (*Z*)- β -substituted α -bromoester **35** afforded single pyroglutamate isomers **36**, which were converted to acid **37** via desulfonation and hydrolysis. Application of Barton's decarboxylation procedure (Barton et al. 1988) followed by debenzoylation yielded pyrrolidine-2-one **38**. Finally, hydrolysis of **38** by HCl afforded racemic baclofen hydrochloride **39**. To access chlorphleg **40**, acid **37** was directly subjected to debenzoylation and hydrolysis.

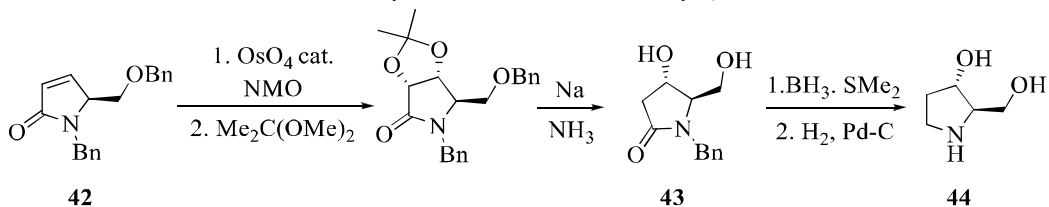


Scheme 10: Synthesis of baclofen **39** and chlorphleg **40** via 3-arylpyroglutamic acid²⁴

Qiao et al. (Qiao et al. 1998) described the stereoselective synthesis of pyrrolidones **41**, which are very active as protein kinase C (PKC) modulators (Scheme 11).



Scheme 11: Synthesis of PKC modulators by Qiao et al.

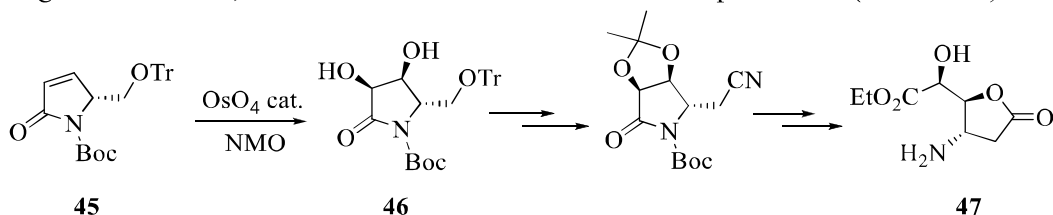


Scheme 12: Synthesis of (2*R*,3*S*)-3-hydroxy-2-hydroxymethylpyrrolidine **44**.



Pyrrolidinone and pyroglutaminol derivatives have importance for the synthesis of bio-active compounds. The dibenzyl-protected dihydroglutaminol **42** can be used as a precursor to prepare lactam **43** via dihydroxylation and reduction. Lactam **43** was transformed to castanodiol hydrochloride **44** by reaction with borane followed by hydrogenation (Scheme 12, Ikota et al. 1988).

The (*R*)-pyroglutaminol derivative **45** has been used by Ikota et al. (Ikota et al. 1989) for the synthesis of compound **47**, a precursor of (*2S,3S,4S*)-4-amino-2,3-dihydroxyhexanedioic acid which is a component of the gastroprotective substance AI-77-B (Shimajima et al. 1982). The transformation starts by *cis*-hydroxylation of **45** to **46**, as a single diastereomer, which was transformed into the desired product **47** (Scheme 13).



Scheme 13: Synthesis of **47**, a precursor of (*2S,3S,4S*)-4-amino-2,3-dihydroxyhexanedioic acid derivative

Yamada et al. (Yamada et al. 2008) developed the methodology for an efficient asymmetric synthesis of the functionalised pyroglutamate scaffold **48** common to oxazolomycin A and neoxazolomycin (Fig. 5).

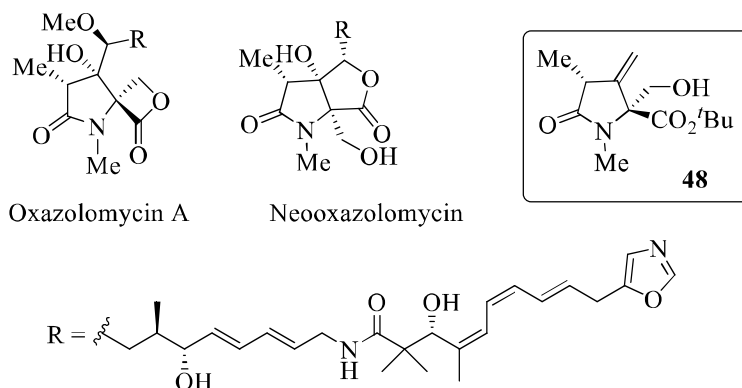
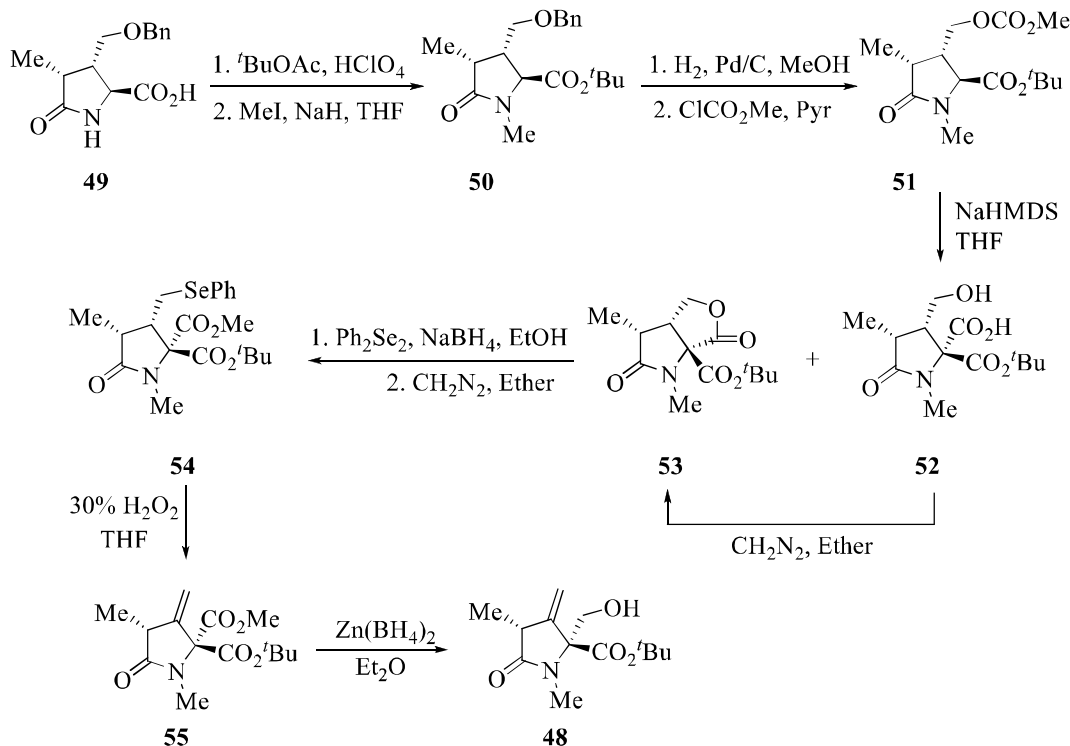


Fig. 5: Structure of pyroglutamate scaffold **48** common to oxazolomycin A and neoxazolomycin

The 3,4-disubstituted pyroglutamic acid **49**, after protection of carboxyl functional group as *tert*-butyl ester and subsequent *N*-methylation gave **50**, which upon the removal of the benzyl group at C3 followed by carboxymethylation of the resulting alcohol, delivered the



carbonate **51** (Scheme 14, Yamada et al. 2008)). The treatment of **51** with NaHMDS afforded a mixture of γ -butyrolactone **53** and its hydrolysed product **52**. γ -Butyrolactone has been prepared as the only product via treatment of the mixture of **52** and **53** with diazomethane. Lactone ring opening results from phenylselenide attack to introduce a suitable leaving group at C3 and the resultant product was esterified to give diester **54**. In the following step, the leaving group could be removed using hydrogen peroxide. Finally, pyrroglutamate scaffold **48** was accessed by reduction of the methyl ester with $\text{Zn}(\text{BH}_4)_2$.



Scheme 14: Synthesis of pyrroglutamate scaffold **48** common to oxazolomycin A and neooxazolomycin

Some Examples of Lactam-Derived Natural Products

(-)-Bulgecinine

The microorganisms *Pseudomonas acidophila* and *Pseudomonas masoacidophila* (Shinagawa et al. 1984) were found to produce a substance named bulgecin **56**, which induces bulge formation (Tomoshige et al. 2018; Shinagawa et al. 1985) in co-operation with β -lactam antibiotics (Fig. 6).

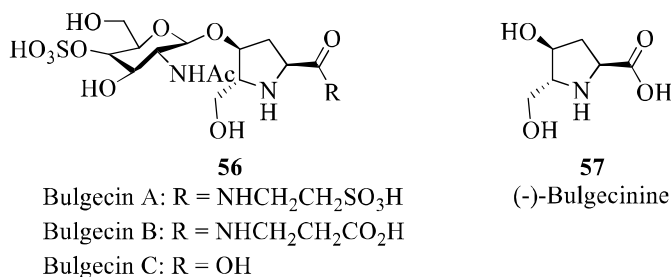
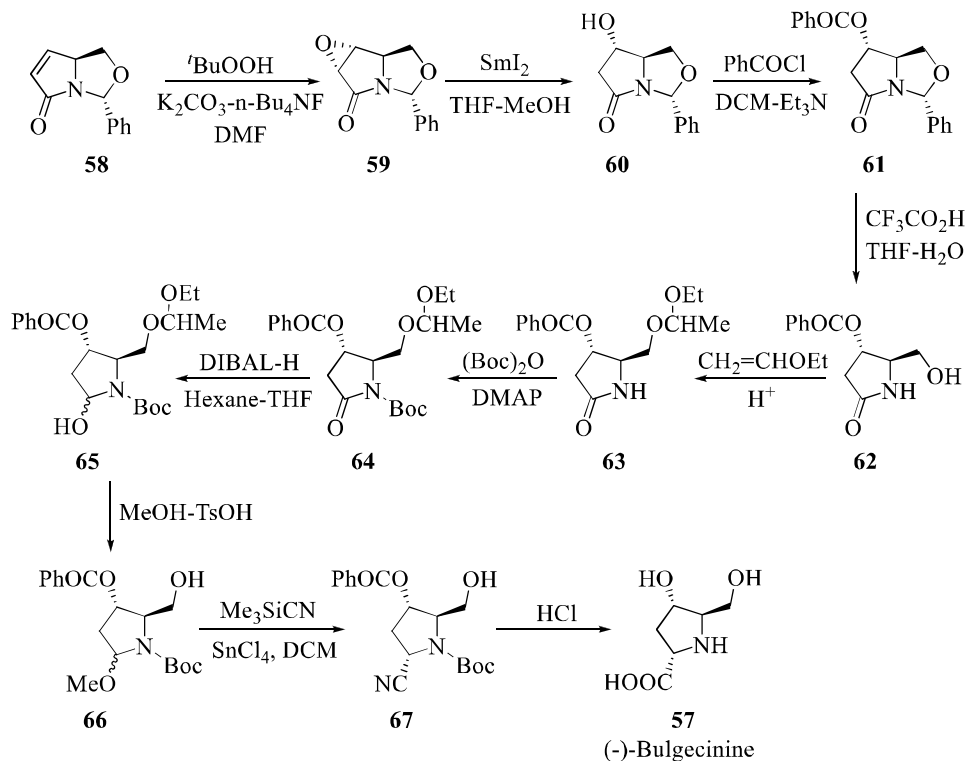


Fig. 6: Structure of bulgecin **56** and (-)-bulgecinine **57**

(-)-Bulgecinine **57** is a non-proteinogenic amino acid, and a common constituent of *O*-sulfonated glycopeptide bulgecins, found in the culture broth of the same organisms (Shinagawa et al. 1984).

Panday et al. (Panday et al. 1997) reported the use of a pyroglutamate derivative for the synthesis of (-)-bulgecinine **57** (Scheme 15).



Scheme 15: Synthesis of (-)-bulgecinine **57** using pyroglutamate derivative



They started with bicyclic γ -lactam derivative **58**, which was converted to 6-hydroxy bicyclic derivative **60** via epoxidation and ring opening. The 6-hydroxy group was protected as the benzoate **61**, which, upon acidic hydrolysis with trifluoroacetic acid, afforded 4-benzyloxypyroglutaminol **62**. The hydroxyl group at C-5 was protected with ethyl vinyl ether prior to *N*-Boc protection of the free amine to give **64**. Selective partial reduction of the γ -lactam carbonyl of **64** with DIBAL-H followed by treatment with MeOH/HCl yielded α -methoxycarbamate **66** as mixture of diastereomers. Stereoselective nucleophilic addition of cyanide to α -methoxycarbamate **66** afforded nitrile **67**, which was hydrolysed with 6N HCl to give (-)-bulgecinine **57**.

Equisetin

Equisetin (Jeong et al. 2015; Kong et al. 2014; Sims et al. 2005) is an example of natural product class containing the 3-acyltetramic acid (2, 4-pyrrolidinone) core structure (Fig. 7).

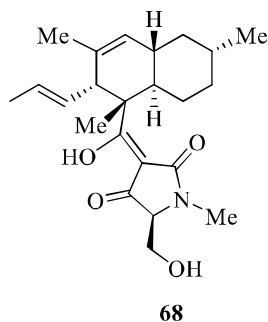


Fig. 7: Structure of equisetin

It was isolated as a metabolite from the white mould *Fusarium hererosporum* by Hesseltine and co-workers in 1974 (Burmeister et al. 1974), which shows potent antibiotic activity and HIV inhibitory activity.

Conclusions

Pyroglutamic acid derivatives has attracted significant levels of interest, and some of the more important aspects are outlined in this review. Detailed study on the pyroglutamate moiety as an important tool in drug discovery, synthetic strategies of 3-substituted pyroglutamates and their immense applications, representative examples of pyroglutamate derived natural products has been carried out enormously and presented all the way through this report.



Acknowledgements

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