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Journal of ISAS

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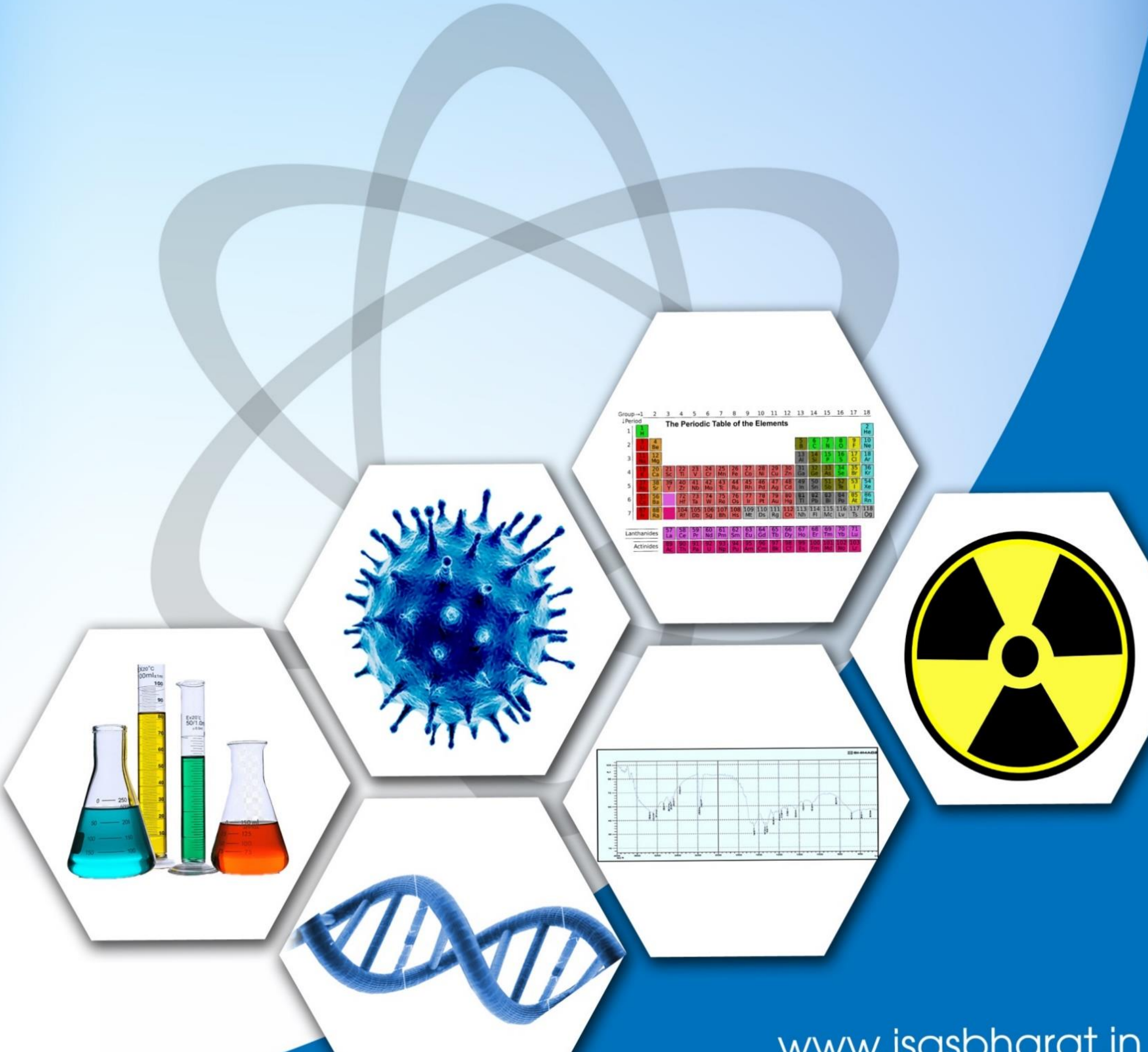
Indian Society of Analytical Scientists



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Journal of ISAS

An open access peer reviewed quarterly e-journal published by Indian Society of Analytical Scientists

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- **Key words: 5-6**
- **Introduction**
- **Experimental**
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No. RCUB/VCO/2023-24/21

Date: 13-06-2023

MESSAGE

I am happy to note that 'Indian Society of Analytical Scientists' (ISAS, https://isasbharat.in/), a prime scientific national body has started its own open access quarterly e-journal (https://isasjournal.isasbharat.in/), **J. ISAS** since July 2022 and the upcoming special `Anniversary Issue', to be published in July 2023 online over scientific deliberations from eminent personalities. I am confident that due to diligent and sincere efforts of the entire team associated with publication process; this journal has a bright future in the coming years by providing an ideal forum for exchange of information from different branches of analytical sciences.

J. ISAS has got ISSN No and each article is assigned with DoI. It is important to note that there is no publication/ processing charge in this open access journal, unlike many other journals by the well-known publishes.

Indeed, it is necessary to encourage the indigenous journals especially by the Professional bodies like ISAS because of the continuously increasing research publications in India (next only to China and USA).

I had the opportunity to inaugurate (as president) the ISAS Belagavi Chapter on 14-05-2021 (which is functioning from Dept. of Chemistry, Rani Channamma University, RCU), and pleased to know that it has received Best Chapter Award 2022 as well as Chairman of ISAS Belagavi Chapter (Prof. J. Manjanna,) has been conferred with ISAS Award of Excellence and ISAS Honorary Fellowship. Further, ISAS Belagavi Chapter has organized National Conference during Dec 15-16, 2022 in RCU campus. I am happy to learn that ***Prof. J. Manjanna*** *has been elected as Vice-President of ISAS HQ for 3 years from April 2023.*

With this background, I sincerely wish a great success to **J.ISAS** for making special impression in the minds of scientific community.

13/6/23

Vice Chancellor
Rani Channamma University
Belagavi

बी. सरवणन
उत्क्रिष्ट बैज्ञानिक एबं
निदेशक
B. Saravanan
Outstanding Scientist &
Director

भारत सरकार
परमाणु ऊर्जा विभाग
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Government of India
Department of Atomic Energy
Atomic Minerals Directorate for
Exploration and Research

June 01, 2023

MESSAGE

I am very happy to note that Indian Society of Analytical Scientists (ISAS) will complete one year of publishing its quarterly, peer reviewed, electronic, open access e-journal, i.e. Journal of ISAS and release the fifth issue of the e-journal during the annual meet on 31.07.2023.

Since its formative days at Bhabha Atomic Research Center (BARC) Mumbai in 1983, ISAS has grown steadily with present strength of 3000 members representing multidisciplinary Indian experts in analytical sciences. It is heartening to note the pan-India presence of ISAS, which is now operating through 10 Chapters across India. Introduction of the e-journal last year is a right step towards popularizing scientific techniques and their role in resolving various societal issues.

In the last four issues of ISAS e-journals, analytical techniques with a wide coverage, starting from in-vogue techniques like ICP-AES, XRD, less common techniques like Electrochemical Impedance Spectroscopy (EIS), and more sophisticated techniques like John-Sivanandan Achari Isotherm were postulated for compositional and structural characterization of various materials. Besides, a large number of research papers are devoted to specific research domains which have tremendous societal impact; these include: (i) Nano technology (ii) Variety of adsorbant molecules (iii)Isolation and characterization of phytochemical constituents (iv) Characterization of traditional Indian medicines and (v)Techniques related to environment and its pollution. It is obvious that all the above mentioned articles have readers from a wider domain including science students, academicians, professionals and science reporters.

I am sure that the fifth issue of the Journal of ISAS will equally be informative and thought provoking and provide a platform for discussions on wide ranging topics, especially in the field of analytical sciences. On this occasion, I fondly congratulate all the members of the ISAS for an eventful annual meet on 31.07.2023 and a grand success for the release of next issue of the e-journal.

(B. Saravanan)

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डॉ. कोमल कपूर
Dr. Komal Kapoor

उत्कृष्ट वैज्ञानिक एवं मुख्य कार्यपालक
Outstanding Scientist & Chief Executive

भारत सरकार
Government of India
परमाणु उर्जा विभाग
Department of Atomic Energy
नाभिकीय ईंधन सम्मिश्र
Nuclear Fuel Complex

MESSAGE

It gives me great pleasure to learn that the Journal of Indian Society of Analytical Scientists (ISAS) is completing one year of publication of its e-version with release of its fifth issue.

Analytical Sciences play a pivotal role in several areas such as environment, forensics, health care, pharmaceutical, linked largely to the traditional drugs, biotechnology, etc., including nuclear science and technology.

Novel researches and their publication form the bone of development making the publication of the journal highly essential. The Journal of ISAS caters to the need efficiently due to its e-version, peer reviewed, open access, free publication charge, and quarterly issues.

I wish the Journal a very bright future.

25/5/23
(Komal Kapoor)

Place: Hyderabad
Date: 25-05-2023

नाभिकीय ईंधन सम्मिश्र (9001, 14001 & 45001 संगठन), ईसीआईएल डाक, हैदराबाद - 500062
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SCIENCE FOR JUSTICE

डॉ. सं.वि. घुमटकर
संचालक

MESSAGE

I am very happy to note that Journal of ISAS is bringing out its anniversary issue after successful launching of four issues with ISSN and doi.

Forensic science refers to the examination of crime scenes, the recovery of evidence, laboratory analysis, interpretation of findings, and presentation of conclusions. As technology continues to advance and become globally accessible, crime is evolving and adapting at an unprecedented rate. New crime trends are emerging, with individuals committing offenses in cyberspace, trafficking occurring in new psychoactive substances and drugs, and so on. Therefore, it is crucial to incorporate new techniques to meet the ever-increasing challenges involved in solving crimes.

In the field of analytical sciences, research based work is progressing day by day and need of accrediting and publishing original work of authors can be addressed in the form high quality standard journals. Indian Society of Analytical Scientists (ISAS) has tried to lay a foundation stone and provided a platform to serve and help analytical scientists to portray their research following international guidelines in publishing field. As evidenced from published issues of the journal, it addresses significant and latest developments in the cross sectional fields of analytical sciences. I am sure untiring efforts of team of dedicated scientists working with J. ISAS will help in scoring the journal high in performance measures and moving up in journal ranking list.

Congratulations to ISAS and my best wishes for bright future of the journal.

Dr. Sangeeta V. Ghumatkar
Director-Directorate Of Forensic Science Lab

ISAS
Indian Society of Analytical Scientists.

Message from President ISAS

It gives me immense pleasure that Indian Society of Analytical Scientists (ISAS) is releasing anniversary issue of its e -Journal, Journal of ISAS (J. ISAS).
The Journal covers a wide spectrum of research activities in Analytical and Allied Sciences with all efforts to retain quality of the Journal.
The issue speaks of tireless hard work of the publication group of ISAS (group of Editors, Advisers and supporting hands). The group deserves due appreciation.
I am sure visibility of the Journal increased with ISSN and DOI would take further leap with the grant of the UGC care in process.

Dr. Raghaw Saran
President ISAS and
Advisor J.I SAS

Editorial

Welcome to the anniversary issue of the J. ISAS. Today marks a momentous occasion as we proudly celebrate the first anniversary of the Journal of Indian Society of Analytical Scientists (J.ISAS). With immense joy and gratitude, we reflect on the incredible journey that has led us to this pivotal milestone. Over the past year, J. ISAS has emerged as a beacon of knowledge and innovation, uniting analytical scientists from across the nation in their pursuit of excellence.

The inception of J.ISAS was driven by a collective vision - to establish a platform that would foster collaboration, disseminate cutting-edge research, and accelerate the advancement of analytical science in India. Today, we stand triumphant, having achieved this and much more. As the editor-in-chief, I take immense pride in the quality of work that has graced the pages of our journal.

Over the course of this first year, J.ISAS has provided an avenue for researchers, scientists, and academicians to share their insights, discoveries, and breakthroughs. It has been awe-inspiring to witness the diverse array of research articles, reviews, and perspectives that have poured in from every corner of the country. Our contributors have consistently demonstrated their commitment to pushing the boundaries of analytical sciences, enhancing our collective understanding and contributing to the betterment of society. The present issue showcases interdisciplinary areas covering research papers, reviews and case study in the area of waste water treatment, copolymer resins, ayurveda, lubricants and forensic case study.

In celebrating this anniversary, we must acknowledge the unwavering support and encouragement we have received from ISAS and its members. Without your dedication and engagement, this journal would not have flourished the way it has. I express my heartfelt gratitude to all the authors, reviewers, editorial board advisory board members for their relentless efforts in maintaining the highest standards of academic excellence. My special thanks are due to Dr. Raghaw Saran, President - ISAS and Chairman - advisory board, J.ISAS and Editorial board members - Dr. Vijayalaxmi Adya and Dr. Vinay Bhandari for their all time support and co-operation. I would like to acknowledge Vaibhav Parse, Maharshi Pandya and Shivani Kantak for technical assistance. I express my sincere gratitude towards esteemed scientists for their insightful encouraging messages and thank all the sponsors being a part of this issue.

As we embark on the second year of this exciting journey, we have set our sights on new horizons. J.ISAS aims to expand its scope further, exploring emerging frontier interdisciplinary areas in analytical sciences. We shall continue to embrace advancements in technology and uphold our responsibility to remain at the forefront of analytical research.

The first anniversary of the Journal of Indian Society of Analytical Scientists is not just a celebration of our achievements, but also a reaffirmation of our commitment to the pursuit of knowledge and the spirit of scientific inquiry.

Thank you for being a part of this remarkable endeavour, and we look forward to your continued support as we usher in another year of scientific excellence.

NRajurkar

Dr. Nilima Rajurkar
Editor in Chief, Journal of ISAS
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Journal of ISAS

Anniversary Issue

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Modification of Activated Carbon by Gamma Radiation - Removal of Acetic Acid

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Abstract:

The present paper deals with the removal of acetic acid using modified Norit Activated Carbon (NAC). Surface properties of NAC were modified by irradiating the sample with gamma radiations from Co-60 Source. Batch adsorption method was used to study removal of acetic acid by adsorption. Characterization differences in the Irradiated and Non-irradiated NAC surface were confirmed by different analytical techniques viz. FTIR, XRD, SEM, BET and EDX. Adsorption equilibrium study shows consistently higher capacities in irradiated adsorbent compared to the non-irradiated adsorbent for adsorption of acetic acid. The results show that the adsorption capacity of irradiated Norit activated carbon increases with increase in the amount of irradiation dose.

Key words: Adsorbent, Acid removal, Activated Carbon, Gamma irradiation, Separation

1. Introduction:

Organic pollutants are commonly found in sewage wastewaters, effluent streams of different industries and even in wastewaters generated in agriculture production due to the use of pesticides/ insecticides or chemical fertilizers[1]. Appropriate treatments are required for these different wastewater streams based on their organic/ toxic load; based on biologically degradable components in industries such as food processing, or industries generating streams containing refractory pollutants such as pulp and paper, dyes and pigments, specialty chemicals and so on. The degradation of organic

S. T. Pandit et al.,

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pollutants requires oxygen and the dissolved oxygen in water bodies can at times get consumed at a rate higher than its replenishment, depleting oxygen levels having adverse impact on the stream biota. Coagulation / clarification is widely used to remove colloidal impurities by the charge neutralization process, and a large number of coagulants/ flocculants can be used including inorganic/ organic/ biocoagulants or using process integration with cavitation, a process modification in the form of cavigulation reported recently[2]. Many other conventional techniques apart from coagulation include ion exchange[3] advanced oxidation processes, cavitation, adsorption etc[1]. Nanomaterials or nanocomposites, biomass derived materials as adsorbents are also being investigated for effective removal of various pollutants[4,5]. In recent years, techniques such as cavitation, an advanced oxidation process is also considered environmentally friendly methodology for the destruction of pollutants[5-7]. Adsorption technique is one of the most widely used technique for the removal of organic compounds[1,8-10]. One of the major organic pollutants in waste water stream is organic acids such as acetic acid. Acetic acid is largely found in wastewaters of industries producing acids or using these acids as catalyst. Removal of these acids is an important operation in the industry for safety of the environment. Industrial effluents containing low concentrations of acetic acid are produced in large quantities by many industries manufacturing acetic acid and also petrochemical, process and fine chemical industries which are using acetic acid as a chemical reagent to produce many chemical compounds[3]. The treatment of wastewater containing acetic acid is a major concern to meet the discharge norms. Although many treatment methods are used for the removal of acids, adsorption is a common methodology for removing the traces of acetic acid. Adsorption is defined as selective removal of one or more components of either a gas or a liquid mixture on the surface of a material (adsorbent) through the application of the forces of attraction or chemical bonding. It is a reversible process and regeneration of adsorbent by desorption of the adsorbed species is also important. The most important parameters of the selection of adsorbent are its surface area, typically ranging from 100 – 1000 m^2/g, porosity, selectivity and adsorption capacity. Both microporous and macroporous carbon adsorbents are made or commercially available having different characteristics for the equilibrium capacity and improved kinetics[11]. The carbon adsorbents can be derived from a variety of natural materials/ bioresources such as wood, coal, lignin and coconut shell[12]. Typically, the selection of the source material, its characteristics and the processing dictates the pore size and pore distribution. Being hydrophobic in nature, the activated carbons are considered to be suitable for removal of organic contaminants due to their affinity toward organic species. The adsorption capacity and selectivity can be further enhanced by modifying the surface of AC either through physical or chemical modifications. The conventional modifications include physical modifications (e.g. heat treatment) and chemical modifications (e.g. acid/ base treatment, surface functionalization etc.)[1,4,12]. Radiation treatment has been reported for altering the surface properties of carbon materials, such as films, fibers, powder etc.[13] An irradiation is known to induce chemical reactions at any temperature in the solid, liquid and gas phase without use of catalyst. It is considered as a safe method. The two main processes of irradiation in use are use of gamma rays and electron beam. Gamma rays from Co-60 source are highly penetrating because of its energetic photons (1.17 and 1.33 MeV).

The present paper deals with a new strategy for the removal of pollutants using gamma irradiated NAC and non-irradiated NAC. Batch adsorption method was used for removal of acetic acid and modified NAC was characterized using different characterization techniques.

2. Experimental

All chemicals, Ferrous ammonium sulphate, Sodium Chloride, Acetic Acid, Sodium hydroxide, hydrochloric acid, Norit activated carbon, phenolphthalein indicator, acetone, methanol were of analytical grade (MERCK).

2.1 Sample Collection and Preparation

The Norit Carbon was ground to fine powder with pastel and mortar. Activation was done by placing the carbon in furnace for 8 h at 500-600 ˚C temperature, this was then cooled and stored in an airtight container for further use.

2.2 Determination of dose rate of gamma source

For gamma irradiation of NAC, Co- 60 Source (Gamma Chamber 900) was used. Its dose rate was measured by Fricke dosimetry. Fricke solution was prepared by dissolving 0.4 g ferrous ammonium sulfate and 0.06 g NaCl in 22 ml of 95-98% H_2SO_4 and diluting it to one liter with distilled water.

5 ml of the solution was taken in 5 tightly capped tubes and then irradiated in Co-60 gamma source, at various time intervals. The dose rate was calculated by plotting a graph of absorbance versus time of irradiation (Fig.1) and using the following equation

$$\text{dose rate} = (\text{slope} \times 10^7 \times 0.965)/(\varepsilon \times \text{d} \times \text{L} \times \text{GFe}^{+3}) \text{---(1)}$$

Where ε is molar absorption coefficient of Fe^{3+} ions (2174 lit $mol^{-1}cm^{-1}$), d is density of solution, l is path length and $GFe^{+3} = 15.5$
The absorbance of the ferric ions, was measured with a spectrophotometer at 304 nm. The dose rate was found to be 52.92 Gy/min

2.3 Sample irradiation

NAC was tightly capped in a test tube and then irradiated in Co-60 irradiator (Gamma Chamber- 900) for a pre-determined time with a dose rate of 52.92 Gy/min. The total dose absorbed was 0, 2,4,6,8 and 10 KGy.

2.4 Batch adsorption method

The batch adsorption method was used to determine the adsorption capacity of NAC for removal of acetic acid. For this purpose, six glass flasks containing known concentration of acetic acid and fix amount of NAC were agitated at constant speed using a shaker and after certain time interval, solution was withdrawn and filtered, the aliquot was titrated with standardized NaOH using phenolphthalein indicator. The adsorption process was carried out at ambient temperature and varying concentrations of acetic acid and amount of NAC. The obtained data was used to calculate adsorption capacity of NAC.

2.5 Characterization studies

Irradiated and non-irradiated samples of NAC were characterized by FTIR, SEM, XRD, BET and EDX techniques

3. Results and Discussion

3.1 XRD analysis

XRD Patterns of non-irradiated and irradiated NAC are shown in Fig. 7 and 8 respectively. The 2Φ value for Non-irradiated NAC was found to be 26.4 and 44.7 which show that crystallite size of carbon was 2.34 A^0 and 2.02 A^0 respectively.

3.2 Scanning electron microscope analysis

Scanning electron microscopy is one of best technique to study topology and morphology of sample. SEM can be used for studying Pore distribution and extent of porosity etc. Irradiated and Non-irradiated NAC samples were observed under electron microscope.

As can be seen from Fig. 9 and 10, pore distribution is getting affected due to gamma radiation, more uniform distribution is observed for irradiated sample so consequently surface area also increases due to high energy radiation.

3.3 BET Surface Area Analysis

Specific Surface area for Non-irradiated NAC was found to be 731.59 m^2/g and for Irradiated carbon it was found to be 847.32 m^2/g so approximately 16% increase in surface area was observed for irradiated NAC.

Maximum Volume of pores was found to be 0.4138 cm^3/g and 0.3791 cm^3/g for irradiated and Non-irradiated NAC respectively. Maximum diameter of pores was found to be 3.98 nm and 3.96 for non-irradiated NAC and irradiated NAC respectively.

3.4 Elemental analysis using Energy dispersive x-ray

Elemental analysis of irradiated and non-irradiated NAC is shown in Tables 1. The major constituent of Irradiated NAC is the carbon (> 90%). In addition, it also contains other atoms. These may be derived from the source of raw material or they may get associated during activation process or other preparation procedure[11,12]. The large difference in carbon and oxygen content in irradiated and non-irradiated NAC is surprising.

3.5 Functional Group Study

FTIR analysis was done using FTIR-84005 model. The obtained spectra are shown Figs. 5 and 6. As can be seen, there are two major absorption bands at 3500 cm^{-1} and 1500 cm^{-1}. The band at 3450 cm^{-1} is attributed to acetic acid adsorption on NAC (O-H stretching) while the band at 2930 indicates C-H interaction with carbon. Further, bands in the range of 3200-3650 cm^{-1} also can be attributed to the hydrogen-bonded OH group.

3.6 Measurement of equilibrium parameters, Effect of concentration and Adsorbent dose

The equilibrium studies were carried out by varying the acetic acid concentration, amount of NAC and contact time. The obtained data was used to study the adsorption capacity.

The effect of initial concentration on adsorption capacity of NAC was studied in the range of 20 to 150 mg/L by stirring 50 mL solution of acid for 20 h with a fix amount of NAC. Residual acetic acid concertation after filtration was determined as described above.

In order to study the effect of dosage of NAC on removal of acetic acid amount of NAC was varied between 0.2-1g and amount of sample solution (50mL) and time of stirring (120rpm) was kept constant

The results for the two adsorbents, irradiated and non-irradiated, are shown in Figs. 2 and 3. A comparative plot of equilibrium concentration versus adsorption capacity is depicted in Fig. 4.

3.7 Equilibrium study

Equilibrium studies were carried out at room temperature (25 ± 1ºC) by employing the batch adsorption technique. The data were analyzed in the light of adsorption isotherms. The sorption data (Fig. 4) shows that irradiated adsorbents have consistently high adsorption compared to the non-irradiated adsorbent, implying positive modification of the adsorbent using the suggested methodology and its practical utility. It is also observed that at higher concentration the capacity reaches a maximum value in the case of both irradiated and non-irradiated adsorbents: the capacity of irradiated adsorbent is ~100% higher than that observed for the non-irradiated adsorbent.

4. Conclusion

Our study reveals that gamma irradiation of NAC increases its surface area and modifies pore size resulting into high adsorption capacity of acetic acid as compared to non-irradiated NAC

The specific surface area of Irradiated and Non-irradiated NAC were found to be 731.59 $\mathrm{m^2/g}$ and 847.32 $\mathrm{m^2/g}$ respectively. Since approximately 15% of surface is observed to be affected due to gamma radiation. Pore size of NAC was found to be 0.31 nm. Also maximum diameter of pore was of the range between 3.96-10.00 nm.

Adsorption capacity of irradiated NAC increases as amount of irradiation dose increases. BET analysis indicated that surface area of irradiated carbon increases with increasing dose. Further, the adsorption increases with an increase in the adsorbent dosage.

Figures

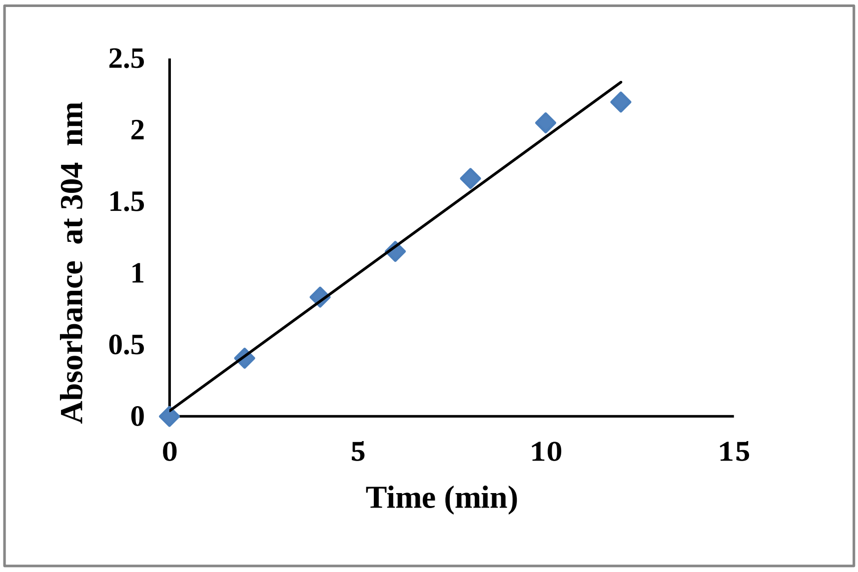

Fig.1 Calibration curve for Fricke dosimetry

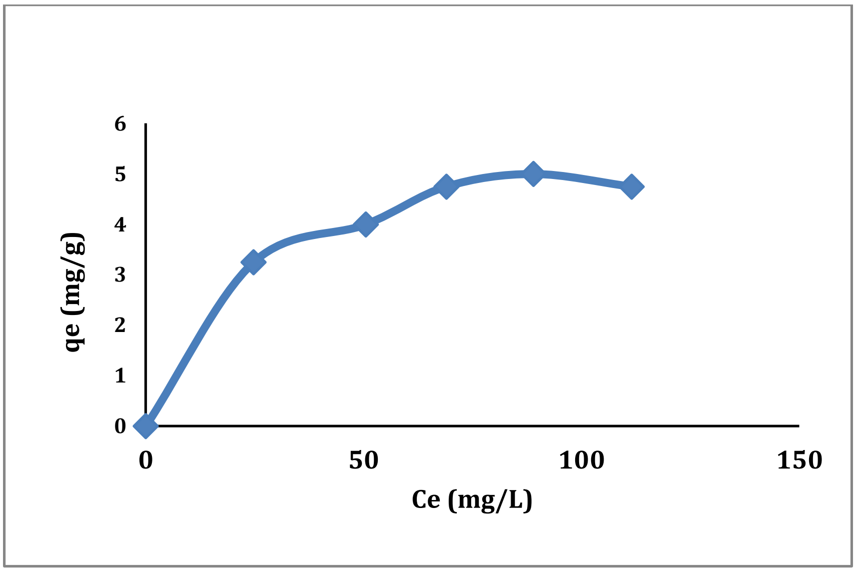

Fig.2. Equilibrium for Non-irradiated NAC

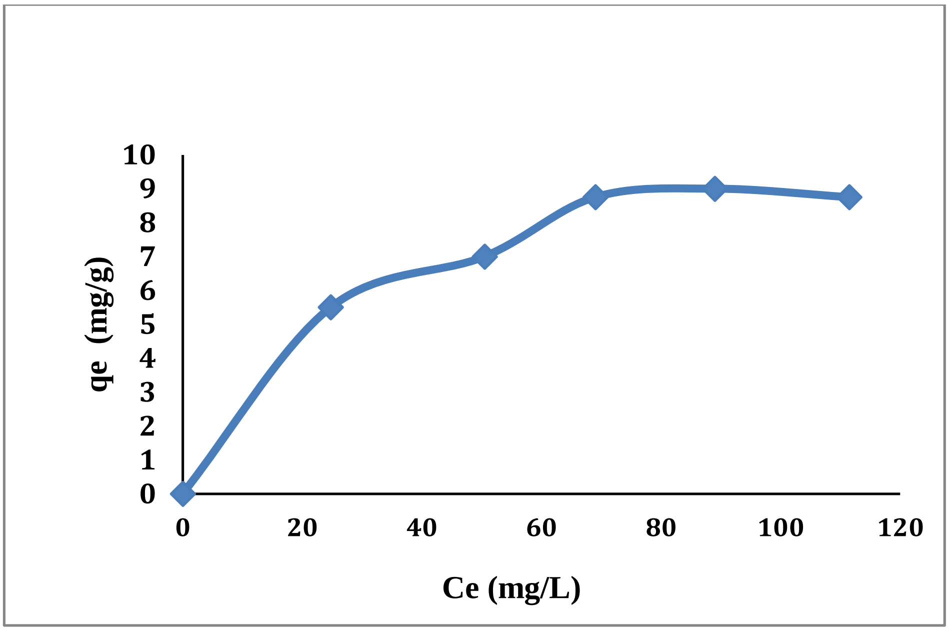

Fig 3.Equilibrium for irradiated NAC

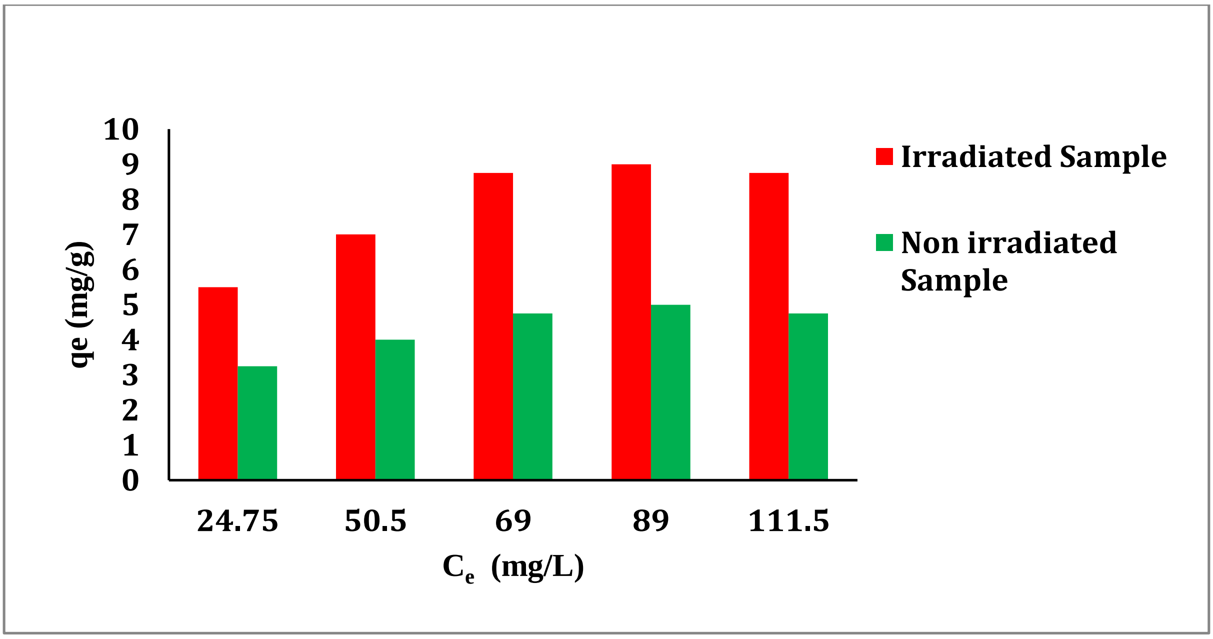

Fig.4. Comparative plot of equilibrium concentration Vs adsorption capacity of NAC

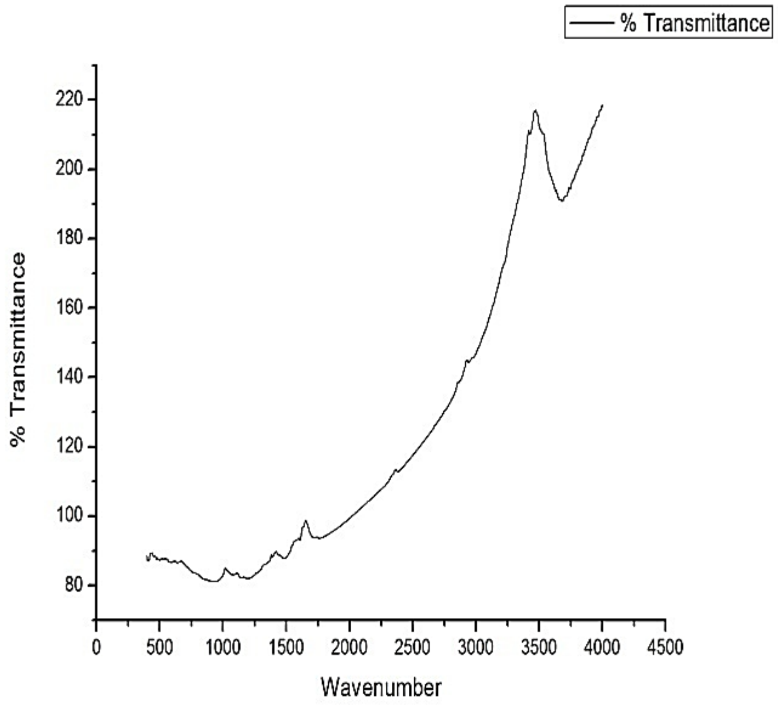

Fig. 5 FTIR of NAC before irradiation

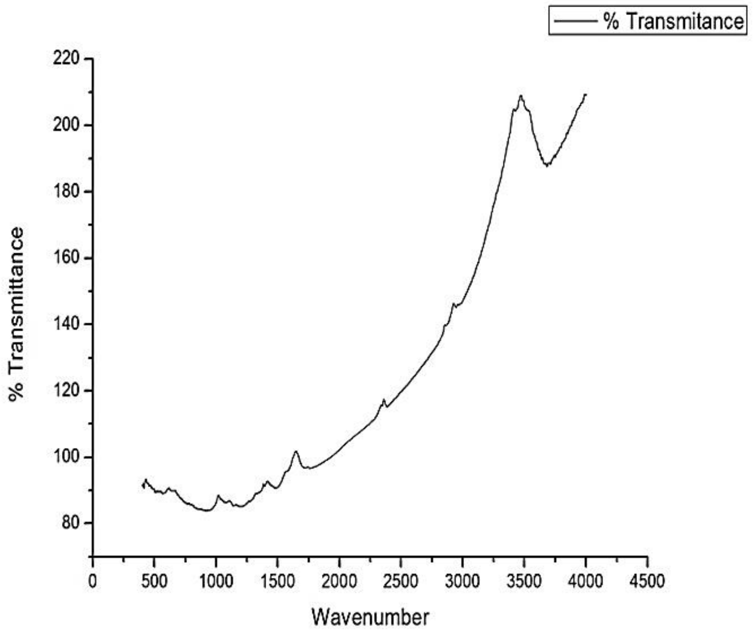

Fig. 6 FTIR of NAC after irradiation

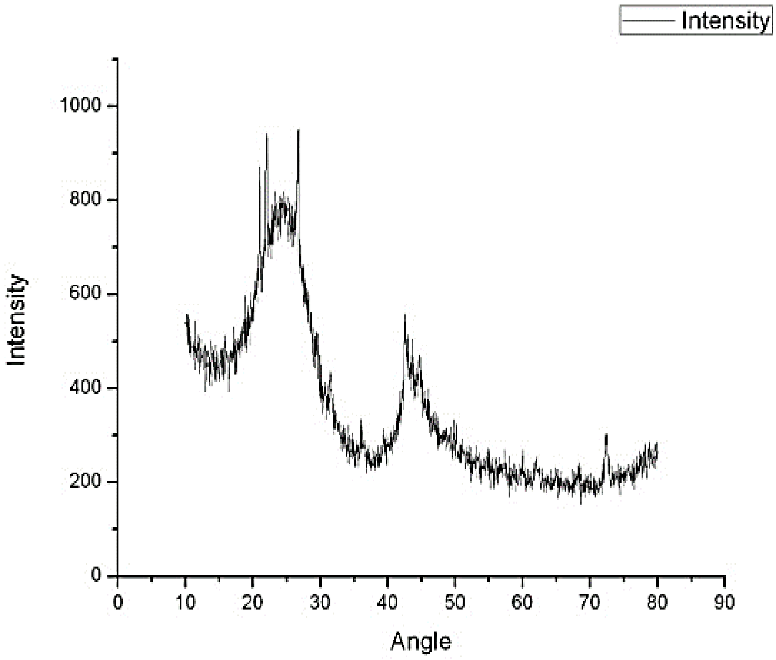

Fig. 7 XRD of Non-irradiated NAC

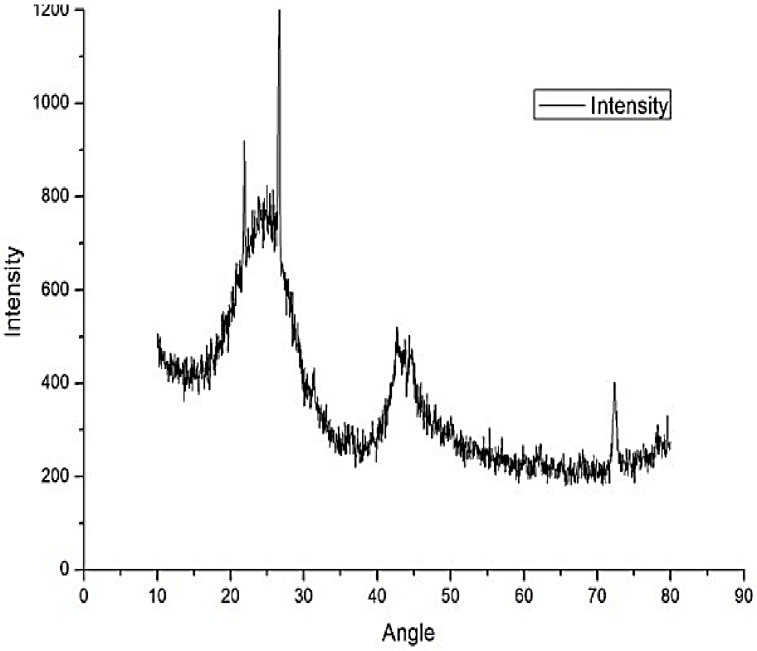

Fig. 8 XRD of Irradiated (10KGy) NAC

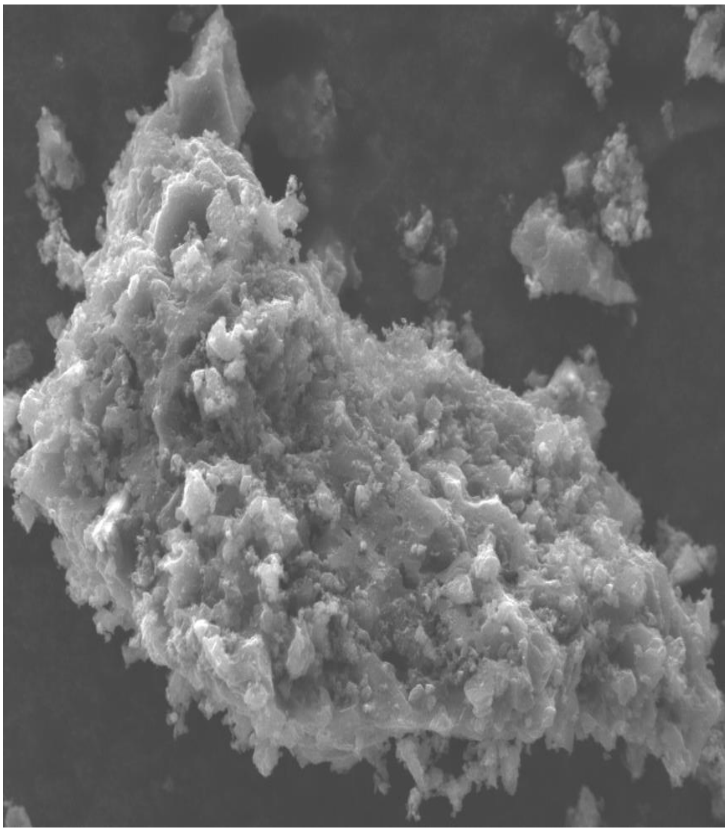

Fig. 9 SEM image of Non-irradiated NAC

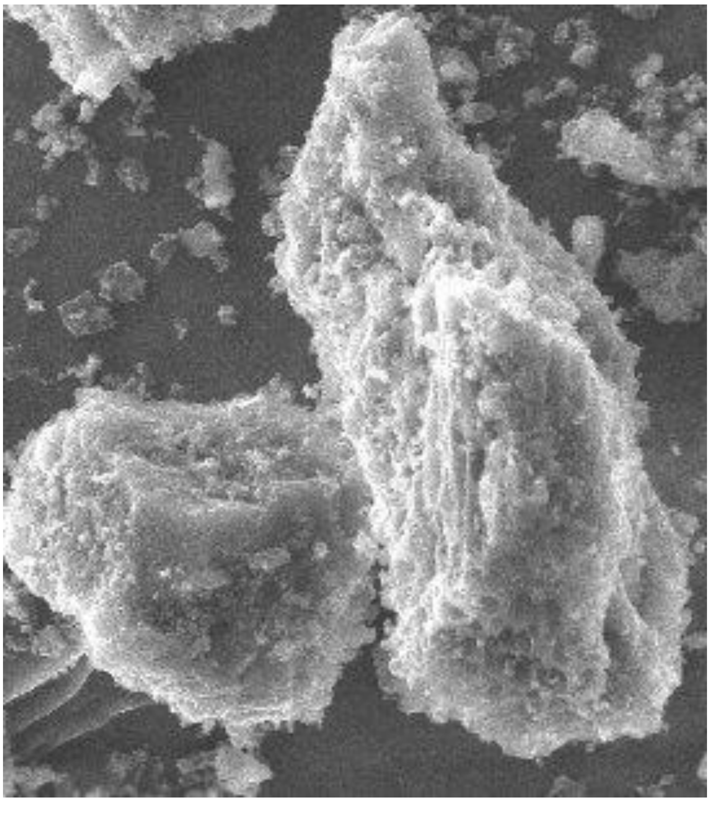

Fig. 10 SEM of Irradiated NAC

Tables:

Table 1. Elemental analysis for Non-Irradiated and irradiated NAC

Elements	**% Weight**	
	Non-irradiated	**Irradiated**
Carbon	56.30	93.58
Oxygen	34.89	4.93
Phosphorous	1.13	0.12
Magnesium	0.17	0.39

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Novel Applications of Some Organic Copolymers Derived From Phenolic and Nitrogen-Containing Compounds- A Review

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Abstract

A variety of organic copolymers have been synthesized from phenolic compounds like p-Hydroxybenzoic acid, p-Hydroxybenzaldehyde, p-Hydroxyacetophenone, and also from nitrogen- containing compound like anthranilic acid, aniline, urea, biurate. These copolymers have been studied for various properties like thermal behavior, kinetic parameters, antimicrobial screening, ion-exchange study, polymer composites, photoluminiscence etc. Kinetic parameters of the copolymers derived from phenolic and nitrogen-containing compounds have been studied using Freeman-Carroll (FC) and Sharp-Wentworth (SW). Based on TGA, thermal stability and decomposition temperature have been studied for the copolymers and composites. Higher thermal stability for copolymer composites has been found as compared to the copolymer because the composite has a high activation energy and more residue left out at the end of the decomposition process. The metal ion uptake capacity of the copolymer have been studied by using the batch equilibrium method and is useful for wastewater treatment. The antimicrobial activity of the copolymers have been studied using the agar diffusion method. Polymer composites have been made from copolymers using an ultra-sonication process and exhibit excellent properties in metal ion uptake for wastewater treatment. The present review paper involves the study of novel applications of the copolymer resins derived from phenolic compound and nitrogen-containing compound.

Keywords: Copolymer, Composites, Ion-exchange, Photoluminescence, Composites.

1. Introduction

Phenolic compounds have versatile applications in the food, pharmaceutical, and polymer industries. They exhibit various biological activities like antimicrobial activity, antibacterial activity, antioxidant and anti-inflammatory, and thermal and electrical conductivity. An intra-molecular hydrogen bonding (Fig.1) is observed in phenolic

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compound[1] like protocatechuic acid, O-Nitrophenol, Salicylic acid, and O-Chlorophenol. Primary and secondary amines form hydrogen bonds. Oxygen is more electronegative than nitrogen, so hydrogen bonds in amines are weaker than phenolic compounds. The inter molecular hydrogen bonding (Fig.2) have been observed in anthranilic acid,Diethylamine, Semicarbazide, Di-amino-benzoic acid.

A large number of useful applications like use in electronic devices, use as insulators, adhesives, in aerospace industries, etc. have been noted in Table (3) for phenolic and nitrogen-containing copolymers, These copolymers have high thermal stability, resistant to bacteria, fungi, chemicals and also have electrical insulating properties[2-7]. In recent years copolymers are widely used as semiconducting material. Because of conducting nature, copolymers are used in solid-state physics and chemistry. In addition to the conductivity, copolymers have been extensively used in Photovoltaic Cells, Organic Solar Cells, Sensors, Light Emitting Diodes, Schottky diodes, Field transistors, Electrochemical batteries, Photoconduction, Luminescence, etc.[8]

The electrical conductivity of the copolymers derived from phenol and formaldehyde has been studied by Pekaln and Kolosonov [9,10] who used them in the field of electrochemistry such as electrodes, the field of electronics sensors, etc. Dewar, et. al.[11] have reported copolymer as an industrially useful semiconducting material. Masram and coworkers [12-15] carried out work on the Study of Kinetics, Thermal degradation, and Electrical Conductivity of copolymers derived from Salicylic Acid and Phenylenediamine containing compounds, butylene-diamine-containing compounds, hexamethylenediamine-containing compounds with Formaldehyde

Gurnule et.al.[16] have reported the study of electrical properties of copolymers derived from 2-hydroxy-4-methoxybenzophenone and 1,5-diaminonaphthalene with formaldehyde. They have also studied the electrical conductivity of novel nanoporous o-aminophenol-melamine-containing compounds-formaldehyde copolymer. Phenol-formaldehyde and amino-formaldehyde copolymers have excellent applications and hence various researchers have synthesized copolymers of salicylic acid- hexamethylene-diamine-formaldehyde, containing compounds. Also some combinations of salicylic acid- catechol-formaldehyde, p-hydroxybenzoic acid- semicarbazide -formaldehyde, salicylic acid- thiosemicarbazide-formaldehyde, anthranilic acid, urea-formaldehyde, 4-hydroxyacetophenone-catechol-formaldehyde, salicylic acid-butylenediamine-formaldehyde, 4-hydroxyacetophenone ethylenedinitrogen-formaldehyde, p-hydroxybenzoic acid- diaminobenzoic acid-formaldehyde, p-cresol- melamine containing compounds-formaldehyde, o-aminophenol melamine containing compounds-formaldehyde have been reported[17-21].

Copolymers derived from phenolic and nitrogen-containing compounds show antimicrobial activity[22-23] (inhibitory activity) against some bacteria such as C. Albicans, S. Typhi, S. Aureus A. Niger, and E. Coli, S. Subtilis, pathogens.

Versatile properties of phenolic compounds have been studied including resistance to high temperatures and excellent thermal insulators, phenolic compounds are resistant to corrosion and exhibit fire-toxic smoke properties[24-30]. Phenolic copolymers are used for various composite manufacturing processes such as filament winding, resin transfer molding, injection molding, and compression molding. Phenolic copolymers provide easy processability, tight tolerances, reduced machining, and high strength[31]. Copolymers derived from phenolic and nitrogen-containing compounds also exhibit excellent photoluminescence properties and have been used in semiconductor devices. This shows that the synthesized coordination polymer can be used as a photoluminescence material for various applications & also as a supporting material for light-emitting devices[32].

A review of some organic copolymers derived from phenolic and nitrogen-containing compounds includes novel applications of copolymer resins like thermal resistance materials, fireproofing materials, molding materials, binders, a Semiconductor, antibacterial materials, antifungal agents, wastewater treatment, Photoelectronic devices, fluorescence sensors, probes, Light emitting, luminescent sensors, Multicolor light emitting device OLEDs.

2.Synthesis of Copolymer Resins

Copolymer resins have been synthesized from phenolic compounds and nitrogen-containing compounds mentioned in Table 1 by using the condensation method with formaldehyde using varied molar ratios of reacting mixture. The reaction has sped up using HCl as a catalyst and heated with occasional shaking at temperature ranges from 125-140 ^{0}C for 5-7 h.[18-20]. The colored copolymer has been separated and then washed with warm water and methanol to avoid unreacted monomers. The synthesis of p-CPBF-II using phenolic and nitrogen-containing compound by condensation method is shown in Fig.3**.** The yield of the copolymer is 90-95% for all the copolymer resins.

3. Properties and Applications of Copolymers

Various properties and applications have been studied for copolymers derived from phenolic and nitrogen-containing compounds. Some of the important properties and applications are given below.

3.1 Thermal Stability

Copolymers derived from phenolic and nitrogen-containing compounds show thermal stability and hence can be used as thermal resistance materials, fireproofing agents, molding materials, and binders. It has been further supported based on low values of frequency factor (Z) and slow rate of the decomposition reaction of the copolymer. The thermal stability of the copolymers at high temperatures have studied based on decomposition reactions started at higher temperatures[18,20-23.] The thermogravimetric analysis method is mostly used to determine the thermal stability of the copolymers. Thermal methods of analysis is an experimental method for determining the thermal stability of the copolymers by measuring changes in physicochemical properties with continuously increasing temperature with time. The thermogravimetric analysis (TGA) of the novel copolymers has also been studied in a stationary atmosphere over a heating rate of 10^0C/min. In the present investigation, thermo-gram of copolymers synthesized from phenolic and nitrogen-containing compounds have been studied with % weight loss of the material (copolymer resin) as a function of temperature and also time. From thermo-grams, activation energy (Ea) have been calculated by adopting an analytical method proposed by Freeman-Carroll (FC) and Sharp-Wentworth(SW)[12-18] as given in Table 2. These methods help to decide the thermal stability of the copolymer resins and also the order of reaction (n), activation energy, entropy, Frequency factor, etc.[26-28].

3.2 Electrical Conductivity

The copolymers synthesized from phenolic and nitrogen-containing compounds have shown good electrical conductivity and can be used as semiconductors[12]. Most of the copolymers derived from phenolic and nitrogen-containing compounds have shown good electrical conductivity and are measured within the range of 303-423 K temperature in their pellets form. The conductivity is further supported based on low activation energy and delocalization of πelectron in polymer chain[13-14]. Experimentally electrical conductivity of the copolymers have determined by making pellets of the finely powdered copolymer in a steel die isostatically at 5-10 tonnes/2inch(1cm^2). Colloidal graphite in acetone has been applied in thin layer form on both sides of the pellets. At room temperature, all pellets have been dried in a vacuum for 6 h. To avoid any leakage across the border precaution has been taken not to apply very high voltages[12-14,16,17]. The rate (slow) of heating have maintained at 1 to 10 ^{0}C / min. during the entire process. The two probes (terminals) method has been used to measure the resistance of the sample pellets. Resistivity (ρ) have calculated using the relations between the resistance of the pellets, surface, and thickness area of pellets as shown in equation (1).

$$\rho = R\ (A/l) \quad \ldots\ldots\ldots\ldots\ldots\ldots(1)$$

Where, R= resistance of the pellets, A = Surface area of pellets & l = Thickness of pellets

The electrical conductivity(σ) may vary exponentially with the absolute temperature according to the well-known Wilson's exponential relationship (2) which is given below.

$$\sigma = \sigma^0 \exp\ [-Ea/kT\ ] \ldots\ldots\ldots\ldots\ldots\ldots..(2)$$

The modified relationship (3) is given as:

$$\text{Log}\ \sigma = \log\sigma 0 + -Ea/2.303kT \ \ldots\ldots..\ldots(3)$$

3.3Antimicrobial Activity

Copolymers synthesized from phenolic and nitrogen-containing compounds exhibit antimicrobial activity against microorganisms, bacteria, and pathogens[18-19]. It is then used as antimicrobial copolymers. The antimicrobial activity of the copolymers is due to the presence of a function group containing nitrogen(amide), oxygen(hydroxyl), and sulfur (thio). Experimentally an agar diffusion method[20-23] has been used to know the antimicrobial properties of the copolymers.

3.3.a. Antibacterial analysis: Antimicrobial screening of the copolymers have been studied by using the agar diffusion method. The test bacterial pathogen like B. subtilis, E.Coli, S.Typhi Klebsiella species, S. Aureus, C. Albicans, C. Tropicals, and A. Niger microorganisms have been used for antibacterial screening of the copolymers. The agar plates of the above media have been prepared along with wells. The agar plates were then incubated at 37°C for 24 h and recorded the diameter of inhibition zones. These were tested at different concentrations to test their efficacy in inhibiting the growth of human pathogens[18].

The antimicrobial activity of the copolymers have been checked using varied concentrations screened 0.0625, 0.125, 0.25, 0.5, 1.0, and 2.0 mg in DMSO. Gentamycin was used as standard antibiotic. The 20 mg sample was dissolved to prepare the above concentrations. The stock Sample was prepared in 20 mg/ml Concentration. The Media Used (Nutrient broth) for the above analysis is Peptone-10 g, NaCl-10g and Yeast extract 5g, Agar 20g in 1000 ml of distilled water. The S. Aureus (MRSA), B. Subtilis, E.Coli (ETEC), S. Typhi Klebsiella species, S. Aureus, and C. Tropicals bacteria were used for antimicrobial analysis[20-23].

3.3.b. Antifungal analysis: The copolymers have been analyzed with 0.0625, 0.125, 0.25, 0.5, 1.0, and 2.0 mg concentration in DMSO. Amphotericin was used as standard Antibiotic. The 20 mg sample has been dissolved to prepare the above concentrations. The Stock Sample was prepared in 20 mg/ml Concentration. The A.Niger, Candida albicans fungi were used for antifungal analysis[18,23].

3.4 Ion-Exchanger for Waste Water Treatment

The copolymers derived from phenolic and nitrogen-containing compounds have also been found suitable and more convenient for the removal of traces of heavy toxic metal ions present in industrial wastewater, domestic water treatment, and nuclear waste treatment. The toxic heavy elements present in wastewater are a serious issue and it creates health-related problems like skin infections, stomach infections, kidney damage, and damage to the nervous system and so on[24]. Therefore, the synthesis of a chelating ion-exchange copolymer has been performed by various researchers from phenolic compounds and nitrogen-containing compounds to assess the ion-exchange characteristics of the copolymer. Ion-exchange process is an efficient and eco-friendly extraction technique for the separation of metal ions and recovery of toxic heavy metal ions from industrial wastes, tannery effluents, sewages, etc[25-30]. The copolymers derived from phenolic and nitrogen-containing compounds are used as ion-exchanger for the removal and pre-concentration of hazardous metal ions such as Cr^{2+}, Mn^{2+}, Cd^{2+}, Pb^{2+} Co^{2+}, etc. found in natural water samples using batch equilibrium method[31,33]. The ion-exchange techniques have been studied by evaluating the following experimental steps.

3.5 Polymer Composites

The polymer composites derived from the phenolic compound and nitrogen-containing compounds exhibit excellent ion exchange properties for wastewater treatment and management[31,32]. Experimentally it has been synthesized from copolymers and activated charcoal in a 1:2 ratio. The copolymer was dissolved in 25 ml of DMF and the activated charcoal was added to it and subjected to ultrasonication for 3 h with constant stirring for 24 h. Finally, the obtained black-colored composite was dried in an air oven at 70°C for 24 h[31,32]. The polymer composites exhibit excellent properties in metal ion uptake for wastewater treatment. Higher thermal stability and decomposition temperature have been found in polymer composites as compared to copolymers[33-38].

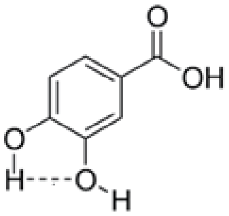
3.6 Photo luminescent copolymers

The copolymer synthesized from phenolic and nitrogen-containing compounds exhibit photoluminescence properties and can be used as fluorescence sensors, probes, Light emitting, photoelectronic devices, luminescent sensors, Multicolor light emitting device OLEDs. The copolymers also worked as ligands as it contains oxygen and nitrogen as donor atoms. When such a copolymer reacts with transition metal ions like Cu^{2+}, Co^{2+}, Fe^{2+}, Ni^{2+}, and Zn^{2+}, co-ordination polymer complex formation takes place in a 2:1 molar ratio. The photoluminescence properties of copolymers derived from phenolic and nitrogen-containing compounds having copolymer metal complex samples have been recorded in photoluminescence spectra[39-43].

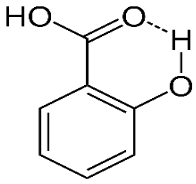
4. Conclusion

Copolymers in the review study have been synthesized from phenolic and nitrogen-containing compounds by poly-condensation method. The kinetic parameters of the copolymers derived from phenolic and nitrogen-containing compounds have been studied using Freeman-Carroll (FC) and Sharp-Wentworth (SW). On the basis of TGA, thermal stability and decomposition temperature have been studied for the copolymers and composites. Higher thermal stability for copolymer composites have been found as compared to the copolymer, because composite has high activation energy and more residue left out at the end of decomposition process. Metal ion uptake capacity of the copolymer have been studied by using batch equilibrium method and useful for wastewater treatment. Antimicrobial activity of the copolymers have studied using agar diffusion method. Copolymers derived from phenolic and nitrogen-containing compounds shows antibacterial activity for certain bacteria and fungi. Polymer composites made from copolymers using ultra sonication process exhibit excellent properties in metal ion uptake for wastewater treatment. Copolymers derived from phenolic and nitrogen-containing compounds have ranked as thermally stable material, semiconductor, ion-exchanger in wastewater treatment also exhibit antimicrobial and photoluminescence properties. The copolymers also exhibit photoluminescence properties and used in photo-electronic devices, fluorescence sensors , probes, Light emitting, luminescent sensors, Multicolor light emitting device OLEDs.

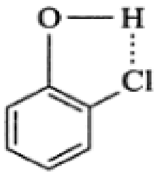
Figures



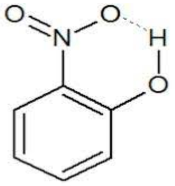
Structure-I: Protocathechuic acid



Structure-II: Salicylic Acid

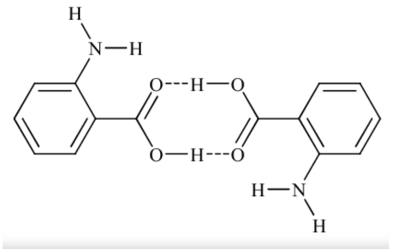


Structure-III: O-Chlorophenol

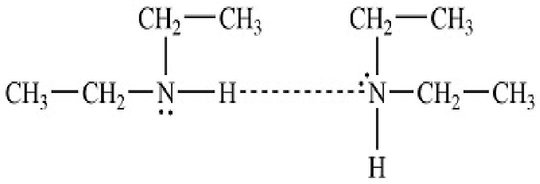


Structure-IV: O-Nitrophenol

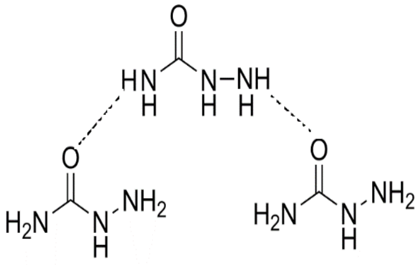
Fig.1: Intra-molecular hydrogen bonding in phenolic compounds.



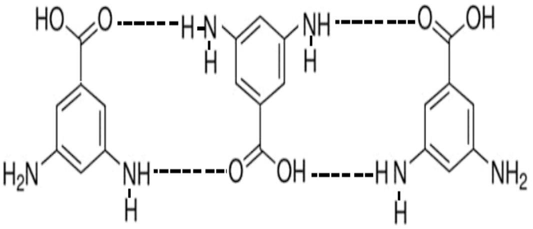
Structure-V: Anthranilic acid



Structure-VI: Di-ethylamine



Structure-VII: Semicarbazide



Structure-VIII: Di-amino-benzoic acid

Fig. 2: Intermolecular hydrogen bonding Nitrogen-containing compounds.

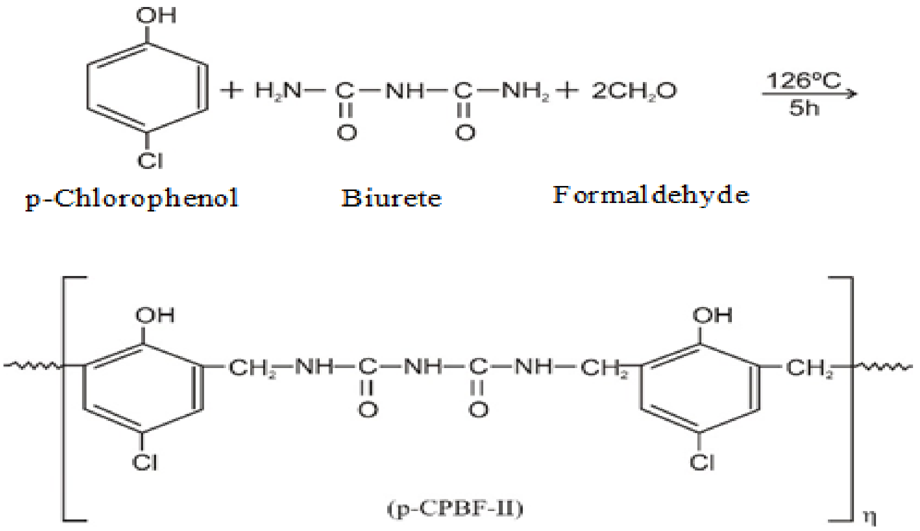


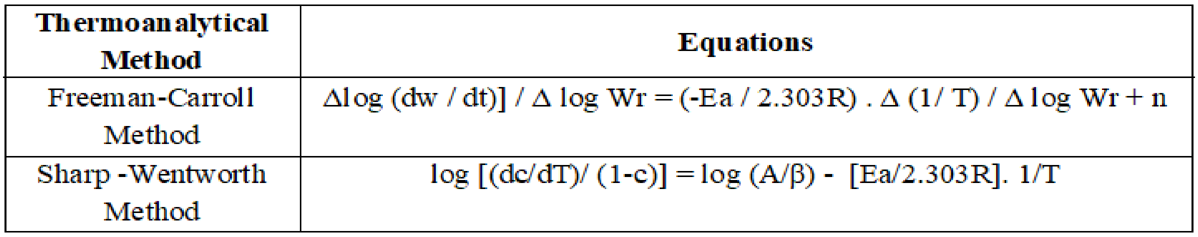
Fig. 3: Synthesis of p-CPBF-II using phenolic and nitrogen-containing compound by condensation method.

Tables

Table-1: List of some phenolic and nitrogen-containing compounds for the synthesis of copolymer resins.

Sr. No	**Phenolic Compounds**	**Nitrogen-containing compounds**
1	Salicylic acid	Phenylenediamine
2	Salicylic acid	Butylenediamine
3	Salicylic acid	Hexamethylenediamine
4	*p*- Hydroxybenzoic Acid	Diaminobenzoic Acid
5	2-Hydroxy 4-Methoxybenzophenone	1,5-diaminonaphthalene
6	o-Aminophenol	Melamine
7	*p*- Hydroxybenzoic Acid	Anthranilic acid + Urea
8	4-Hydroxyacetophenone	Ethylenediamine
9	Salicylic acid	Thiosemicarbazide
11	p-Hydroxybenzoic acid	Semicarbazide
12	p-Cresol	Melamine

Table-2: Thermo analytical methods and important equations



Thermoanalytical Method	Equations
Freeman-Carroll Method	$\Delta \log (dw / dt)] / \Delta \log Wr = (-Ea / 2.303R) . \Delta (1/ T) / \Delta \log Wr + n$
Sharp -Wentworth Method	$\log [(dc/dT)/ (1-c)] = \log (A/\beta) - [Ea/2.303R]. 1/T$

Table-3. Properties and applications of copolymer resins derived from phenolic and nitrogen-containing compound.

Sr. No	Properties of copolymers	Applications
1	Thermal Stability	Thermal resistance materials, Fireproofing agent, Molding material, Binder(adhesive)
2	Electrical Conductivity	As a Semiconductor, In aerospace industries.
3	Antibacterial Activity	Antibacterial material, Antifungal agent, Coating material.
4	Ion-Exchange	Wastewater treatment, Removal of toxic heavy elements
5	Polymer Composites	Wastewater treatment, Engineering Use.
6	Photoluminiscence	Photoelectronic devices , fluorescence sensors , probes, Light emitting, luminescent sensors, Multicolor light emitting device OLEDs. Organic Solar Cells,

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Cypermethrin insecticide in viscera of suspected snake bite case: A Forensic case study

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Abstract:

The present paper reports the use of analytical techniques in identifying the reason of the death of a suspect. After the death of an individual, a post-mortem examination was conducted. As part of the investigation, the viscera (I) and (II) were sent to the Mini Forensic Science Laboratory in Solapur. The Medical Officer, in their report, mentioned that no injuries or defensive marks were found on the body, except for a small prick mark or bite mark with clotted blood observed on the right foot, between the small toe and adjacent fingers. Upon cleaning the area, it was noticed that one spot was more prominent, while the other spot was faint. Since there were no eyewitnesses present at the crime scene, the police recorded in their inquest that the death might be a result of a snake bite. No formal complaint was registered at that time. However, the viscera samples were preserved for further examination and a final opinion. In the analysis of the viscera, techniques such as Thin-Layer Chromatography (TLC) and Gas Chromatography-Mass Spectrometry (GC-MS) were employed. The results of the analysis revealed that the cause of death was cypermethrin poisoning, as indicated by the presence of cypermethrin in the viscera samples

Keywords- Snake bite, Cypermethrin, poisoning case, TLC, GC-MS

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1.0 Introduction

Analytical techniques play a crucial role in forensic studies by providing valuable information and evidence that can be used to investigate crimes, identify suspects, and support legal proceedings. These techniques help in identifying and characterizing various types of evidence collected from crime scenes, such as fingerprints, DNA, fibers, drugs, poisons, gunshot residue, etc. and enable forensic scientists to determine the nature, composition, and origin of the evidence, which can link suspects to the crime or provide valuable information for the investigation. The present paper demonstrate use of GC-MS and TLC techniques in identifying the cause of the death of a victim

Systematic analysis procedure of analysis of viscera is very important and Forensic laboratory Maharashtra is having facility to analyze unknown poisons by using different analytical techniques including modern instrumentation[1]. In poisoning cases, determination of pesticide, insecticide and drugs is common practice in forensic science laboratory but in this case there is unknown poisoning and from the history it appears to be natural death.

Chromatographic techniques are discussed in literature analyzed for poisons in food[2], food products, biological samples…etc, Detection of pesticide of 11 pesticide residue samples from 70 postmortem cases is discussed[3] by Shailesh Kumar Rai *etal*. Thin layer chromatography is commonly used in organophosphorus pesticide analysis and tremendous work is done by using this technique[4-6]. The review of Mass spectrometry in application of toxicology revealed that the technique is really useful in forensic toxicology[7]

It is possible to analyse inorganic poisons as well by using techniques like ICP-MS, whereas LC-MS and GC- MS are used for analysis of organic poisons[7-8]. The separation of cypermethrin and deltamethrin is also important as they are from synthetic pyrethroid category[9]. Pesticides of organochloro, organophosphorus, carbamate group are generally used in suicidal, homicidal and even accidental cases; hence it was necessary in this case to check all types of poisons.

The case study was carried out on a 46-year-old male who was found to be dead in a prone position under a mango tree. According to the medical officer's report, the body exhibited the following observations: there were no injuries or defensive marks present on the body and the estimated time since death was 24 to 48 hours. Additionally, two small prick marks with clotted blood were observed on the right foot, specifically between the small toe and adjacent finger. Upon cleaning the area, one mark appeared more prominent while the other was faint. Hence, he was suspected to have a snakebite The suspected case was analyzed in forensic laboratory, Solapur

2.0 Experimental

2.1 Chemical and reagents

Chemicals used for the analysis were potassium iodide, sulphuric acid, hexane, diethyl ether, acetone, methanol, chloroform, Ammonia, benzene and acetonitrile. All chemicals were used of A. R grade and are of Merck. The spray of chemicals used as Mercuric nitrate- Potassium Ferro cyanide, Mercuric nitrate- Diphenylamine, potassium iodate-starch, Alkaline resorcinol, Sodium carbonate - chloronil in acetone, O- Tolidine thereafter kept under UV, NaOH-Nickel amine, Copper acetate, O-tolidine, Dragendorff's and sodium hydroxide- ferrous sulphate, Standards like cypermethrin, Dichlorvos, Dimethoate, Malathion, glyphosate and parquet.

2.2 Procedure

Viscera samples were initially tested for volatile poisons like ethanol, methanol…etc, thereafter it was tested for inorganic poisons and organic poisons. Alkaline extraction of viscera I and II in chloroform was taken for further analysis, Acidic and neutral extraction of viscera I and II in ether was taken for further analysis.

2.3 Thin layer chromatography

Above extract was spotted along with standard poisons like cypermethrin, Dichlorvos, Dimethoate, Malathion, glyphosate and parquet on thin Layer chromatography of Silica gel and run in solvent system - Hexane:Acetone (8:2), Standard poisons and thereafter the plate was developed by using reagent mentioned in 2.1 for screening of all types of organic poisons.

2.4 Gas chromatography-Mass spectrometer

The Neutral ether extract was injected to GC-MS (Agillent technologies). HP- 5ms capillary column 25m x 0.25mm x 0.1µm was used, the method was set as inlet temperature 150^0C, MS source temperature-230^0C, QP temperature 150^0C, initial temperature of oven was kept 70^0C and hold for 5, Ramp was kept 5^0C per min heated up to 280^0C, helium was used as carrier gas with flow rate 1ml/min.

3 Results and Discussion

Volatile poisons like methanol, ethanol were not found and Inorganic poisons like arsenic, Mercury were absent in viscera samples. It was further screened for organic poisons like orgaochloro, organophosphorus, herbicides, cypermethrin and drugs by using TLC. Presence of cypermethrin was revealed in viscera sample (Fig.1). 10 TLC plates were run in solvent system- Hexane:Acetone (8:2) and separately treated by using above reagents. The observations are given in Table 1.

The neutral ether extract of viscera I & II was further injected to GC-MS which showed presence of cypermethrin. Mass spectra m/z- 39, 51, 77, 91, 115, 127, 141, 152,163, 181, 191, 197, 209 tallies with cypermethrin.

Conclusion

In summary, although no visible injuries were found on the body, the examination of the viscera using analytical methods (GC-MS, TLC) revealed that the individual's death was a result of cypermethrin poisoning and not due to the snakebite. This finding provides important evidence for the investigation into the circumstances surrounding the death.

Figure:

1 2 3

1-Standard cypermethrin, 2-Viscera II sample, 3- Viscera I sample

Fig.-1 Thin layer chromatography of viscera samples

Table:

Table 1 Observation of viscera sample treated with spray reagent

Sr. No.	Reagent	Observations
1	Mercuric nitrate- Potassium ferrocyanide,	No spot
2	Mercuric nitrate- Diphenylamine	No spot
3	Potassium iodate-starch	No spot
4	Alkaline resorcinol	No spot
5	Sodium carbonate- chloronil in acetone	No spot
6	O- Tolidine thereafter kept under UV	No spot
7	NaOH-Nickel amine	No spot
8	Copper acetate, O-tolidine	No spot
9	Sodium hydroxide- ferrous sulphate thereafter plate was heated in oven there after hydrochloric acid	Bluish green spot at Rf -0.67 it tallied with cypermethrin
10	Dragendorff's	No spot

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Removal of Ni (II) ions from aqueous solution using chitosan and activated carbon: isotherms and kinetics

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Abstract

The present study deals with adsorption of Ni (II) ions from aqueous solution using chitosan (CHI) and activated carbon (ACC) as adsorbents. Several parameters such as pH, contact time, adsorbent dosage, concentration of adsorbate and radiation dose were varied to achieve an optimized adsorption of the metal ions. It was concluded that maximum removal of Ni (II) ions (92.2%) using CHI was observed at pH 3, dosage 1 g and contact time 240 min. Maximum removal of Ni (II) ions (82.3%) was achieved using ACC at pH 2, dosage 2.5 g for 120 min. The percentage removal of Ni (II) ions increases slightly after irradiation with Co-60. The adsorbents were characterized before and after irradiation and adsorption using FTIR and SEM techniques which clearly indicated the occurrence of adsorption of metal ions. Harkin-Jura and Jovanovic isotherms study indicated multilayer adsorption. The adsorption process follows pseudo-second-order kinetics.

Introduction

In the modern civilization and progressive industrialization, the level of nickel pollution is intensifying in water bodies like surface water, soil water, and shallow groundwater. Wastewater from electroplating and battery production industries are common sources as waste for nickel. Some other sources are metal mining, vehicle emission, smelting, fossil fuel combustion, domestic, municipal and industrial waste disposal, fertilizer applications and organic fertilizers[1].

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Nickel shows many adverse effects on human beings, for instance, it is responsible for most common skin allergies called dermatitis, cardiovascular and kidney diseases, lung fibrosis and lung and upper respiratory cancer[2]. Nickel is considered as the most hazardous element to the environment due to its toxicity and carcinogenicity. Generally, the levels of Ni (II) ions in air is 5-40 ng/m^3, in agricultural soils is 3-1000 mg/kg and less than 2 µg/L in fresh water and oceans. (WHO). It has become essential to explore all its sources so that new efficient technologies can be developed for decreasing its concentration. Some of the existing methods which are routinely used for removal of nickel ions are ion-exchange, precipitation, reverse-osmosis and more. The reason for not choosing these techniques are the high cost and foul smell of loaded resins, expensive chemicals and membranes for long-term investment, respectively. Adsorption is found to be the cost-effective technique compared to other ones and this is the reason for choosing it for the study of removal of Ni (II) ions. Nowadays, more and more importance are being given on research into materials suitable for cheap and efficient removal of nickel ions from the environment. In addition, there is high availability of the adsorbents. Few of the adsorbents are organic, mineral sources biomass[3], agricultural waste or synthetically developed material are being used for removal of metallic ions.

This research is devoted to the study of adsorption of nickel ions on chitosan and activated carbon. CHI and ACC are comparatively cheaper and thus they were selected for this study. Chitosan is obtained from chitin by enzymatic or chemical deacetylation of chitin (removal of $-COCH_3$ group). Chitin is a biopolymer of the exoskeleton of living organisms such as shrimps, crabs, lobsters, beetles and in the cell walls of certain fungi. Therefore, β-D glucosamine is the monomer unit present in chitosan which is soluble in dilute acids and hence helps in enhancing the complexion with metals compared to chitin[4-6]. Chitosan is in a form of a white powder and is commercially available.

Globally, adsorbent activated carbon has been widely used in wastewater treatment. The process for production of activated carbon is to dehydrate, carbonize and activate raw materials. The starting material is dehydrated and carbonized by slowly heating it in the absence of air. During the step of carbonization, organic material is converted to primary carbon forming a mixture of ash, tars, amorphous carbon and crystalline carbon where some decomposition products or tars are deposited in the pores, which are later removed during the activation step. The current research gives an overview on adsorption of Ni (II) ions from aqueous solution using chitosan (CHI) and activated carbon (ACC) as adsorbents. In literature, there exists more data on types of modifications of CHI and ACC while only few work has been done on the modification using gamma irradiation. The adsorbents were irradiated with Co-60 gamma chamber 900A in order to examine any structural change responsible for increased adsorption. The effect of pH, contact time, adsorbent dosage and initial concentration of Ni (II) ions on the process of adsorption were monitored. Adsorbents were characterized using FTIR and SEM techniques. Isotherm and kinetic studies were performed on the obtained data.

2. Experimental

2.1. Adsorbate and adsorbent material

AR Grade nickel sulphate ($NiSO_4.7H_2O$) was purchased from Sisco Research Laboratories Pvt. Ltd. Chitosan of Otto brand was purchased from S. D. Fine-Chem Ltd., India. It is a fine powder of off-white color. Activated charcoal was supplied by S. D. Fine-Chem Ltd. It is in the form of black color powder. The commercially obtained CHI and ACC were irradiated in Co-60 gamma chamber 900A for three different doses 1, 5 and 9 kGy with a dose rate of 2.0838 Gy/ min, estimated by Fricke Dosimetry.

2.2. Batch adsorption process

Adsorption was performed by batch adsorption process at room temperature. In this process, aliquot of 25 mL of 2000 ppm of Ni (II) ion solution was placed in a round bottom flask at the pre-determined pH of the solution. An initial dosage of 1.0 g of adsorbent was added to the flask and was agitated on magnetic stirrer for 1 h at room temperature. The solution was then centrifuged and the supernatant solution was analysed for Ni (II) ions concentration using UV-Vis spectrophotometer. The experiment of the adsorption batch were repeated three times and mean values were presented.

The amount of nickel ions adsorbed by the adsorbent is given by equation (1)

$$q = \frac{C_0 - C}{m} \times V \qquad (1)$$

where q is the amount of metallic ion adsorbed by the adsorbent (mg/g); C_0 is the initial concentration of Ni (II) ions in contact with the adsorbent (mg/L), C is the equilibrium concentration of Ni (II) ions in aqueous solution (mg/L) after batch adsorption. V is the volume of Ni(II) ions solution (L) in contact with the adsorbent and m is the mass (g) of adsorbent.

The various parameters *viz* pH, contact time, dosage with initial concentration of metal ion were optimized for achieving maximum removal of Ni (II) ions.

2.3. Irradiation of adsorbents

The adsorbents (ICHI and IACC) were irradiated using a Cobalt 60 Gamma Chamber 900A. The γ radiation dose was measured using Fricke Dosimeter. The effect of radiation dose (1, 5 and 9 kGy) on removal of Ni (II) ions was studied to examine the changes in the structure of CHI and ACC induced by γ-radiation which may increase the percentage removal.

2.4. Characterization of adsorbent

FTIR spectra of virgin adsorbent, irradiated virgin adsorbent and loaded irradiated adsorbent obtained by using FTIR spectrophotometer (Shimadzu 8400) in the range 4000-400 cm^{-1} having KBr disk as reference. were analyzed for their vibrational frequency (transmittance) changes in the functional groups of the adsorbents.

Scanning electron microscope (SEM - JEOL, JSM 6360 LV) was used to investigate the texture and porosity of the adsorbents before and after adsorption at the optimized conditions. A thin layer of platinum was sputter-coated on the samples for charge dissipation during SEM imaging. The sputter coater (Eiko IB-5 Sputter Coater) was operated in an argon atmosphere. The coated samples were then transferred to the SEM specimen chamber and observed at an accelerating voltage of 20 kV.

3. Results and discussion

3.1. Effect of pH

One of the most significant aspects in adsorption studies is effect of pH of the medium. The percentage removal of Ni (II) ions with pH is shown in Fig. 1. The range of pH was varied from 2 to 7. In case of CHI, the adsorption was found to be almost constant from pH 2 to 7 and a slight increase at pH 3. This increase could be by the fact that total number of negative groups available for binding of metal ions increased and therefore competition between proton and metal ions became less pronounced and thus indicated higher adsorption. pH 2 shows a higher percentage removal of the metal ions onto ACC. The removal was found to be almost constant from pH 3 to 7. For further studies, pH 3 for CHI and pH 2 for ACC were used as optimized pH.

3.2 Effect of contact time

The effect of contact time for adsorption of Ni (II) ions was studied by varying the agitating time from 60 to 240 min (Fig. 2). As the contact between adsorbate and adsorbent increases, efficiency of removal also increases in the case of CHI. While in case of ACC, the percentage removal was almost constant (slightly higher at 120 min). After the adsorbed material form one molecule/ ion thick layer, the capacity of adsorbent gets exhausted and the metal adsorbed rate is controlled by the rate at which the adsorbate is transported from the exterior to interior sites of the adsorbent particle. In further study, 240 and 120 min are taken as equilibrium time for CHI and ACC, respectively.

3.3 Effect of adsorbent dosage

The effect of adsorbent dosage was studied by varying its amount from 1 to 2.5 g (Fig. 3). Adsorbent dosage seems to have great effect on adsorption process. It was found that 1 g of CHI was sufficient to achieve maximum removal of Ni (II) ions (92.2%) whereas 2.5 g of ACC shows maximum percentage removal of Ni (II) ions (82.3%). The phenomenon of increase in percentage removal of Ni (II) ions with increase in adsorbent dosage of adsorbent ascribed to the availability of surface area for the solute to adsorb.

3.4 Effect of concentration

The initial concentration of Ni (II) ions was varied between 400 to 2000 mg/ L at 25 °C at optimum pH, adsorbent mass and contact time. The percentage removal of Ni (II) ions with initial concentration remains almost unchanged for CHI and found to decrease for ACC (Fig. 4). The higher initial metal ion concentration provides a strong driving force between the liquid/ solid phases as reported by Mustapha et. al[7]. At lower concentrations, the ratio of available binding sites to the initial metal ion concentration appeared to be larger, while at higher concentrations overloaded adsorption sites could have been formed. This behavior is attributed to less availability of surface-active sites.

3.5 Effect of radiation dose

The percentage removal of Ni (II) ions using ICHI and IACC at optimized condition is illustrated in Fig. 5. It was found that in case of irradiated CHI there was slight increase of 0.2 % at 9 kGy dose and 3.38 % at 1 kGy for irradiated ACC in removal of Ni (II) ions. This is attributed to the insignificant changes in terms of structure for better adsorption of adsorbate ions on CHI and ACC. Similar results were observed for irradiated bentonites studied for adsorption properties as reported by M. Galamboš *et. al*[8].

3.6 Characterization studies

The spectra of the adsorbents were obtained by using FTIR. Fig. 6. shows that the adsorption peak for CHI is nearly at 2400 cm^{-1} which is responsible for combinations of C-H and C-C bonds for binding of Ni (II) ions. Few peaks are observed in the range of 1700 – 1500 cm^{-1}. This is attributed to the presence of double bond of C=C, C-O, and C-N of bond order 2, which vibrates to higher frequencies. For ACC, peaks around 2400 and 1500 cm^{-1} are responsible for alkyl groups and more specifically methyl group ($-CH_3$) (Fig. 7). Further examination of Fig. 6 and 7 shows slight change in peak intensity which indicates only slight increase in adsorption.

Morphological characteristics of adsorbents were studied with SEM and the corresponding micrographs are shown in Fig. 8 and 9. SEM micrograph (Fig. 8 (a)) of virgin CHI possesses irregular cavities of variable sizes from small to large. The surface areas seem highly porous with mean surface area of 6194 µm^2 and with mean length of 40.6 µm (measured by ImageJ software). These pores seem occupied after adsorption of Ni (II) ions on CH surface as shown in Fig. 8 (b) as no empty cavities are observed. Micrograph of virgin ACC (Fig. 9 (a)) shows homogeneous tiny size pores of mean surface area of 20.92 µm^2 with mean length of 5.65 µm. As the pores seem tiny, adsorption found to be occurred on the surface of ACC (layers) (Fig. 9(b)).

3.7 Adsorption Isotherms

An adsorption isotherm is the relationship between the adsorbate in the liquid phase and the adsorbate adsorbed on the surface of the adsorbent at equilibrium at constant temperature. The equilibrium adsorption is essential in designing the adsorption systems. For solid-liquid systems, several isotherms are available in the literature.

Langmuir isotherm

Langmuir isotherm represents equilibrium distribution of metal ions between solid and liquid phases. The linear Langmuir isotherm is expressed as follows[9].

$$\frac{1}{q_e} = \frac{1}{ab} \times \frac{1}{C_e} + \frac{1}{b} \qquad (2)$$

where q_e is the amount of adsorbate at equilibrium (mg/g); a, Langmuir adsorption constant related to the affinity of the binding sites (mL/g); b, the adsorption capacity (mg/g); C_e, the equilibrium concentration of Ni (II) ions in the solution after adsorption (mg/L). The essential characteristics of Langmuir isotherm can be expressed in terms of dimensionless separation factor, R_L which is defined as equation (3)[9].

$$R_L = \frac{1}{1+aC_0} \qquad (3)$$

where C_0 is the initial concentration (mg/L). The value of R_L indicates the shape of isotherms to be either unfavourable ($R_L > 1$), linear ($R_L = 1$), favourable ($0 < R_L < 1$) or irreversible ($R_L = 0$).

It was observed that CHI follows Langmuir isotherm (Fig. 10). The constant, b (67.11 mg/g) (Table 1) indicates the good relation with the variation of suitable area and porosity of CHI which implies that large surface area and pore volume resulted in moderate adsorption capacity. The constant, R_L (1) (Table 1) indicated that the adsorption of Ni (II) ions on CHI is favorable[9]. It was observed that the adsorption of Ni (II) ions on ACC did not fit Langmuir isotherm and thus was not shown in article.

Harkin-Jura Isotherm

The model assumes the possibility of multilayer adsorption on the surface of adsorbents having heterogeneous pore distribution[10]. It is expressed as follows:

$$\frac{1}{q_e^2} = \frac{B}{A} - \left(\frac{1}{A}\right)\log C_e \qquad (4)$$

where B and A are Harkin-Jura constants which can be obtained from the plot $1/q_e^2$ versus log C_e. It was observed from Fig. 11 and Table 1that the adsorption of Ni (II) ions on CHI fit well the Harkin-Jura model. It can then be concluded that the adsorption of Ni (II) ions is a multilayer adsorption applicable to heterogenous surfaces of CHI. Similar results were reported by Foo and Hameed[11] for adsorptive removal of reactive black 5 from wastewater using bentonite clay.

Jovanovic Isotherm

The model is based on the assumptions of Langmuir model and in addition, it explains the possibility of some mechanical contacts between adsorbate and adsorbent[11]. The linear form of Jovanovic isotherm is expressed as follows[12]

$$\ln q_e = -K_J C_e + \ln q_{max} \qquad (5)$$

Where q_e is the amount of Ni (II) ions adsorbed by the adsorbents at equilibrium (mg/g), q_{max} is maximum uptake of adsorbate and K_J is Jonanovic constant obtained from plot ln q_e versus C_e.

The adsorption of Ni (II) ions on CHI and ACC were tested Jonanovic. It was found from the correlation coefficients (0.9228) that adsorption of Ni (II) ions on ACC followed Jovanovic isotherm better than the others (Fig. 12 and Table 1).

3.8 Adsorption kinetics

Adsorption kinetics was studied by using pseudo-first-order and pseudo-second-order kinetics. It was observed that the adsorption of Ni (II) ions did not follow pseudo-first-order kinetics.

Pseudo-second-order:

The pseudo-second-order model is represented as follows[13]

$$\frac{t}{q_t} = \frac{1}{(K_2 q_e^2)} + \frac{t}{q_e} \qquad (6)$$

where K_2 is pseudo-second-order rate coefficient (g/mg/min) and q_e^2 (mg/g) is the maximum adsorption capacity. A graph (Fig. 13 and Fig. 14) of t/qt versus t is plotted from which the intercept and slope can be determined and they are presented in Table 2.

The adsorption of Ni (II) ions using both the adsorbents CHI and ACC obeys pseudo-second-order model (0.993 and 0.9074, respectively). This concludes that the overall rate of Ni (II) ion adsorption process seemed to be controlled by the chemical process through sharing of electrons or by covalent forces through exchange of electrons between adsorbent and adsorbate.

Conclusions

The current research showed the effectiveness of both adsorbents CHI and ACC in the removal of Ni (II) ions from aqueous solution. The study of adsorption of Ni (II) ions concluded that the maximum removal of metal ions (92.2 %) was observed at pH 3 with 1 g of CHI in contact for 240 min. 82.3 % removal of Ni (II) ions was achieved using pH 2 with 2.5 g of ACC in contact 120 min with the adsorbate. The percentage removal of Ni (II) ions increases slightly after irradiation with Co-60. FTIR and SEM studies clearly indicated the occurrence of adsorption of metal ion. Langmuir, Harkin-Jura and Jovanovic isotherms study indicated multilayer adsorption with adsorption capacity of CHI is found to be 67.11 mg/g for Ni (II) ions. Both the adsorption processes follow pseudo-second-order kinetics and the adsorption capacity for ACC was found to be quite less for Ni (II) ions (1.05 mg/g). It may be concluded that CHI may be used as a potential adsorbent for adsorption of Ni (II) ions (adsorption capacity 67.1 mg/g) compared to synthesized adsorbent developed with plant extract[15] (MWCNTs-KIAgNPs: 40.1 mg/g). However, ACC (1.0 mg/g) seems to have least (and closely to 4.0 mg/g-beech sawdust) adsorption capacity as compared to other adsorbents.

This work concludes that CHI can be used as a potential adsorbent compared to ACC for effective removal of Ni(II) ions and can also be applied to industrial effluents for treatment.

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Figures:

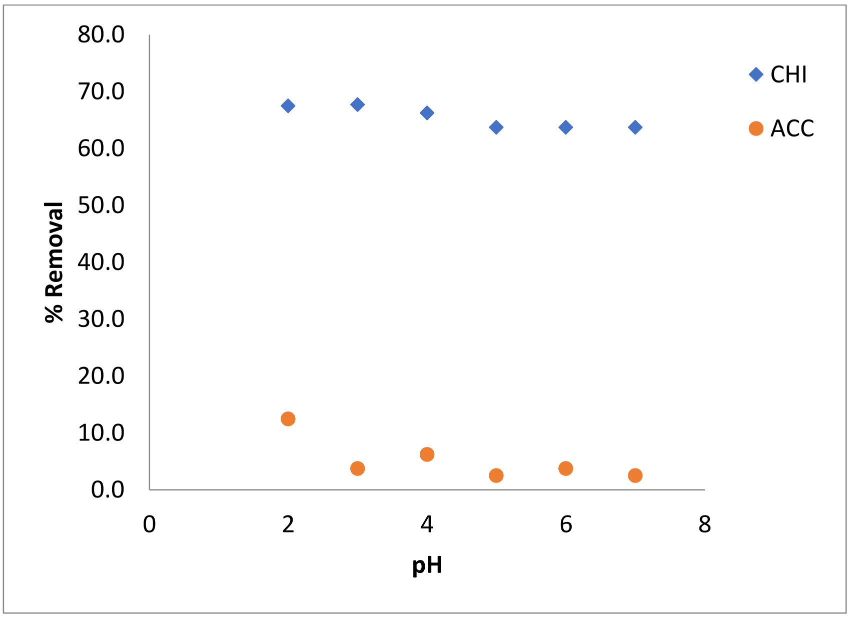

Fig. 1. Effect of pH of solution on adsorption of Ni (II) ions using CHI and ACC

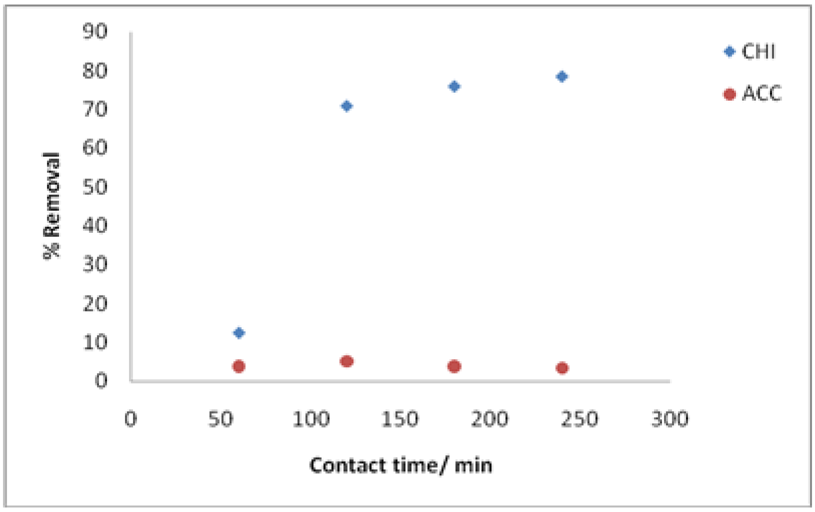

Fig. 2. Effect of contact time on adsorption of Ni (II) ions using CHI and ACC

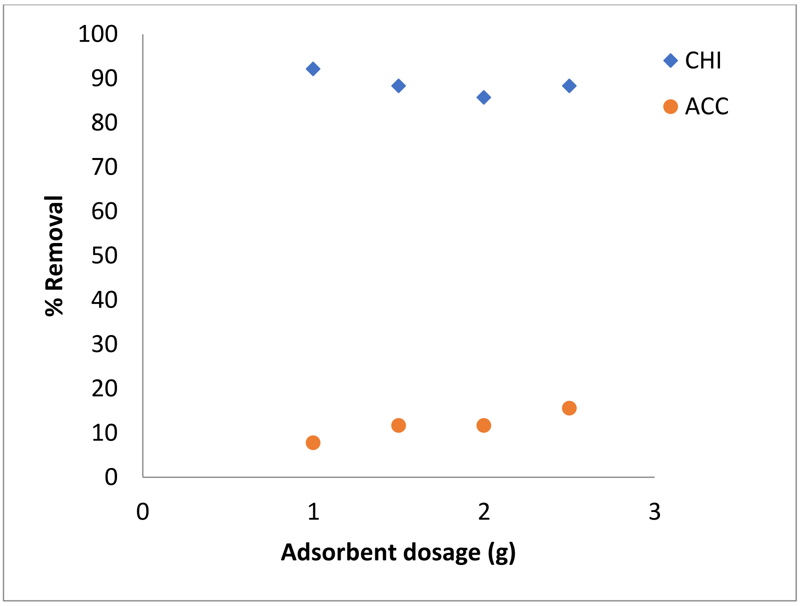

Fig. 3. Effect of adsorbent dosage on adsorption of Ni (II) ions using CHI and ACC

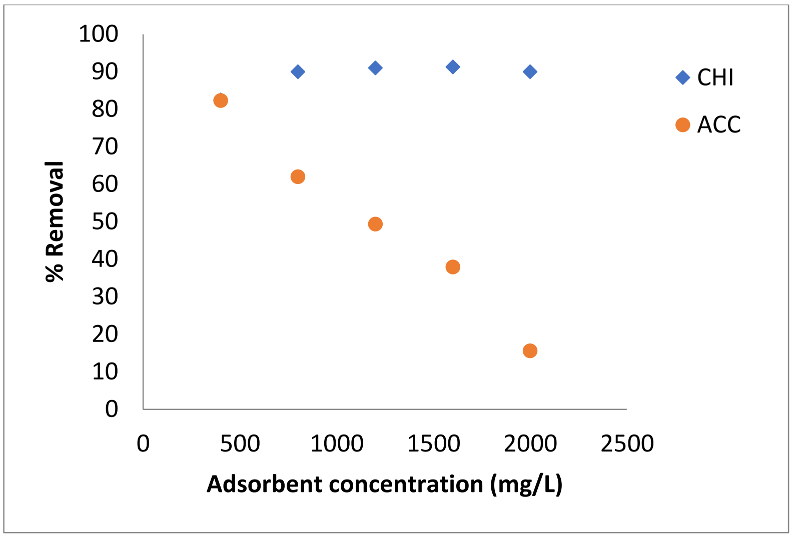

Fig. 4. Effect of adsorbate concentration on adsorption of Ni (II) ions using CHI and ACC

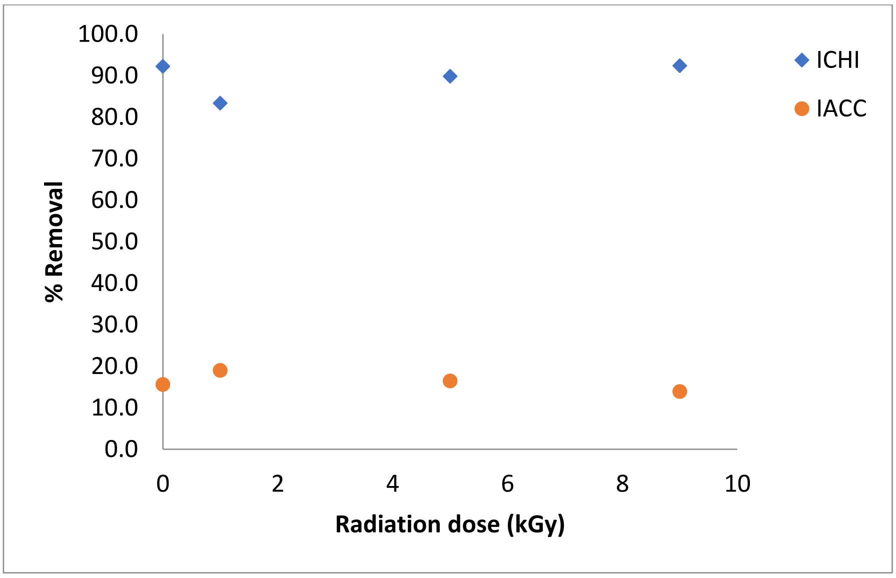

Fig. 5. Effect of radiation dose on removal of Ni (II) ions using ICHI and IACC

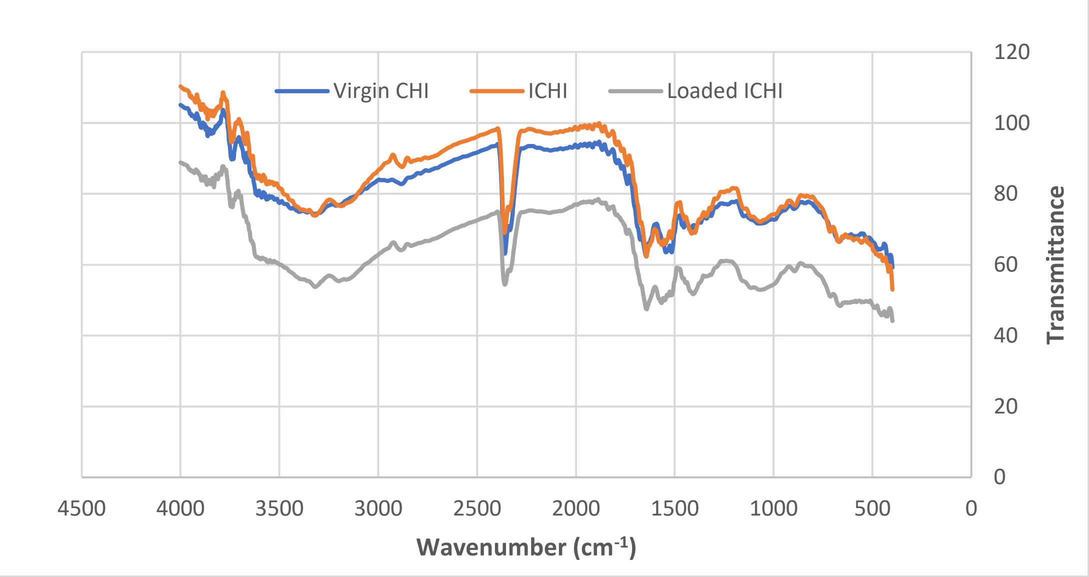

Fig. 6. FTIR spectra for CHI

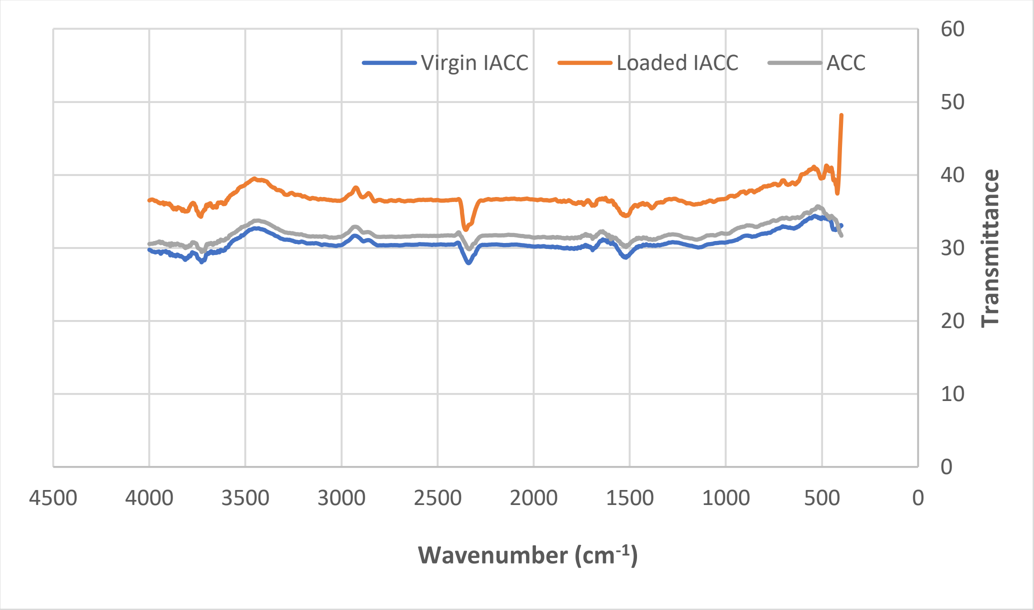

Fig. 7. FTIR spectra for ACC

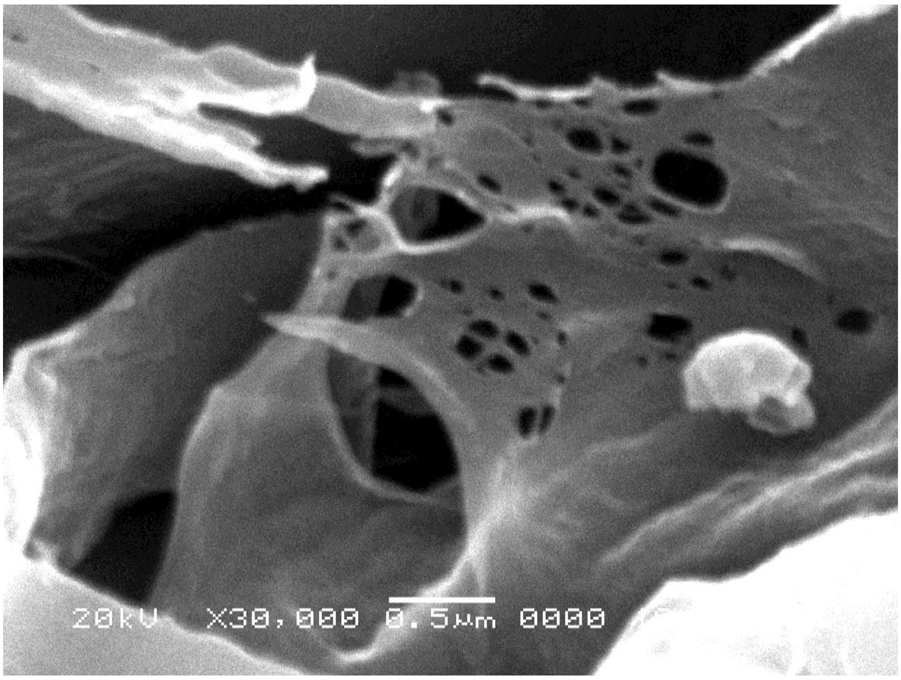

Fig. 8. SEM micrograph of **(a).** virgin CHI

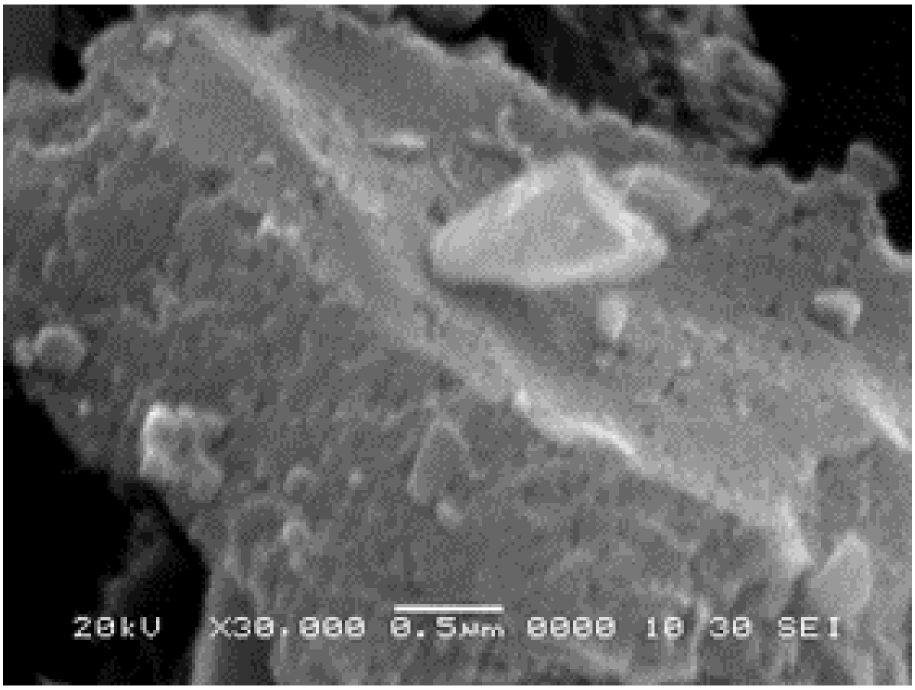

Fig. 8 (b) Ni (II) loaded CHI

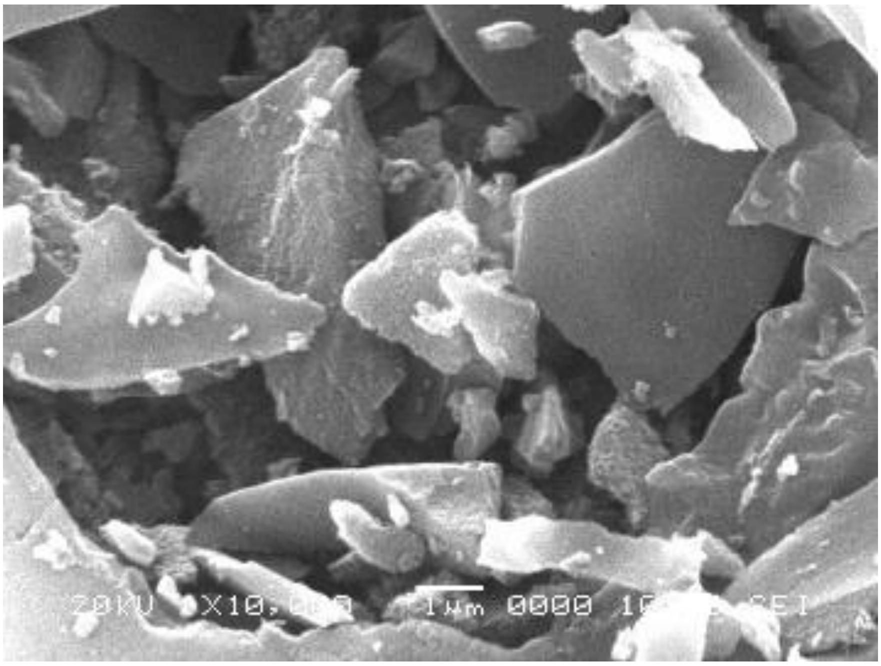

Fig. 9. SEM micrograph of **(a)** virgin ACC

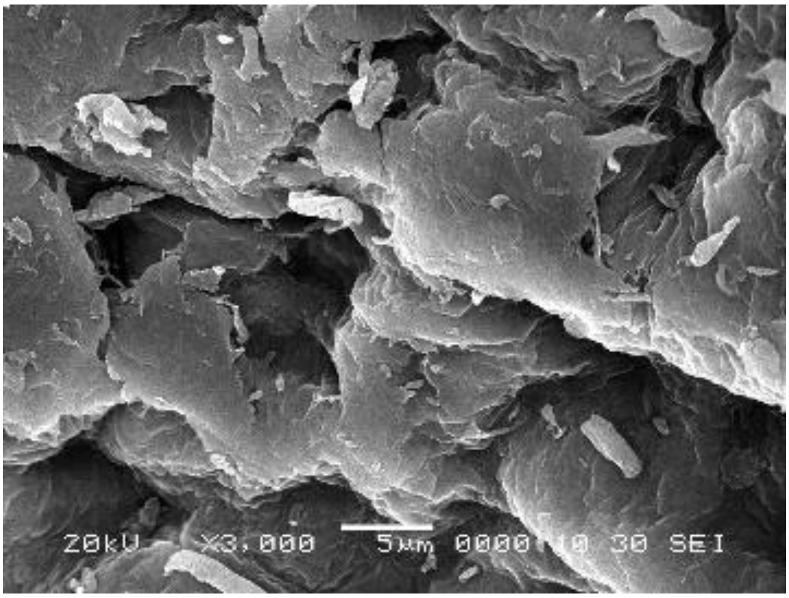

Fig. 9. (b) Ni (II) loaded ACC

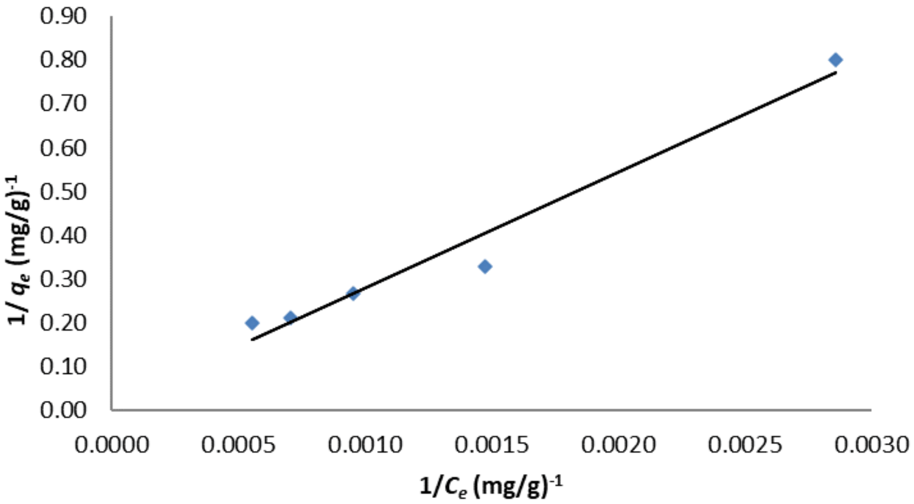

Fig. 10. Langmuir isotherm for adsorption CHI

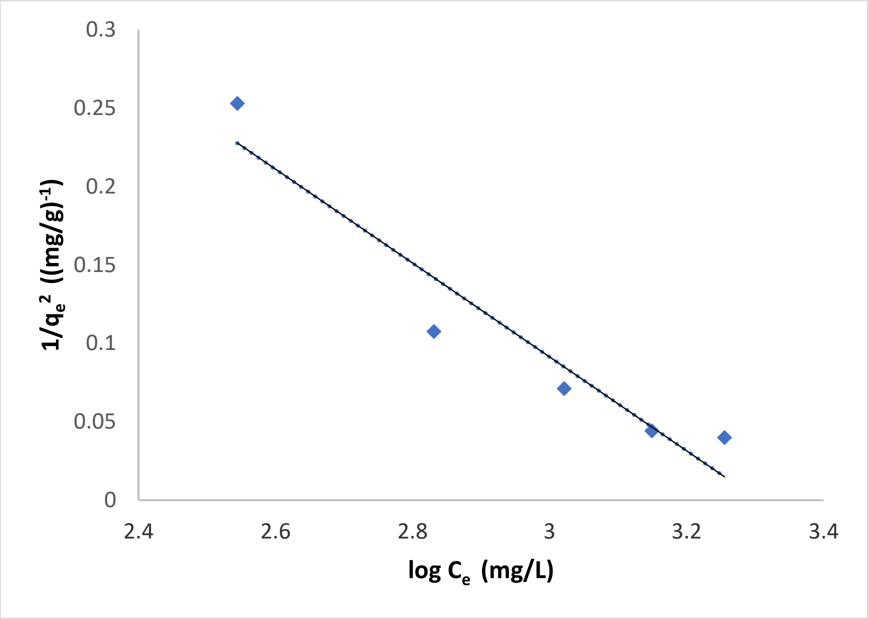

Fig. 11. Harkin-Jura isotherm for adsorption CHI

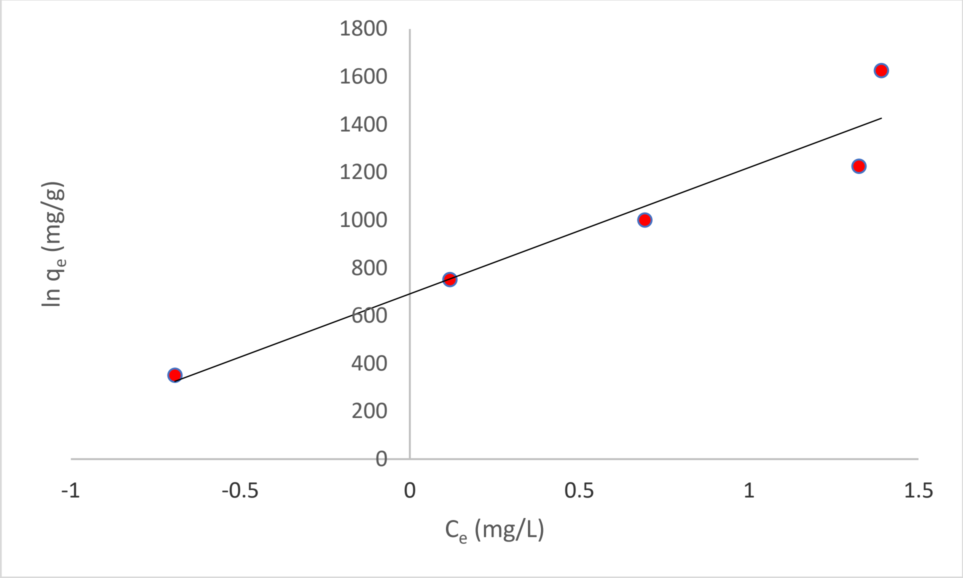

Fig. 12. Jovanovic isotherm for adsorption of Ni (II) ions on ACC

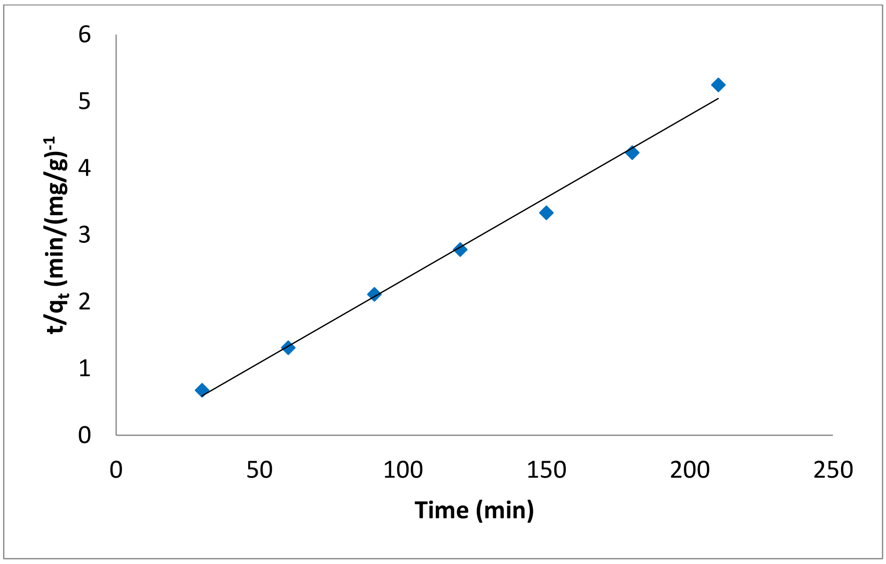

Fig. 12. Second-order kinetic plot of adsorption of Ni (II) ions on CHI

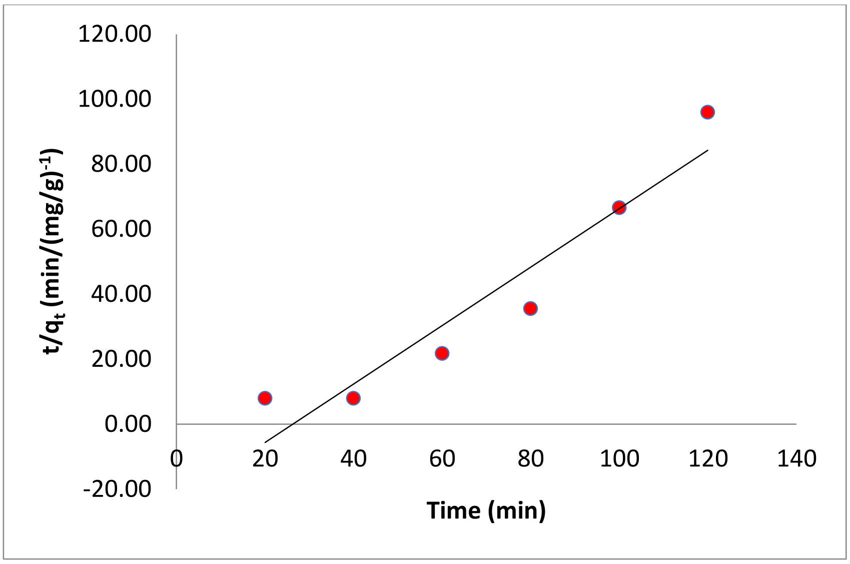

Fig. 13. Second-order kinetic plot of adsorption of Ni (II) ions on ACC

Tables:

Table: 1. Adsorption isotherm parameters for adsorption on Ni (II) ions on CHI and ACC

	Langmuir			
CHI	**a (10^{-5}) mL/g**	**b (mg/g)**	**R_L**	**R^2**
	5.64	67.11	1.00	0.9668
	Harkin-Jura			
	A	**B**		**R^2**
CHI	3.34	3.30		0.9146
	Jovanovic			
	K_J	**q_{max}**		**R^2**
ACC	-528.51	2.04		0.9228

Table 2. Kinetics Parameters for adsorption of Ni (II) ions using CHI and ACC

	Pseudo-second-order		
	q_e^2 (mg/g)	K_2 (g/mg/min)	R^2
CHI	40.49	$-3.938\text{x}10^{-3}$	0.9930
ACC	1.11	$-34.24\text{x}10^{-3}$	0.9074

Table 3. Comparison on adsorption capacities of adsorbents for removal of Ni (II) ions

Adsorbents	Adsorption capacities (mg/g)	Reference
Composite-$CaCO_3$	769.2	14
Composite-biopolymer base material	500	14
MWCNTs-KIAgNPs	40.1	15
Sodium hydroxide treated rice bran	153.6	16
Acid treated sawdust	74.1	17
Beech sawdust	4	18
Chitosan (CH)	67.1	This study
Activated carbon (ACC)	1.0	This study

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Metallic *Bhasmas*: A Review on Chemical Characterization, Particle Size and Toxicity

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Abstract

Bhasmas are unique metallic-herbal preparations of Indian origin, widely recommended for the treatment of chronic ailments. These intriguing formulations of metals are associated with organic macromolecules derived from the medicinal herbs. *Bhasmas* are often prepared by repeated incineration of metals with herbs and its extracts by alchemic processes and are taken along with honey, milk, butter, or ghee. Besides primary constituent of metals, *bhasmas* also contain other metals as minor constituent or in traces. Commercially available seventeen *bhasmas* based on Ca, Fe, Zn, Hg, Cu, As, Ag and Sn were characterized by instrumental neutron activation analysis (INAA) for up to 20 elements. The technique involves irradiation of the sample with thermal neutrons in a nuclear reactor followed by assay of gamma activity by high-resolution gamma ray spectrometry. Concentrations of major, minor, and trace elements vary in a wide range even in *bhasmas* of the same primary element depending on its preparation method. C, H, and S were also found in significant amounts suggesting the possible presence of organic macromolecules that may act as ligands. Transmission electron microscopy (TEM) studies have shown that the *bhasmas* as available in the market are not really nano particles contrary to claims of some literature reports. Westerners think *bhasmas* to be highly toxic especially those of As, Hg, and Pb, highly toxic elements. Still *bhaasms* of these elements are widely recommended. Clinical evidences suggest that the *bhasmas* taken in small doses are highly beneficial to the body system and do not cause any adverse effects. It is essential to follow quality control in the preparation of *bhasmas*. A review of our earlier work is also presented.

Keywords; *Bhasma*, Chemical characterization, Instrumental Neutron Activation Analyis (INAA), Transmission Electron Microscopy (TEM), Particle size, Toxicity.

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Introduction

Ayurveda, the traditional Indian health care system has been in vogue since the Vedic period. It advocates holistic approach to the human health care thus presenting a balance between the physical, mental and spiritual functions of the body and strengthening its immune system. Study of ancient *Ayurvedic* literature indicates the use of metals, minerals and gems since 7th century B.C.[1]. Siddha Nagarjuna considered to be the father of Indian alchemy and *Rasa Shastra,* first suggested the use of precious metals *viz* silver, gold, copper, zinc as medicines and described the preparation of their *bhasmas.* In spite of many processes described for the preparation of *bhasmas,* no scientific process control has been discussed/developed. Many world civilizations such as those of Africa, China, Egypt, and South America have described the use of herbs as medicines but no where metals or metallic-herbal preparations are described. Therefore, Indian system of medicine is unique where the importance of metals in life processes was first recognized.

Bhasma, literally means ash, is unique *Ayurvedic* herbomineral/metallic formulation of nano dimensions and of high potency, recommended for the treatment of chronic ailments. These intriguing formulations of metals are associated with organic macromolecules derived from herbal extracts/juices by alchemic processes making these biologically assimilable with least side effects[2]. *Bhasmas* are often prepared by repeated incineration of metals with medicinal herbs and are taken in small doses along with honey, milk, curd, butter, ghee etc so as to eliminate their harmful effects[3]. Besides primary constituent metal such as Ca, Fe, Zn, Ag, Au, Hg, As these also contain other metals as minor constituents or in trace amounts[4]. The metals are mostly present as oxides, sulfides, and carbonates or as complex with organic ligands derived from the herbs. These additional elements play an important role in the treatment of diseases and hence it is essential to determine for their quality control or toxic effects, if any.

Bhasmas are prepared from precious metals and their naturally occurring salts by calcination process called *putas*. However, before calcination, the metal must go through two main processes, physical purification called *shodhan* and chemical detoxification called *maran,* both terms derived from Sanskrit, an ancient Indian language. The primary steps of preparation method include crushing, boiling and repeated incinerations in earthen crucible at specified temperature that make the minerals ready for human consumption. This purification process is different from chemical purification and is carried out in a special vessel under the earth and incinerated using cow dung's dry cake[1]. In chemical purification only the foreign matter is eliminated whereas *Ayurvedic* purification is aimed at -

i) Removal of harmful effects from the crude material.

ii) Alteration in undesirable physical properties of the crude material.

iii) Changing some of the characteristics of the crude material.

iv) The enhancement of therapeutic action making it biologically assimilable and maintaining its potency for a long period of time.

When *bhasma* is finally prepared it should be tested to meet following requirements-

a) It should have no metallic luster (*Nishchandrika*).

b) The *bhasma* powder should be fine enough so that when rubbed between the index finger and thumb, it should go into the grooves (*Rekhapurit*).

c) When a small quantity of *bhasma* is sprinkled onto cold water, it should float on the surface (*Varitaram*).

d) The *bhasma* should not revert to its original state (*Apurnabhava*).

In *Ayurveda* minerals remain combined with herbs so as to help in the assimilation and deliver the ingredients to the human body. It is now well established that several metals play a vital role in the biochemical and enzymatic processes as well as in the cure of many chronic diseases. Minerals are essential constituents of the bone, teeth, muscles, blood and nerves and play a vital role to our overall mental and physical wellbeing[5,6]. Whereas proteins, enzymes and vitamins are manufactured in human body by physiological processes, minerals cannot be manufactured in a similar manner but supplemented only. Hence, minerals of Fe, Ca, Mg, Mn, Cu and Zn found in the soil are first absorbed directly in plant roots and then dispersed in different parts. These mineral elements are then supplied to our body through the food chain. Perhaps the metal in *bhasma* bound to carrier macromolecule, acts as a catalyst or alters the membrane fluidity. Apparently, the organic ligands derived from the herb render the metal easily assimilable/bioavailable. Another aspect of *Ayurvedic* preparations is synergism, which is apparently achieved by selectively blending of many plants, minerals and animal products, and thus maintaining the active ingredients at a minimum level and reducing or eliminating its side effects.

In earlier days, the physicians called *Vaidyas* were preparing these *bhasmas* and other herbal preparations according to well laid procedures described in old texts. Hence, the quality of these preparations was not subjected to any review but was based on the sacred faith between the physician and the patient. However, in modern times these are manufactured by pharmaceutical firms who may or may not be following the exact procedure. Therefore, a physician or a patient seeks assurance for the quality, safety and efficacy of any herbal *Ayurvedic* medicine more so because of Government regulations especially for export in the western market. Hence, any *bhasma* or other herbal preparation needs quality control as many of them have been found to contain toxic substances. In recent years many reports from USA, Canada and other western countries have banned Indian herbal preparations because of toxic element contents[7]. In view of these reports, it has become essential to standardize these herbal formulations and maintain quality control. Ingredients and uses of seventeen metal based *bhasmas* analyzed in this study are listed in Table 1.

Several workers have analyzed *bhasmas* of various metals, alloys and minerals, for major, minor and trace elements by employing a variety of classical and instrumental analytical methods *viz* flame photometry, atomic absorption spectrophotometry (AAS), inductively coupled plasma-atomic emission spectrometry (ICP-AES), particle induced X-ray emission (PIXE), X-ray diffraction[8-14]. Earlier in our laboratory, we have extensively employed INAA for major, minor and trace element of a large number of commercial *bhasmas*[15,16]. In continuation, we present here a review of our earlier work and report data on C, H, and S contents that may be present as minor constituents. Toxicity of some elements is discussed because of prevailing controversy. Also our results on particle size by transmission electron microscopy (TEM) are presented for the first time.

Experimental

Sample collection and reactor irradiation All the seventeen *bhasmas* analyzed in this study were procured commercially from M/s Dabur India Ltd (Delhi), Baidyanath Ayurved Bhawan Ltd (Jhanshi), Deshrakshak Aushdhalaya (Haridwar), and local Ayurvedic physicians in Roorkee. Names of all the bhasmas, its ingredients and their uses as described in literature are listed in Table 1. Two Reference Materials Peach Leaves (SRM 1547) and Mixed Polish Herbs (MPH 2), used as comparator standards, were procured from NIST, USA and INCT, Poland respectively. All the samples and RMs were stirred well and dried at 80 ^{o}C in oven for 2h before use. 30-50 mg each of the sample and RMs were weighed accurately, and packed in Alkathene/aluminum foil for short and long irradiations respectively in APSARA/ CIRUS reactor at BARC, Mumbai. Other details are the same as described earlier [15,16].

Activity measurements After suitable cooling, samples were unwrapped, swiped with acetone for decontamination and mounted on a Perspex sheet. Gamma activity was assayed by using high resolution gamma spectrometry at different intervals of time. Other details of experimental setup and counting schedule are same as reported earlier [15,16].

Main constituent of the metallic *bhasma* was analyzed by conventional classical methods. C, H, N, and S were determined by using Elementar Vario-EL III (Germany) after prior calibration. N content was also analyzed but found in insignificant amounts and hence not reported.

Results and discussion

Elemental concentrations are calculated by comparator method using RMs with certified elemental contents. NAA has the unique advantage of being multielemental, nondestructive and higher sensitivity requiring small sample size only. Main constituent of the *bhasmas* analyzed in this study was found at % level whereas other nutrient and toxic elements were found at minor and trace level. All the elemental contents of major, minor and trace constituents are listed in Tables 2 and 3. Multiple *bhasmas* of the same element such as that of Ca (4), Fe (4), Zn (3) and Hg (3) were analyzed as each one differs in preparation methodology and so also these have different medicinal importance. Significance of variation in elemental contents of these is discussed here briefly.

Calcium based *bhasmas*: Calcium forms >1% of the total body content and Ca along with P are considered structural elements playing an important role in correcting bone metabolic disorders[5]. With increasing industrialization, skeletal disease of osteoporosis characterized by low bone mass and micro structural deterioration of bone tissue leading to enhanced bone fragility, has become a major health problem. In *Ayurveda*, several Ca preparations from natural/sea sources are recommended for supplementing its deficiency to growing children and ladies especially after 50 years of age. All the *bhasmas* were prepared by repeated incineration/calcination of pearls, oyster or conch shell in a covered vessel under reducing atmosphere. Four preparations analyzed in this study show a varying content of 29.5 - 41.9% Ca, 2.73 - 22.1 mg/g Mg, 0.29 - 0.96 mg/g P and a number of other elements such as Na, K, and Fe which all play a vital role in life processes[5,6]. Variation in range and mean elemental concentrations of these elements along with As and Hg, the two toxic elements are illustrated in Fig. 1. Several workers have reported antacid activity of these preparations and studied their role in enhancing effectiveness of antibiotics [17,18]. Surprisingly, all the Ca-based *bhasmas* showed high C (11.8 – 15.1 %), H (0.25 – 0.81 %) and S (0.12 – 0.81 %) suggesting the possible presence of carbonate and sulfate[8]. Interestingly all the four *bhasmas* contain higher amounts of As and Hg than permissible limits that may possibly be attributed to polluted marine environment.

Iron based *bhasmas*: Iron is an essential trace element, that nourishes blood, enhances vigour and its astringency prevents blood from becoming too hot or too fluid[4]. Pandit et al[19] evaluated chemical and pharmacological action of different Ayurvedic preparations in iron deficient anemic patients. These *bhasmas* are mostly prepared from pure iron filings/ferric oxide or magnetic iron incinerated with decoction of *Trifala, ghritkumari ras,* vinegar and sesame oil. Iron content varies in a much wider range of 5.31 - 56.9% with least amount in *Trifala yog lauh* and highest in *Vanaspati yog lauh*. Other minor constituents are Na, K, Mn and P besides trace amounts of Co, Cu and Zn including toxic elements (As and Hg). Ranges and mean elemental contents in 4 *bhasmas* analyzed in this study are shown in Fig. 2. Treatment of iron deficiency anaemia with iron salts like ferrous sulfate results in gastrointestinal irritation, cardiovascular collapse, damage to brain and liver. A perusal of C, H and S data in small amounts (Table 1) suggests the possible presence of organic macromolecules that may act as ligands. Jani et al[20] have detected trace amounts of polycyclic aromatic hydrocarbons (PAH) by HPLC in *Ayurvedic* preparations.

Zinc based *bhasmas*: Zinc is an essential constituent of many enzymes in the human body as more than hundred metalloenzymes are known. Its deficiency may cause reduction in cell division resulting in failure of growth, weight loss impairment of tissue repair[5,6]. Out of three zinc based *bhasmas* analyzed in this study, its content varies in a wide range of 0.012 - 60.0% and these contain higher amounts of iron (3.87 – 22.8 mg/g), besides K and P. Even two *yashad* bhasmas procured from different pharmaceutical firms differ in their elemental contents significantly. *Kharpar* is primarily $ZnCO_3$ though it also has Ca (23.9%) and C (8.4%) suggesting that some $CaCO_3$ may have been added. Khosa and Dixit[21] have shown *yashad bhasma* to increase virility and intelligence. Also Puri et al[22] have suggested its role in the treatment of myopia. An elemental variation plot of zinc based *bhasmas* is shown in Fig. 3. It is observed that high amounts of Mn (117 - 334 µg/g) along with significant amount of S (0.257 – 0.436 %) seem to be always associated in these *bhasmas*. Several zinc based wound healing ointments and eye drops (Zincorin and Occulus contain ~0.1 5 % $ZnSO_4$) are being marketed by various pharmaceutical firms.

Mercury based *bhasmas*: Mercury is an industrial hazard and occurs in environment as heavy metal contaminant. Any form of mercury (inorganic or organic) is considered to be highly toxic, causing *Minimata* disease[23,24]. If inhaled in trace amounts, it exhibits purgative effect. However, in *Ayurveda* its preparation especially *Makaradhwaja* is considered as a marvel drug[25] that can cure all diseases if properly prepared and used. However, if improperly prepared then it may cause all kinds of diseases[26]. In our study, we have found *Siddha makaradhwaj* to be stoichiometrically pure HgS with no other element including gold being found even in traces except trace amounts of C (0.06%) and H (0.03%). In another brand of *Makaradhwaja gutika* with swarnakalp marketed by Dhootpaeshwar Ltd, Mumbai, only trace amounts of Hg (168 μg/g) but significant amount of Au (462 μg/g) was found. We presume it is not real or a duplicate sample may have been sold as a branded product.

Other metal *Bhasmas*: We also analyzed one each of Ag, Cu, Sn and As based *bhasmas.* Of these As is highly toxic. Copper, silver and gold have long been known as coinage metals but these are also considered for medicinal purposes. *Rajat bhasma* is recommended for epilepsy, neuropsychobehavioural effects, and tuberculosis[27]. Besides 23.4% Ag, *rajat bhasma* also contained As (14.2 %), P (5.14%) and Na (1.28%) as major constituents along with trace amounts of Mn (183 μg/g) and Au (140 ng/g). Arsenic is considered to be the king of poisons but it is also known to be a possible essential element in *Unani* system of medicine with analgesic activity and proconvulsant effects[28]. Arsenic based *kushta khas* shows As (3.65 %) along with Ca (30.1 %) and S (21.1%) as major components. It also contains Na (0.83 mg/g), K (2.42 mg/g), P (1.06 mg/g) and Cl (0.20 mg/g) as minor constituents along with Mn and La in trace amounts. Thus As might be present as sulfide (As_2S_3). Copper is an integral part of several enzymes influencing our immune system. It also acts as antioxidant and plays an important role in scavenging superoxides[29]. Sample of *tamra bhasma* contained Cu (44.1%), Fe (7.12%), P (1.09%) and K (2.37%) as major constituents and As (~20), Mn (134) and Zn (358) in µg/g amounts. Higher amount of S (22.0%) may be indicative of presence of CuS. Tin based *vanga bhasma* contained Sn (43.8%) and Ca (7.35%) as major constituents besides Fe (0.3%) and K (0.88%) as minor constituents and P (720), Mn (257), Zn (67) including In (17.1) in µg/g amounts. Chopra et al[30] first reported synthesis of tin based *bhasma* in 1936. In *Ayurvedic* literature, tin based *bhasma* has been recommended for diabetes, semen disorder, skin disease and syphilis[3].

Particle Size Studies

A *bhasma* is suitable for drug use if it has no metallic luster. It must be extremely fine powder such that the particles are smaller than skin ridges of the index finger and the thumb, float on cold water, does not revert to metallic form, maintains its potency indefinitely and manifests no toxicity[3]. The processing technology during the preparation of *bhasma* is very complex and specific according to ancient literature. It has been observed that micro cracks are developed at the grain boundaries during thermal cycling. It is supposed that microfine medicinal product has easy digestive power and quick reaction with the bile juices. Some workers have suggested *bhasmas* as biologically produced nano particles. Prakash[1] has reproduced some photographs showing microstructures of gold, zinc and lead *bhasmas*. However, no experimental measurements have been reported confirming the nano-sized particles. In order to confirm these literature claims, TEM photographs were recorded for a few *bhasmas* of *shankh* (Ca), *yashad* (Zn), *vanga* (Sn), and *Vanaspati Yog Lauh* (Fe) shown in Fig. 4. It is observed from the photographs that the particle size of *yashad* (Zn) was found to be 520 nm and those for *shankh* (Ca) and Fe these correspond to 260 nm. *Vanga* containing Sn showed a much bigger particle size of 2 µm. Thus, our experimental observations do not clearly show the *bhasma* to be of really nano particle size (< 100 nm) but as somewhat of larger particle size.

Bhowmick et al[12] have reported physicochemical characterization of *yashad* (Zn) *bhasma* and detected nanoparticles containing nonstoichiometric zinc oxide with irregular shape and 15-25 nm size by TEM. Paul and Sharma[31] have prepared nano size (~15 nm) particles of *swarna* (Au) *bhasma* and studied its blood compatibility to evaluate cytotoxicity. In a recent study Kantak et al[13] have prepared *Abhraka bhasma* and shown crystalline nature of different sizes and shapes ranging from 50 nm to 1 µm. It may be mentioned that our *bhasma* samples were not freshly prepared and these being old, aggregation might have occurred. It is suggested that more thorough experimental evidence using high resolution TEM is required to confirm the nano particle size of *bhasmas* of freshly prepared samples.

Toxicity of *bhasmas*

Sometime back a bunch of Ayurvedic medicines including *bhasmas* were sampled from an Indian store in New York and analyzed. Subsequently a report was published by Saper et al[7] in the Journal of the American Medical Association (JAMA) which created a whirlwind of controversy that wreaked havoc on the export market of *Ayurvedic* medicines from India. The study was carried out in the context of toxicity of As, Hg and Pb that remain associated with the use of herbal medicines. Unlike many trace elements required by the body as minerals, toxic heavy metals do not play any role in the metabolic processes in human body[5]. In fact these toxic elements tend to accumulate in tissue causing toxicity, damaging the body organs. Several diseases such as *Minamata, Itai-Itai* etc are known to be caused by these toxic elements[5]. Yet, metals are the starting point of *bhasmas*. It is argued that toxicity can arise only from a particular metallic species and not all forms are toxic. However, a *bhasma* prepared according to the classical methods never contains a free metal. Since metallic preparations have been in use since ages and no toxicological studies are reported, it is assumed these are safe to consume in small doses. Of course, along with their dose and mode of administration, dietary restrictions are also very important. A *bhasma* is always consumed with honey, milk, curd, butter milk, butter or ghee whereby their harmful effects may be neutralized. It seems that due to commercialization, some manufacturers may not be following the recommended procedure (good practices) in the preparation of these medicines[32]. Therefore, it is essential to have quality control and provide analytical data for all the herbal preparations so as to ensure that no toxicity due to metals is added to herbo-mineral preparations. In this regard, Chan[32] has emphasized the essentiality of following good agricultural practices (GAP), good laboratory practices (GLP), good manufacturing practices (GMP) and good supply practices (GSP). Recently Department of AYUSH, Ministry of Health & Welfare, Government of India has come out with a notification with permissible limits for As, Pb, Hg and Cd[33]. Nagarajan et al[34] have reported the preparation and characterization of lead based *Naga bhasma* whereby they have emphasized that repeated calcination leads to the formation of nano crystalline lead sulfide. Though lead is heaviest of all toxic metals but it is still recommended as *Ayurvedic* medicine in minute amounts. Recently Liu et al[35] have studied a number of metallic *bhasmas* of Tibetian origin and reviewed their therapeutic effects and toxicity aspects. It has been emphasized that chemical form of the metal in *bhasma* plays a role in risk assessment for its disposition, efficacy and toxicity.

A cursory look of data in Tables 2 and 3 including Figs 1 to3, it is clear that most *bhasmas* analyzed in this study contain significant amounts of As and Hg both of which are highly toxic but their dosage taken with honey as recommended in old texts are useful. Our composition data show the need for quality control of *Ayurvedic* preparations manufactured by pharmaceutical companies with state of art R&D laboratory. In order to derive benefit from such preparations, it is imperative to prepare *bhasmas* as per recommended procedure and subject them to toxicity testing thus ensuring their efficacy and safety. Following motto must always be remembered:

"When processed properly and used under the expert guidance of a trained clinician, bhasmas are safe"

Conclusion

Bhasmas of metals, alloys and minerals have been known in Indian subcontinent since ages and widely used for treatment of many chronic diseases. Seventeen metal based *bhasmas* of Ca, Fe, Zn, Hg, Cu, Ag, Sn and As were analyzed for major, minor and trace constituents by INAA. Presence of significant amounts of C, H and S suggests that some organic molecules may possibly be acting as ligands or involve in compound formation. Concentrations of elements in different *bhasmas* of the same element vary in a wide range depending on the method of preparation. Particle size of *bhasmas* is likely to be of nano size but more studies are required to confirm it. These are consumed in small doses and with honey, milk, curd, ghee etc so that harmful effects are likely to be avoided. Toxicity aspects of elements such as As, Hg, Pb as major/minor or trace constituent is discussed. Presumably chemical form of metal plays an important role in toxicity of a *bhasma.*

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Figures:

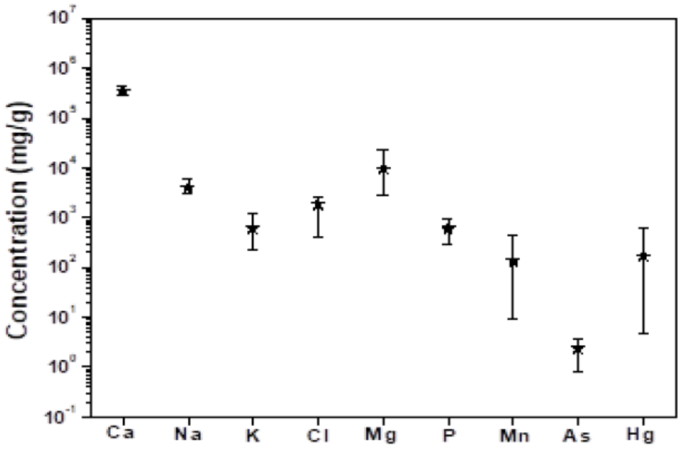

Fig. 1 Range and Mean Elemental Contents in Ca based *bhasmas* (n=4)

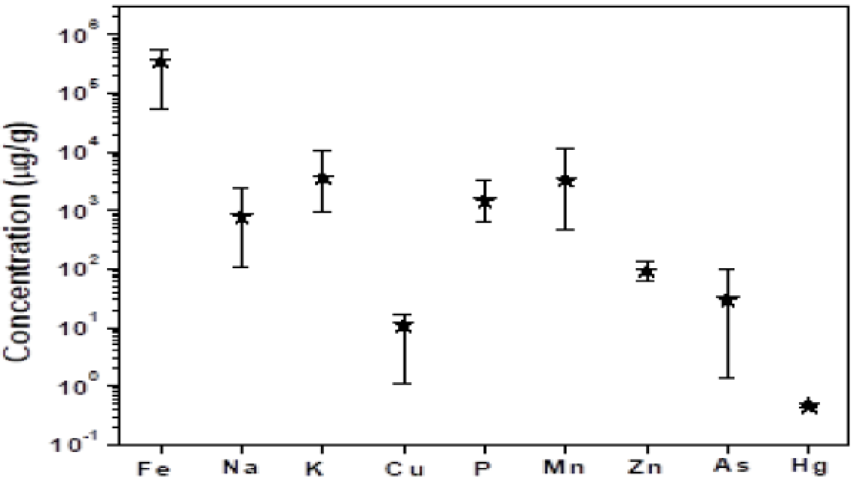

Fig. 2 Range and Mean Elemental Contents in Fe based *bhasmas* (n=4)

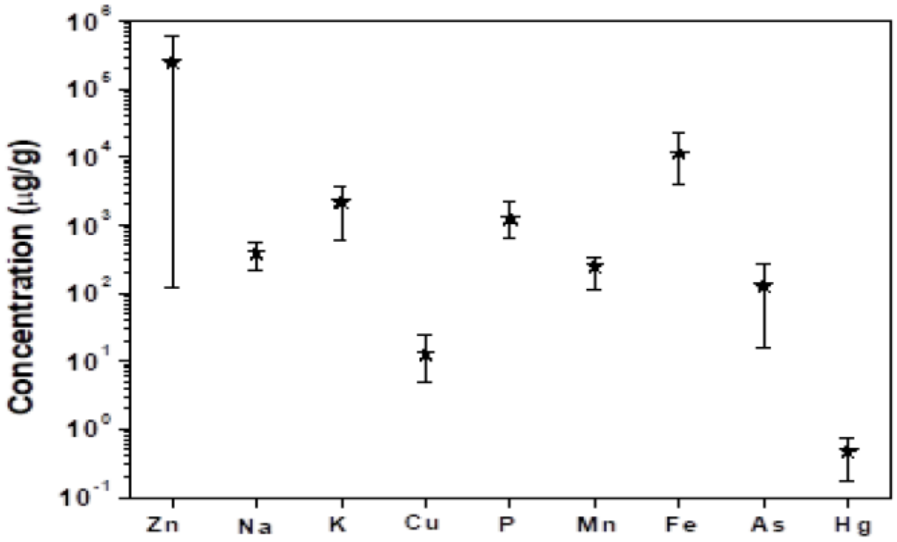

Fig. 3 Range and Mean Elemental Contents in Zn based *bhasmas* (n=3)

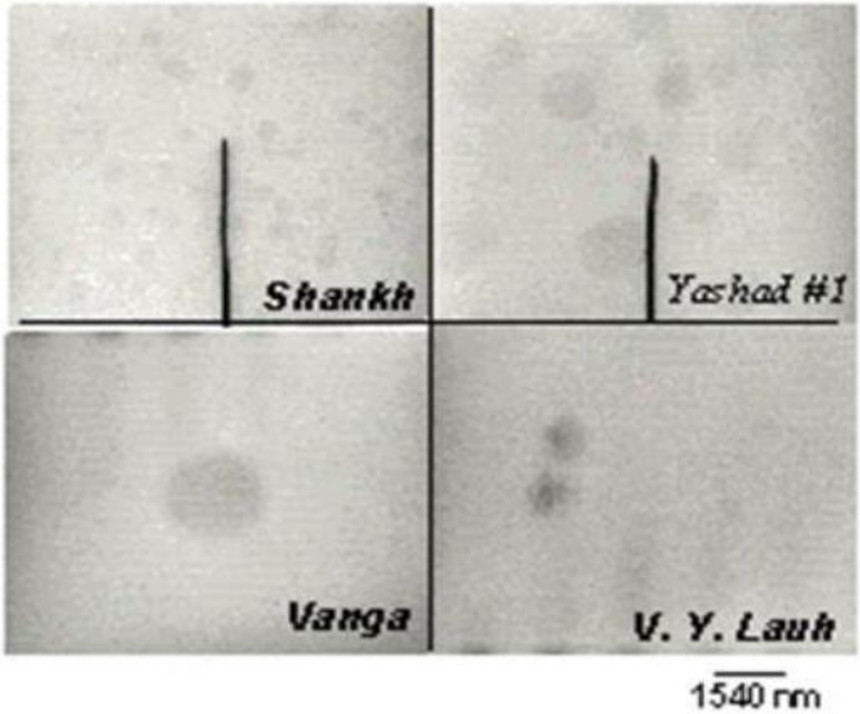

Fig 4 Transmission electron micrographs of some bhasmas; Shankh (Ca), Yashad (Zn), Vanga (Sn) and Lauh (Fe)

Table 1 Metal *Bhasmas*, their ingredients and uses.

Bhasma (Metal)	**Ingredient/ Description**	**Uses**
CALCIUM (Ca) BASED		
1. Mukta Moti	*Pearls and Ghee (milk preparation)*	Cough, impotency, eye disorders, tuberculosis, sprue, nervine sedative, used in hyperacidity, asthma, cough and nervous excitement in growing children and pregnant women.
2. Mukta Shukti	Pearls and Rose water	Respiration, cough, heart diseases, stomach, liver, intestine
3. Praval Pishti	Pearls	Antacid, used in cough, phthisis, scrofulous, affections, spermatorrhoes, pulmonary hemorrhage and calcium deficiency.
4. Shankh	Conch shell	Antiperodic, carminative and analgesic, used in colic flatulence and tympanites.
IRON (Fe) BASED		
5. Vanaspati Yog Lauh	Magnetic iron (purified)	Sprue, stomach disorders, anaemia, diabetes, blood disorders, restorative, haematinic, astringent, jaundice, disorders of liver and spleen
6. Kant Lauh	Magnetic iron (purified), Ash of incinerated magnetic iron	Ant rheumatic, haematinic and used in anaemia
7. Mandoor	Ash of incinerated purified ferric oxide	Alterative, haematinic, diuretic, used in anaemia, oedema, chlorosis, rickets and jaundice.
8. Trifala Yog Lauh	Ferrum (purified), incinerated and potentiated, rubbed with Trifala decoction	Strengthening the body, deficiency of iron, anaemia, indigestion
ZINC (Zn) BASED		
9. Yashad	Zinc/ Shudh Yashad	Dysentery, sweating, phthisis, tuberculosis, diabetes, hypoglycemic, astringent, used in urinary disorders
10. Baidyanath Deshrakshak Kharpar	Zinc carbonate/ash of incinerated purified zinc carbonate	Antacid, Bone strengthening,
MERCURY (Hg) BASED		
11. Sidhmakardhwaja	Mercury	Physical disorders, strengthening the body, fever, malaria, asthma
12. Parad	Mercury	Syphilis, genital disorders, rejuvenation
SIVER (Ag) BASED 13.Rajat	Silver	Wasting, nerve disorders, brain functions, eye disorders, tuberculosis
ARSENIC (As) BASED 14.Khushta **khas**	Arsenic	Nervine tonic, Asthma, leucoderma, paralysis and impotency
COPPER (Cu) BASED 15. Tamra	Ash of incinerated purified copper	Acidity, ascites, jaundice, piles, leprosy, leucoderma, asthma, tuberculosis, cough, skin diseases, obesity, chronic bloating, spleen and liver enlargement, cirrhosis.
TIN (Sn) BASED 16.Vanga	Tin	Asthma, cough, sweating, blood disorders, diabetes, diuretic and urinary antiseptic, semen disorder, syphilis and gonorrhea

.Table 2. Elemental concentrations in calcium (4) iron (4) and tin based *bhasmas*

Element	Calcium				Iron				Tin
	Mukta Moti	Mukta Shukti	Vanga	Shankh	Vanasp-ati Yog Lauh	Kant Lauh	Triphala yog Lauh	Mandoor	Vanga
Al (mg/g)	0.13±0.01	0.70±0.03	1.62±0.15	0.30±0.04	2.44±0.05	2.50±0.27	3.52±0.04	ND	0.13±0.01
As (µg/g)	1.29±0.18	0.82±0.04	3.61±0.03	3.67±0.40	1.39±0.15	10.6±1.0	97.3±16.8	9.59±1.0	24.1±6.4
Ca (mg/g)	31.0±2.6 %	33.6±2.4 %	29.5±2.0 %	41.9±4.0 %	ND	2.37±0.25	ND	ND	73.5±2.9
Cl (mg/g)	2.66±0.35	0.40±0.06	2.08±0.30	2.27±0.18	ND	0.24±0.03	0.22±0.03	0.21±0.03	0.24±0.03
Co (ng/g)	123±12	27±2	147±15	910±100	416±40	340±25	610±45	510±40	880±40
Cu (µg/g)	ND	ND	1.52±0.15	ND	1.08±0.12	15.0±0.3	16.9±0.5	ND	ND
Fe (mg/g)	ND	1.28±0.12	2.83±0.19	ND	56.9±5.6%	42.9±0.5%	5.31±0.53%	35.1±5.4%	1.34±0.06
Hg (µg/g)	19.0±2.0	4.75±0.55	627±20	14.3±1.2	ND	0.49±0.04	0.42±0.03	0.45±0.04	0.97±0.08
K (mg/g)	0.22±0.02	0.59±0.01	1.26±0.07	0.35±0.01	1.83±0.07	1.18±0.11	0.93±0.04	10.3±1.6	0.26±0.03
Mg(mg/g)	3.45±0.29	ND	22.1±4.3	2.73±0.21	ND	1.26±0.11	0.96±0.05	ND	ND
Mn (µg/g)	28.0±0.6	445±35	49.4±3.8	9.35±1.25	596±47	467±25	465±30	11.4±0.4*	257±25
Na(mg/g)	3.80±0.39	3.13±0.29	5.91±0.51	3.11±0.03	0.41±0.04	0.11±0.01	0.21±0.02	2.33±0.11	0.47±0.01
P (mg/g)	0.96±0.03	0.29±0.01	0.77±0.02	0.38±0.01	0.62±0.02	0.96±0.01	0.86±0.04	3.26±0.04	0.72±0.01
Zn (µg/g)	176±20	ND	125±10	ND	ND	61.2±4.5	79.9±1.0	135±24	67.0±4.9
C (%)	11.8	12.1	11.9	15.1	1.22	0.11	0.12	0.07	4.15
H (%)	0.364	0.245	0.299	0.81	0.01	0.04	0.02	0.01	0.64
S (%)	0.39	0.12	0.38	0.81	0.12	0.05	0.03	0.16	0.152

ND = Not detected, * = Concentration in mg/g, In Vanga bhasma, Sn and In contents were found to be 43.8±2.4 % and 17.1±0.7 µg/g respectively

Table 3. Elemental concentrations in zinc (3), silver (1), arsenic (1), copper (1), and Mercury (3) based *bhasma*

	Zinc			**Silver**	**Arsenic**	**Copper**	**Mercury**		
Element	Yashad #1	Yashad #2	Kharphar	Rajat	Kushta Khas	Siddha Makardhwaja	Siddha Makardhwaja	Parad	Makaradhwaja
	Baidyanath	Deshrakshak							Gutika with Swarnakalp
Al (mg/g)	3.03±0.14	1.02±0.05	1.70±0.02	7.08±0.5	0.71±0.08	ND	ND	0.53±0.12	ND
As (µg/g)	15.3±1.4	89.6±13.5	269±30	142±19*	3.65±0.6%	19.7±1.0	ND	ND	0.40±0.01
Ca (mg/g)	ND	193±5.5	239±20	ND	301±2	ND	ND	247±5	ND
Cl (mg/g)	ND	0.21±0.03	0.59±0.15	ND	0.20±0.02	ND	ND	ND	ND
Co (ng/g)	188±10	205±20	310±25	387±24	ND	810±55	ND	ND	30.5± 1..2
Cu (µg/g)	5.05±0.8	9.03±0.78	23.7±1.8	ND	ND	44.1±3.0%	ND	ND	17.9 ± 1..3
Fe (mg/g)	22.8±2.4	3.87±0.24	7.14±0.45	ND	ND	71.2±3.1	ND	ND	6.68± 0.30
Hg (µg/g)	ND	0.75±0.03	0.17±0.01	ND	ND	0.23±0.01	85.3±7.0%	0.018±0.002%	168±11
K (mg/g)	0.59±0.02	2.22±0.16	3.59±0.09	ND	2.42±0.05	23.7±2.0	ND	ND	4.47± 0.12
Mg(mg/g)	ND	67.2±5.6	ND	ND	ND	ND	ND	65.8±7.2	ND
Mn (µg/g)	116±13	334±13	288±12	183±18	84.0±1.0	134±12	ND	252±23	ND
Na (mg/g)	0.21±0.02	0.57±0.02	0.37±0.08	12.8±0.1	0.83±0.08	0.25±0.01	ND	ND	3.15±0.17
P (mg/g)	2.19±0.06	0.92±0.04	0.65±0.03	51.4±1.5	1.06±0.04	10.9±0.2	ND	0.97±0.04	ND
Zn (µg/g)	60.0±7.0%	13.4±2.4%	0.01%	ND	ND	358±26	ND	ND	86.4±2.2
C (%)	0.087	7.13	8.37	0.631	0.242	0.088	0.064	13.4	ND
H (%)	0.039	0.424	0.214	0.252	0.049	0.511	0.034	0.03	ND
S (%)	0.436	0.257	0.383	19.9	21.1	22	14.2	0.04	ND
ND = Not detected, In Rajat *Bhasma* Ag was found to be 23.4 ± 2.5 %, * concentration in mg/g									

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Role of Lubricants in Industry: A Review

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Abstract:

Lubricants are available in our daily lives for functioning as coolants, to dissipate heat and lubricate different surfaces which can be either in solid, liquid or gaseous forms. It reduces friction by the formation of thin film between two surfaces in contact and by improving efficiency and reducing wear. For any system to work efficiently and effectively appropriate lubricant is needed.

Fresh lubricating oil needs to meet specifications of Original Equipment Manufacturers (OEMs). Applying lubricant regularly on tool increases life on usage and durability but a situation comes when the oil starts degrading may be due to depletion of additives or tool break down. Degraded oil is tested by using different physicochemical properties and also by employing different sophisticated analytical techniques like infrared spectroscopy (FTIR), Gas chromatography (GC), Inductively coupled plasma atomic emission spectroscopy (ICPAES), etc.

In this article, we shall discuss some basics of lubrication, different lubrication regimes and various kinds of lubricants used for various industrial and automotive applications. Some case studies of oil and also their representative formulations, testing and interpretation of results is being presented for understanding of various lubricants.

Key words: Lubricant, lubrication, Analytical techniques

Introduction:

Lubricant assists in reducing friction between two surfaces in contact and thereby lowers the heat generated by cooling immediately. They are also referred as lubes. These can function by

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removing the metal debris (metal particles removed due to two moving contacts abrading each other or by additive depletion).

Lubricants have a great impact on reliability by increase in shelf life of equipment, energy efficiency, thereby reduction of different machinery wear[1] and by friction. Lubricants can also function as a tool for heat dissipation. These exotic chemicals are applied on surfaces of substances which are referred to as substrate. They can be either as phases like lubricating oil in liquid or grease in semi solid state. These can be applied on substrate to minimize friction, wear, heat and cooling and allowing smooth functioning of part and are often referred as lubricity[2].

Basics of Lubrication

Lubrication is a process of reducing friction and wear between two surfaces that move relative to each other[1,3,4]. This is done by introducing a substance called lubricant between two surfaces to build an oil film separating them and prevent these metals from contacting each other. Lubricants can be in the form of a lubricating oil or grease[1].

In the case of boundary lubrication (BL) condition, metal surfaces are usually in contact and load is carried by the surface asperities. In mixed lubrication (ML) the load is carried by both the lubricant film and the asperities in contact whereas in the case of hydrodynamic lubrication (HL), a full film of lubricant carries the load and the surfaces are not in contact. The contact occurs at the peaks of the surfaces called asperities and amount of extent of the asperity contact depends on many factors like surface roughness, fluid film pressure, normal load, hardness, elasticity of the asperities, etc[5].

Boundary Lubrication

When there is a metal-to-metal contact taking place between two sliding surfaces we can say boundary lubrication exists. In this regime the lubricant film is worn away and there is severe contact between the two metal asperities which takes place usually during the start or shut down of equipment.

Mixed Lubrication

Mixed lubrication regime is referred to the stage when the metal-to-metal contact between the two asperities substantially reduces along with coefficient of friction. This is due to the fact that a lubricant film between the surfaces in motion has been created reducing the friction. Here there is minimal metal to metal contact taking place.

Hydrodynamic (HD) Lubrication

Here the metal contacting surfaces are not in contact with each other. An oil film of 1-micron thick exits between the two metal surfaces and metal slides over the oil film. Here the coefficient of friction is the least when compared to the three regimes. There should be a geometric conformity between machine moving parts and low contact pressure (100 to 300 psi in industrial journal bearings) between the moving parts[6].

Elastohydrodynamic lubrication conditions occurs when there is a no contact between the moving components. This regime is considered to operate on a full fluid film and oil thickness is about 1 micron.

The different lubrication regimes are shown in Fig. 1

Generally, lubricants can be formulated by using class of base oils which can be either mineral oil base or synthetic base. Mineral base oils are usually natural in origin whereas synthetics are prepared artificially. Mineral base oils are found to be containing elements of carbon and hydrogen called hydrocarbons of different molecular structure and molecular weights distribution, chain length. Mineral lubricants are complex mixture of paraffin based, naphthenic and aromatic hydrocarbons of 20 to 50 carbon atoms. This being obtained naturally also may contain small fraction of nitrogen, oxygen and sulphur[7].

Mineral base stocks are used for making industrial lubricants whereas combination of mineral and synthetic base stocks or only mineral base oils are used for formulating automotive lubricants.

Looking at the nature of the base oil, which is the key to lubricants, they are classified as mineral oil which are derived from petroleum resources, synthetic oil (eg., polyalphaolefins, polyalkylene glycols, synthetic esters, silicones, etc.) Synthetic base oils can be manufactured by using different small moieties which can be used as building blocks for further use. Molecular weight and viscosities of these oils can be tailor made as per requirement of supplier and are also stereo specific in nature[7].

Base oils are divided into 5 broad categories and are listed in Table 1

Usually mineral base oil is obtained by distillation of petroleum crude by different fractions. They are further processed using different procedures. Base oils of different groups as per API classification with different reactivity levels and concentration of sulphur can be obtained as per distillation procedure employed and so does the viscosity index of different group of base oils changes.

Use of mineral and synthetic base stocks has grown up exponentially in the last few decades. These are used for making different automotive lubricants like motor oils, gear oils, marine, railroad lubricants and for various industrial lubricants like compressor, gear, hydraulic oils, etc[3]. Synthetic base oils are usually used for manufacturing high end products.

Lot of crisis are going on as the petroleum crude is getting depleted fast due to its limited availability. So the synthetic base oils prepared chemically have come into existence. Mineral base oils obtained from crude are not biodegradable whereas synthetic base stocks prepared artificially are partially biodegradable and due to which recent trend shows a shift towards the use of biodegradable and low toxic synthetic lubricants[3,4,8]. Mineral lubricants have poor biodegradability. Vegetable oils have low ecotoxicity and are biodegradable[9].

Nanolubricants is another important class of lubricants wherein nanoparticles either are imparted in the lubricating oil in small dosages to form suspensions or are employed in lubricating oil in the form of friction modifiers and have to be dispersed uniformly. Effect of addition of nanoparticles is seen in the lubricating oil by the decrease in the coefficient of friction compared to lubricants with no nanoparticle additives. Examples of nanoparticles used in lubricating oils include titanium dioxide, graphene, zinc oxide, molybdenum disulfide, etc.[10]. Nanotechnology is an emerging field and a potential source to enhance the tribology performance of different lubrication system[11].

Biobased lubricants are the substitutes to mineral based oil and are found to exhibit superior lubricating properties over mineral oil. These are biodegradable to water and carbon dioxide. One of the limitations of bio based lubricant is low temperature characteristics and oxidative stability which can be overcome by incorporating proper additive package in the bio based lubricant[12].

Lubricants are a mixture of oil and additives. It can have from 90 to 100 % oil and 0 to 30 percent additives. Common lubricants include engine oils, gear oils, compressor oils, hydraulic oils, turbine oils, transformer oils, stamping oils, wind turbine oils and many more to name a few.

Additives can be in the form of antioxidants, antiwear agents, extreme pressure agents, detergents, dispersants, foaming agents, etc.

Lubricants can also be in the form of semi solid which is grease. Grease can be thought of sponge oil and consists of three fundamental components: a lubricating base fluid, a thickener and additives. It can have from 80 to 90 % oil, 7 to 15 % thickener and 0 to 10 percent additives.

Chronology of Lubrication:

Viscosity of a fluid can be referred to as resistance to flow of liquid. There are two kinds of viscosities which are kinematic and dynamic viscosities and the units are centistokes and centipoise respectively. Newton's law of viscosity says the shear stress is directly proportional to the velocity gradient. The friction responsible for creating viscosity is responsible for both molecular and mechanical stresses.

Tribology is the science which usually deals with friction and wear of material covering lubricants as one of the major field of study. This subject also covers design of bearings and science of interaction of surfaces in relative motion. It is an interesting and interdisciplinary science covering physics, chemistry, materials science and engineering and also chemical thermodynamics.

A brief history covering this wonderful subject is presented in the below in Table 2.

Various physico-chemical properties like kinematic and dynamic viscosities, moisture content, density, volatility, iodine number, saponification number, functional groups, carbon length distribution, elements, etc are used to find out some qualitative analysis and quantitative estimation of the base oils and finished lubricants[16]. Further some analytical sophisticated precise techniques like Fourier Transform Infrared Spectroscopy, Gas Chromatography, Inductively Coupled Plasma Atomic Emission Spectroscopy etc. are used for further information like purity, carbon chain length, predicting molecular structure.

Typical properties of Lubricating oil are given in Table 3:

In the present manuscript, we shall cover few case studies of lubricating oil along with their testing methods and their interpretation for the same (for fresh and used lubricating oils) using various sophisticated analytical techniques.

Properties of Oil

Viscosity

Oil analysis is needed to know the life, condition used in particular instrument.

In the case of gear oil, viscosity is generally tested in terms of kinematic viscosity at two different temperatures (40 ^{0}C and 100 ^{0}C) and having the units in centistokes (cSt). Dynamic viscosity is recorded at 25 ^{0}C and having units in centipoise (cps).

Kinematic viscosity is measured by knowing the time lubricant flows through a capillary at a defined temperature. Viscosity for the oil could be affected due to insolubles present in the lubricant, soot and oxidation of the lubricant.

Viscosity Index

Viscosity Index is a value calculated from the two measurements of viscosity at 100°C and 40°C or some typical two temperatures and describes the viscosity-temperature relationship of the oil. Higher value of Viscosity Index indicates small change of viscosity with temperature.

Moisture

Water ingress will increase the viscosity of the lubricating oil. Water content of fresh and used lubricating oil is measured by Karl-Fischer titration (either potentiometric or coulometric) method or by infrared spectroscopy method. When moisture content is greater than 50 ppm potentiometric method is used and when moisture content in the lubricating oil is less than 50 ppm coulometric titration is the preferred method.

Total Acid Number

Acid number in a lubricating oil specifies the amount of acidic components in the oil and is calculated by titration either manually or automatically determined by Volumetric Titration using KOH. Acid number could be starting point to detect the oxidation content in the oil.

Flash Point

Flash point of a lubricant oil is determined at which vapor may cease to burn when source of ignition is removed. Open cup and closed cup are commonly methods used for Flash point determination of lubricating oils. Lubricating oil with greater viscosity tend to have a higher flash point[17].

Pour Point

Pour point is determined by temperature at which oil becomes semi solid and loses its flow characteristics. Lubricating oil with greater viscosity tend to have a low pour point.

Some brief method of description of sophisticated instrumentation techniques used is presented below -

FT-IR Spectroscopy

Fourier Transform Infrared Spectroscopy (FT-IR) also referred as infrared spectroscopy is an experimental analysis technique which is used to detect functional groups of organic material. The nature of carbon as aromatic, paraffinic and napthenic in lubricating oil along with their proportion can be estimated. This method is also used for finger printing of functional groups present in the material.

FTIR spectroscopy is a technique for determining molecular structure by assigning each absorbance band to a specific functional group[18]. FTIR spectroscopy allows to quantify the total carboxylic compounds generated during the thermal oxidation of the lubricating oil. One can also find out purity of the material.

Ageing of oil leads to oxidation, nitration and sulphonation. This is seen by observing a shift in bonds in the used oil and correction is applied with respect to blank referred to as fresh oil.

Some of the advantages of the FT-IR technique over the other conventional systems are ease of sampling and sample preparation, quick and reliable results and robust nature of equipment. Exposure of operator to minimum quantity of solvents[19].

20 mg of solid in case solid (nujol), 1 drop of oil is needed in case of ATR to cover the crystal.

Inductively Coupled Plasma Spectroscopy

Initially AAS (Atomic Absorption Spectroscopy) was used for rapid trace metal analysis but it had limitations as only single metal could be analyzed at a time and it is cumbersome and time consuming. Detector used in AAS is a Photomultiplier tube and the same tube is commonly used as detector in AAS and electron multiplier for ICP.

Inductively coupled plasma atomic emission spectrometry (ICP-AES) is a multi elemental, rapid, simple technique for the determination of trace level analytes[18]. This method can detect elements of low concentrations at ppm and ppb for metals as well for as non-metals. ICP uses inductively coupled plasma to ionize the sample and creates atomic ions which are detected after the sample is atomized.

Sample weight varies as per concentration of metals and non-metals present. Multiple samples of different concentrations can be tested together with ease. Accurate determinations for Al, Ba, Ca, Cd, Cr, Cu, Fe, Mg, Mn, Mo, Ni, Pb, Si, Ti, V, Zn, P, S, Na, B and S can be acquired by analysis for fresh and aged oils[20].

Low viscosity oil sample are used as such whereas high viscosity samples are diluted and then used. Liquid samples can be detected after diluting with suitable solvent like xylenes, petroleum ethers or any low volatile solvents which can instantly form aerosols on injection and solid samples which are to be digested and then used. Argon is usually used as carrier gas which assists in the formation of aerosols (propagating tiny droplet samples) across plasma which is maintained at a very high temperature[21]. Solid samples are digested in aqua regia.

The oil samples is diluted and 5 µL sample volume injected into an air carrier stream leading to a conventional pneumatic concentric nebulizer which gives rise to a signal or peak.

Gas Chromatography

Gas chromatography is a tool used for separating and analyzing compounds. Gas chromatography can be used for testing purity of a substance.

Sample being tested should be thermally stable, be soluble in desired solvent and have different boiling points. Gas chromatography coupled with mass spectrometry (GCMS) can be utilized to check fresh and used lubricating oil and also to predict the probable molecular structure of oil. Oil analysis is used to find out shelf life and residual life of the oil after service.

Packed column holds the stationary phase which is made of steel or glass tube whereas capillary column is made of silica. GC usually uses different types of detectors like GC-FID, GC-TCD, etc. GC-FID (GC Chromatography Flame Ionization Detector) respond to wide range of hydrocarbons. GC-TCD (Gas Chromatography Thermal Conductivity Detector) detector can detect air, hydrogen, carbon monoxide, nitrogen, sulfur oxide, inorganic gases and many other compounds. GC-ECD (GC Chromatography Electron Capture Detector) is used to detect atoms and molecules in a gas. Of these, GC-FID is used for lubricating oil.

For GC, few microliters of sample is sufficient when using GC-FID, GC-TCD

Gas Chromatography separates organic compounds in mixture based on boiling point and retention time and carbon chain length distribution. Process is carried out by injecting liquid sample consisting of sample with carbon disulphide used as solvent and n-decane as standard using different carrier gas[22].

Usually GC analysis has two phases which are stationary and a mobile phase. A stationary phase would absorb the sample and release them whereas, a mobile phase is a stream of carrier gas used for carrying the sample from the injection port to column and finally to detector[23]. Detector is a device which gives signal response with respect to counts and detect as a peak.

Some of the findings observed by previous workers are discussed below as case Studies

Reig[24] studied an used oil and tested using FTIR by placing one to two drops of the oil sample between the two potassium bromide crystal windows using a spacer. Intense heating of the lubricating oil led to formation of carboxylic compounds. Triglyceride esters have a strong absorption band at 1743 cm^{-1} due to stretching of carbonyl group. Aldehydes and ketones have an absorption band at 1725 cm^{-1} and 1715 cm^{-1} respectively.

Infrared spectroscopy is used to measure the oxidation of the lubricating oil. The oxidation peak is usually observed at 1710 cm^{-1} wavenumber measured by infrared spectroscopy. Oxidation products within the oil reacts with hydrocarbon molecules forming insoluble carbonaceous residues and resins.

Nitration is due to lubricant oil degradation and results from the reaction of the oil with NOx. The nitration peak is usually observed at 1620 cm^{-1} wavenumber measured by infrared spectroscopy.

Sulphation give an indication of the degree of degradation of the lubricant which are typically from sulfur based additives. Sulphation is measured by infrared spectroscopy at an infrared wavenumber of 1150 cm^{-1}.

Lubricating oil when fresh is devoid of any oxidation, sulphation and meets the specification and ready to be used in machine. It is observed that when fresh lubricant oil is depleted in additive content then oxidation of the oil takes place or in another scenario viscosity of the oil can increase due to wear of metal debris from the walls of the instrument in running condition. Wear metal which are worn out from the walls of the machine tend to mix with the fresh oil making them dark in color increasing their viscosity and making them not suitable for further usage.

Common cases for increase in viscosity is by the oxidation, nitration and sulphation of the lubricating oil.

Oxidation occurs when there is availability of oxygen and is dependant on temperature and contamination. As the temperature of the lubricating oil increases, wear metal content increases, oxidation of the oil also increases.

Martinez et al[20] analyzed the elemental content of vegetable oils through inductively coupled plasma optical emission spectroscopy (ICP-OES). ICP-OES can be used for multielemental analysis for elements from Lithium to Uranium at ppm and ppb levels[2]. We have mentioned above a few critical parameters used in the interpretations of lubricating oil. It is essential to interpret the fresh and used lubricating oil samples. Whenever used lubricating oil is sampled it is compared to the fresh lubricating oil and then an inference is drawn.

Todorova et al[25] had carried out analysis using distilled lavender oil with GCMS.

They had used Bruker BR-5 MS fused silica capillary make column. Standards were utilized to optimize various parameters of the instrument. Distilled lavender was diluted with hexane and was analyzed using GCMS. GCMS using internal libraries revealed that the oil of lavender contained 35 compounds, which represent 94.13% of the total oil. A total of 50 volatile compounds were found in lavender oil. These studies were useful to conclude the essential oil content and quality of the commercial products with respect to the standards.

Typical specification of an oil is given in Table 4 and elemental content for fresh and used oil is given in Table 5.

Table 4 is just a representative example of an oil. Fresh oil meets the specification and is without contamination. When an oil is used for its application, it lubricates the internal components of machine and a stage is reached where the fresh oil which is transparent in color becomes darkish. This is the stage we need to test the darkish oil. Fresh oil is used as a standard and being compared to the used darkish oil.

From Table 4 we can infer that, Viscosity at 40 ^{0}C and 100 ^{0}C has increased in the used lubricating oil as compared to the fresh oil. This is due to the oxidation of the used oil as compared to the fresh oil, increase in Acid Value of the oil and few system component elements which gets worn out mixing with the lubricating oil.

Acid number gets increased due to oxidation of the used lubricating oil and depletion of additives (antioxidants and antiwear).

Table 5 represents the elemental contents for the fresh and used Lubricating Oil. Fresh oil contains higher contents of Silicon, Phosphorous and Sulfur which are due to the additives. Elemental Phosphorous is an antiwear additive, Silicon is from the antifoaming agent. We can infer from the Table 5 that increase in Aluminum and Iron content in the used lubricant as compared to the fresh lubricant is due to wear of metals from different machine components during its operation. Wear metals once worn off mix with the lubricating oil leading to increase its viscosity.

Yan et al[26] have reported the analysis data for oils derived from 35,000 km of regular oil monitoring for an E-axle used in a truck oil. Oil used was 75W/90. Oil test data was based on a reliability road test data on a test gourd at Chongqing, China. Oil samples were tested for the physical and chemical properties after the road test which predicted the deterioration of oil, additive depletion and oxidation of the oil. Wear was in the form of iron debris from transmission gear, the rolling bearing, etc. When E- axle is operational, worn-out iron debris mixes with the oil causing abrasive wear of the E-axle. Iron in the oil will act as catalyst leading to the increase in debris concentration and finally degradation of the oil. Oxidation of the oil is tested by FTIR, additive depletion of the wear elements in the used oil was measured by ICP-AES.

Conclusions:

In this review, basics of lubricant and lubrication are discussed in brief. This is followed by description of various different types of lubricants used in industry which are mineral, synthetic (biodegradable), etc and brief history of lubrication. The application of different analytical techniques, namely, FT-IR, ICP-AES, GC in lubricant industry including different regimes are discussed at the end along with some case studies.

Figure:

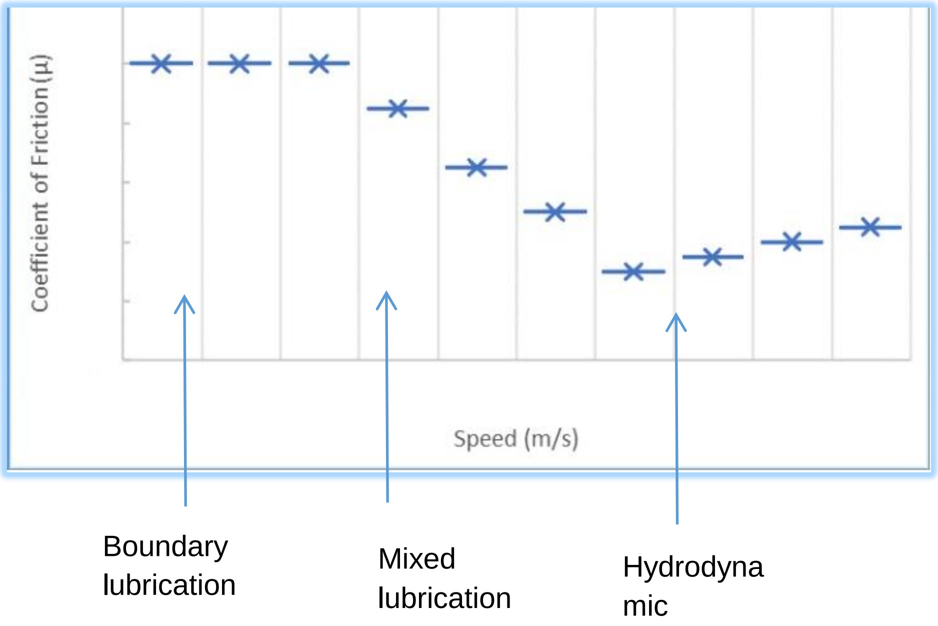


Figure 1: Lubrication regimes

Tables:

Table 1: Base oil Categories

Base Oil Category	Percent Saturates		Percent Sulfur	Viscosity Index	Types
Group I	< 90	and / or	> 0.03	80 to 119	Mineral Oil composed of Wax
Group II	≥ 90	and	≤ 0.03	80 to 119	Hydrotreated mineral oil
Group III	≥ 90	and	≤ 0.03	≥ 120	Naphthenic Oils
Group IV	Polyalfaoleofins				Polyalfaoleofins
Group V	Anything not covered in Groups I to IV				Polyol Esters Synthetic Oil

Table 2: Brief history of Lubrication

Year	Details
1400 BC	Greases were made from calcium and fats used to lubricate chariot wheels.
1450 AD	Herodotus described pits observed in Iraq as containing three different kinds of substances like asphalt, soil and oil which were in different forms like Asphalt and soil are solid and oil is liquid.
1596 AD	First use of petroleum products was evolved in Egypt. Piny and Pedanius described Sicilian oil which was burnt for illumination during beginning of Christian era. Walter Rayleigh discovered deposits of bitumen in Trinidad in 1596.
1629 AD	Joseph Roche of Cuba found petroleum being used medicinally and to bind pigments which were used in body adornments.
17th to 18th Centuries AD	John Theophilus developed a tribology model of cohesion and adhesion on friction[13]. Molecules of a liquid experience friction having like behaviour when flowing due to molecular interaction within.
1769 AD	James Watts was responsible for development of practical steam engine[14].
1833 AD	Benjamin Sillmann described petroleum sold in Eastern states under name of Senaca Oil found to be brown in color present between tar and molasses and its degree of consistency was not matching to temperature[14].
1859 AD	W.A. Smith, a blacksmith and brine well driller, began drilling

	and went down 69.5 ft and was discovered on drilling an incredible quantity of 20 barrels of oil a day can be obtained[15].
1850 to 1875 AD	Between 1850 to 1875 period products of petroleum distillation and also an investigation of substitutes for vegetable and animal oils were found out.
1900 AD	In 1900 crude oil demand increased due to importance in gasoline[15].
1910–1918 AD	Lubricants started being used in mechanical equipments like turbines and automobiles.
1930 to 1940 AD	Additives started gaining importance in 1930s covering corrosion inhibitors, pour point depressants, viscosity index improvers, etc to be used in lubricants in 1940s[15].
1950 AD	Esters were produced in 1950 by US and British researchers which were the same in engines of jet aircrafts[14].
1970 to 1980	Process of hydrocracking started in 1970s and 1980s.
1990s AD	Isomerization became common in 1990s[13]. Hydroisomerization technique was used to basically remove the wax from Group I (solvent extracted) base oils and converted them into oil without wax (mostly Group I)
21st century AD	Evolution of mechanical lubrication progressed with oil / grease products with more productivity leading to advances in industry[13].

Table 3: Properties of Lubricating Oil

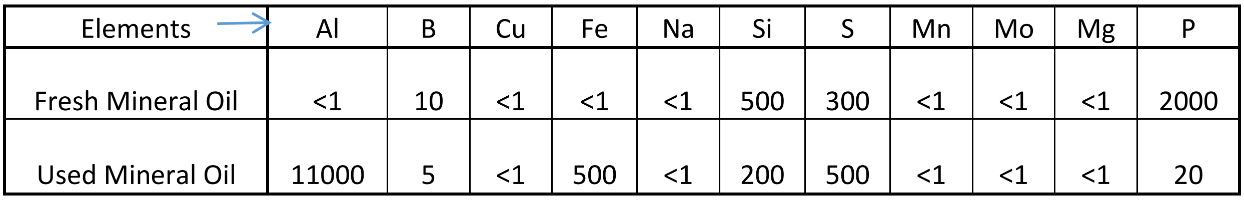
Instrument	Testing method followed	Tests performed	Detection Limits	Details
Viscosity	ASTM D445	Viscosity and Viscosity Index	2 cSt to 1000 cSt	Viscosity is measured at 2 tempe ratures, 40 °C and 100 °C
Moisture Content	ASTM E1064	Trace Level Moisture in lubricants	< 10 ppm	Determined by potentiometric / coulometric titration using the Karl Fisher Reaction
Total Acid Number	ASTM 974	Calculates Acidity in lubricants	0.01 mg KOH g/oil	Determined by Volumetric Titration using KOH
Flash Point	ASTM D92	Flash Point		Determined by the point at which

		determination in oils		vapor may cease to burn when source of ignition is removed (25 to 250 °C)
Pour Point	ASTM D97	Pour Point determination for oils		Determination by temperature at which oil becomes semi solid and loses its flow characteristics (25 to -50 °C)
Fourier Transform Infrared Spectroscopy		Detection of functional groups in oils, greases, polymers and gels		Used to obtain infrared spectrum of solid or liquid
Inductively Coupled Plasma AES	ASTM D5185	Determination of elemental contents in oils		Used to determine additive concentrations in oils.

Table 4: Representative example of Lubricating oil (Fresh and Used)

Parameter	Fresh Oil	Used Oil
Viscosity, Kinematic @ 40 ^{0}C	162	178
Viscosity, Kinematic @ 100 ^{0}C	19	24
Viscosity Index	135	165
Flash Point, ^{0}C	210	220
Pour Point, ^{0}C	-36	-35
Acid Value, mg KOH g/ oil	0.1	2.5
Moisture, ppm	100	500

Table 5: Elemental content for fresh and used Oil.



Elements →	Al	B	Cu	Fe	Na	Si	S	Mn	Mo	Mg	P
Fresh Mineral Oil	<1	10	<1	<1	<1	500	300	<1	<1	<1	2000
Used Mineral Oil	11000	5	<1	500	<1	200	500	<1	<1	<1	20

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Latent TB is a condition that occurs after an individual is infected by TB bacteria, M. tuberculosis, but does not show symptoms of TB. Unlike patients with active TB, individuals with latent TB do not transmit the disease. In simple terms, people in this situation are infected with TB, but the infection is essentially dormant. Although most of the infected persons do not manifest the disease, they are at high risk of developing active infection and hence represent a reservoir of TB bacteria. In India, the prevalence rate of latent tuberculosis is very high, around 40% of the population.

The reservoir of latent TB infection (LTBI) is a major barrier to the control and elimination of tuberculosis. Various studies indicate that a higher prevalence of LTBI would contribute to higher incidence and mortality of TB. In order to achieve the TB elimination target, testing and treatment of LTBI is essential.

Detection of Latent TB

Many individuals with high immunity affected by LTBI, can typically resist the bacteria and prevent them from multiplying. However, if latent TB bacteria become active in the body, usually due to weak immunity, the person will develop an active infection. Those who have LTBI run a considerably higher risk of developing active TB or having it reactivated than healthy individuals. Thus, people with latent TB infection should be effectively diagnosed and treated to prevent them from developing TB disease.

Until recently, for detecting the latent TB cases, the two most widely used tools are the tuberculin skin test (TST) and interferon-gamma release assays (IGRA). However, TST has poor specificity and low sensitivity as it also shows positive for those who have received the BCG vaccine for TB, while IGRA results are influenced by an individual's immunity status. Additionally, IGRA is expensive, needs specialized instruments, trained personnel and labs. Aside from sensitivity issues, neither the IGRA nor the TST can reliably differentiate between active TB disease and LTBI, nor can they predict LTBI reactivation.

Conclusion

TB continues to be a significant public health issue in our country. Therefore, the TB programme should lay emphasis on detection and treatment of LTBI to decrease the likelihood of active TB and to achieve the targets of TB elimination.

CY-TB is the third-generation test for latent TB detection

The Cy-Tb test is one of the most recent advancements in LTBI diagnosis and is a novel form of the TB skin test. It strikes the right balance. Developed by the Serum Institute of India, this test combines the cost-effectiveness and the ease of the TST with the specificity of the IGRA in the diagnosis of LTBI, and remain unaffected by the BCG vaccination.

The test kit is designed to detect two major secretory proteins, namely, culture filtrate protein-10 kDa (CFP-10) and early secreted antigenic target-6 kDa (ESAT-6), thus solving the problem of false positive results. The test kit comprises Mylab C-Tb SmartPatch which has a SmartCut-Flap, to ensure easy access to the skin for injection. It also has QR code which certifies its authenticity and links observation with UHID. The Guidemark on the SmartPatch enables image processing by AI algorithm and injecting CTB, while the Colour Calibrator allows precise image correction.

Since most people in India have received the BCG vaccine, the 5mm cut-off for the wheal (skin bump) used by the world does not work in India. We have to keep the cut-off at 10 mm and this might be leading to us missing several cases. It also does not work very well with those who have HIV. With the Cy-TB test using a specific infection-causing part of the TB, the 5 mm cut-off for a test to be positive can be followed for all, including HIV patients.

The test can be used to detect latent tuberculosis in contacts of a patient with active TB and among those with conditions such as HIV and cancers who are at a higher risk of developing active TB.

Not only does the Cy-TB test produce more accurate results, it also does not need extracts from the actual bacteria, making the manufacturing easier.

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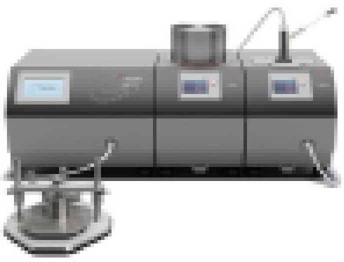

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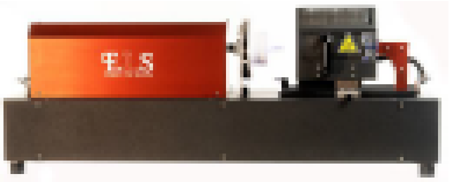

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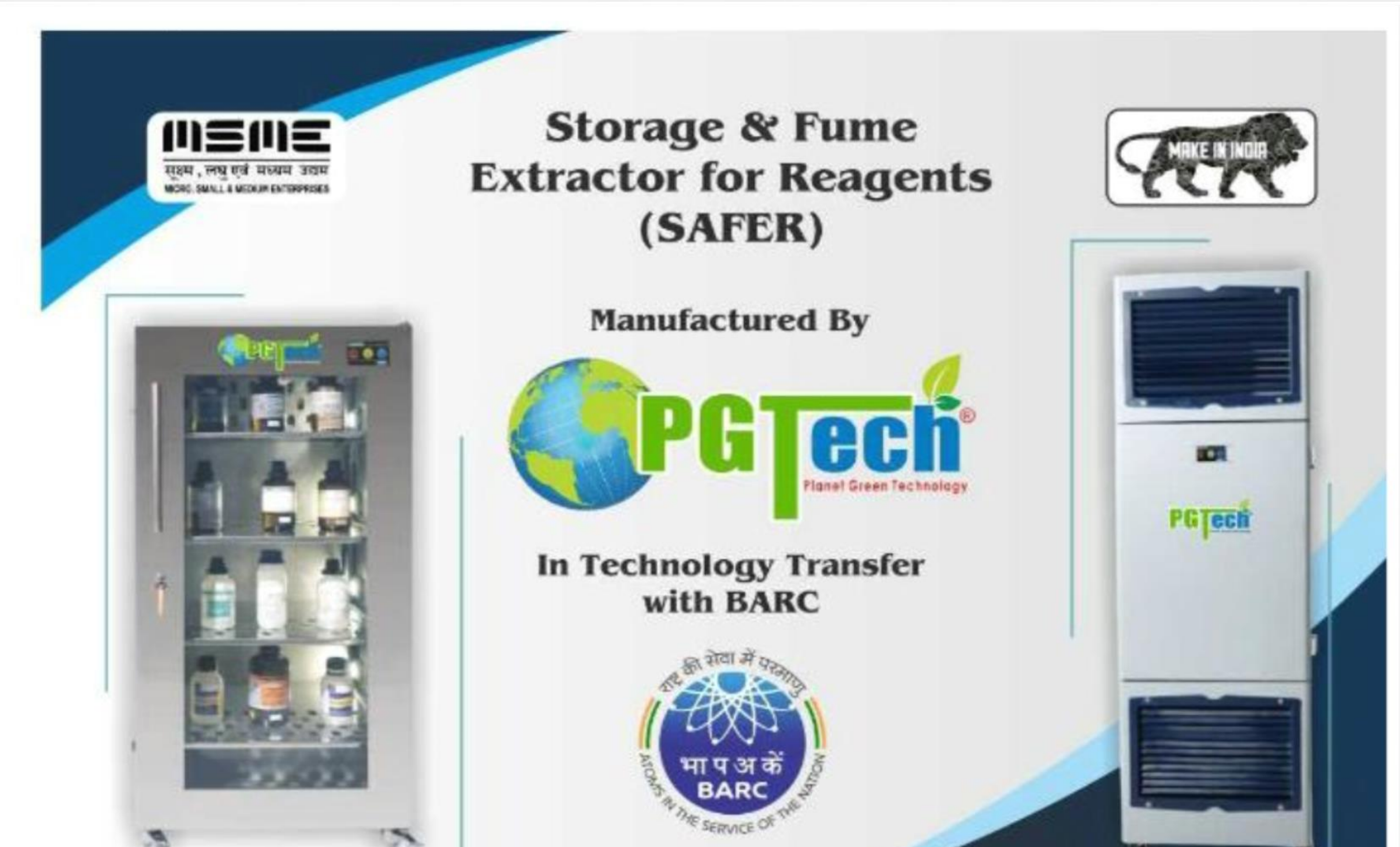

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