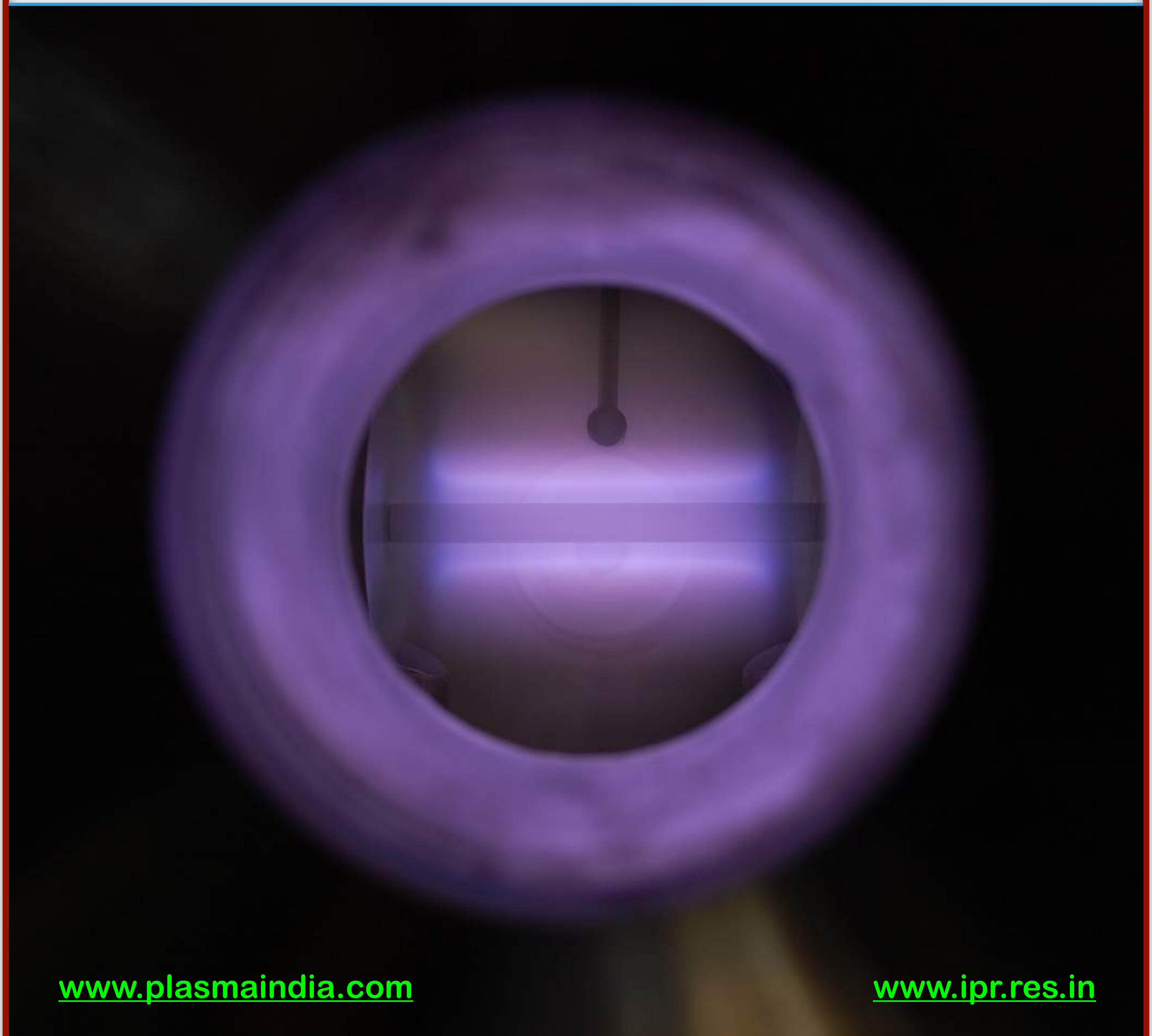
Plasma Processing Update

A Quarterly Newsletter from FCIPT, Institute for Plasma Research

Issue 99 July 2024



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Newsletter Team : Satyaprasad A. Kushagra Nigam

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RESEARCH ARTICLE

High Temperature Plasma Process for Synthesis of Magnetic Nanoparticles

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Magnetic Nanoparticles (MNPs) are of significant interest among researchers due to their applications in various fields like biomedicine, magnetic fluids, spintronics, magnetic resonance imaging, data storage etc. Various methods are used to synthesise MNPs like co-precipitation, sol-gel, thermal decomposition, laser ablation, plasma processing etc. Main problems in large scale synthesis of MNPs are broad size distribution of nanoparticles (NPs), poor crystallinity, longer time scales of production, scalability issues, use of toxic reagents, complicated synthesis steps, contamination of products etc. [1] [2]. Some of the challenges are manufacturing of MNPs having tunable properties like controlled narrow size distribution, well- defined shape, good magnetic properties and monodispersivity etc. Also search for novel synthesis method and detailed understanding of the mechanism is still a challenge [1].

Iron and iron oxide nanoparticles have drawn special attention due to their strong magnetic properties and biocompatibility. Below certain size, they show super-paramagnetic (SPM) behaviour. Super-paramagnetism is observed in extremely small nanoparticles that consist of single magnetic domains. These magnetic domains keep flipping from one direction to other due to thermal motion. This flip-flop – also called as Neel relaxation – has typical time scales of 10^{-9} to 10^{-10} seconds. Due to this flip-flop the resultant magnetization is measured to be zero i.e. the material behaves similar to a non magnetic material. However, upon application of even a very small external magnetic field, the magnetic domains get aligned in the direction of the applied field and results in a strong magnetization of the material. These SPM particles are characterized by nil or negligible coercivity, high saturation magnetization (as compared to paramagnetism) and negligible remanent magnetization. These characteristics of SPM particles increase their application-potential tremendously and they find demand in various fields including bio-medicine. It may be noted that, not only their size but the stresses and defects present in the nanoparticles can also lead to super paramagnetism. In high temperature plasma processing, significant thermal stresses develop in nanoparticles due to the existing sharp temperature gradients. Studies were carried out to find the suitability of thermal plasma and the parameters that control the formation of SPM particles. Preliminary results of this exploratory study are presented here.

At FCIPT, Iron and Iron Oxide Nanoparticles (I&IONPs) were synthesised by high temperature transferred arc plasma process. In this process, micron sized iron powder was placed in a graphite crucible which also acts as an anode, while a graphite rod with sharp tip is used as cathode. The anode (graphite crucible) can be moved up and down so as to vary the distance between the electrodes. An electric arc is struck between the electrodes by bringing them into a momentary contact with each other. Subsequently a fixed distance of few mm is maintained between the electrodes between which plasma is created. Schematic diagram of the experimental setup is shown in Figure 1. Due to the high heat produced in plasma column iron powder in the anode-cup is evaporated. While moving away from this high heat plasma-column, these vapours nucleate and grow in the gas phase and get settled on the inner walls of the experimental chamber.

Since material evaporation, nucleation, growth, structure formation etc. of the produced nano-particles depend on the plasma temperature, it was decided to study the effect of temperature on the properties of MNPs (both morphological & magnetic). This variation of temperature was achieved by controlling the plasma current – high current leads to higher heat flux. As the ambient gas also influences, to some extent, the growth of NPs, this aspect was also studied.

Iron oxide NPs were synthesised at atmospheric pressure under different ambience (air and helium), and at 50A & 100A of plasma arc current. Experiments in He ambience were done after evacuating the experimental chamber to a base vacuum of 10^{-2} mbar and then filling it with He gas upto one atmospheric pressure. The collected powder was analysed for phase by x-ray diffraction (XRD), for morphology by Scanning Electron Microscopy (SEM), and for magnetic properties by Vibrating sample Magnetometer (VSM).

NPs synthesised in He ambience were observed to be black in colour (Figure 2). XRD analysis of these samples indicated significant presence of α- Fe phase. However traces of α-Fe_2O_3 (for arc current of 100A only) was also observed. Presence of this oxide is due to higher base pressure. A better base vacuum of 10^{-3} or 10^{-4} mbar would have resulted in pure iron NPs. Further, NPs synthesised in air ambience are found to be in rust colour (Figure 2), indicating iron oxide formation. XRD analysis of these samples shows the presence of mixed phases of α-Fe_2O_3, γ-Fe_2O_3 or Fe_3O_4. Results are shown in Figure 3.

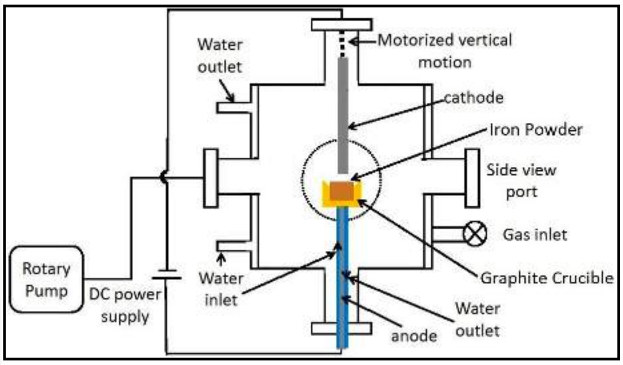

Fig. 1: Schematic diagram of the experimental setup

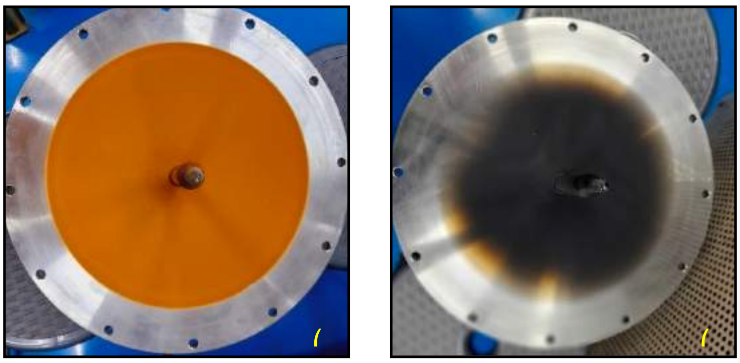

Fig. 2: Nanoparticles deposited on flanges of experimental chamber (a) in air; (b) in helium

To investigate the size distribution of the NPs SEM was used. SEM images of NPs synthesised at 100A arc current are shown in Figure 4. It is clear that they are typically spherical in shape. The average size of the NPs produced in He ambience is observed to be lower than that of those synthesised in air ambience. This is consistent for both the arc currents. Average sizes obtained are ~ 41nm and ~ 23nm at 50A, in air and He respectively; and ~ 49nm and ~ 21nm at 100A in air and He respectively.

Magnetic properties of the synthesised NPs was studied using VSM. M-H curves of the samples are shown in Figure 5. It is clear from the figure that saturation magnetization is almost same for NPs produced at 50A arc current, in both the ambience of air and helium. However coercivity values of NPs produced in helium ambience, though low, is still relatively higher than that of those synthesised in air. However, in the case of NPs produced at 100A arc current, the coercivity is almost same and negligible in both the ambience. Further, the remnant magnetization of air ambience NPs is found to be lower than those synthesised in He ambience. It should be noted that coercivity and remnant magnetisation are the two important characteristics used for qualifying the synthesised particles as SPM particles.

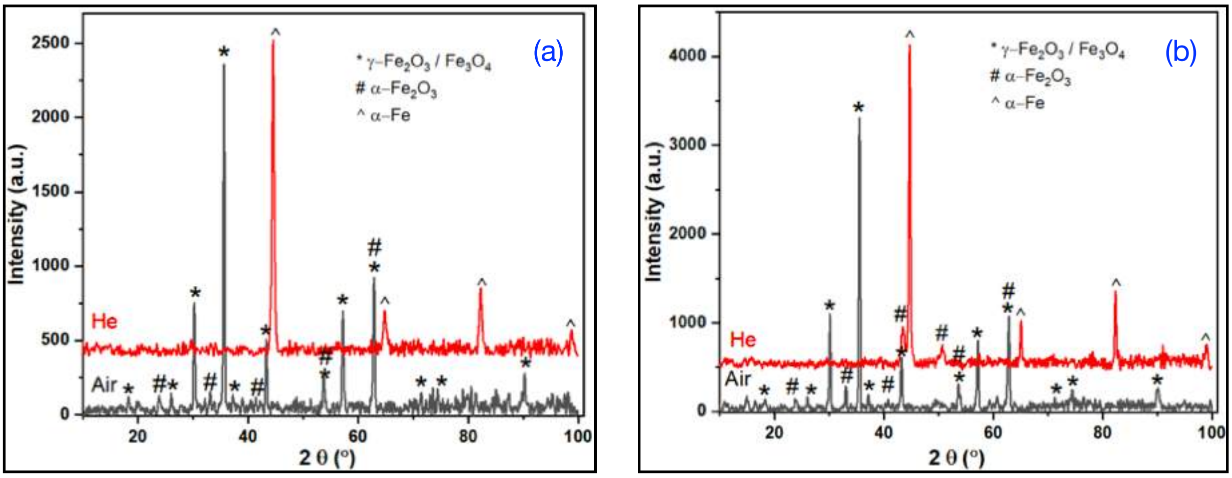

Fig. 3: XRD spectra of iron/ iron oxide samples prepared at arc currents of (a) 50A and (b) 100A

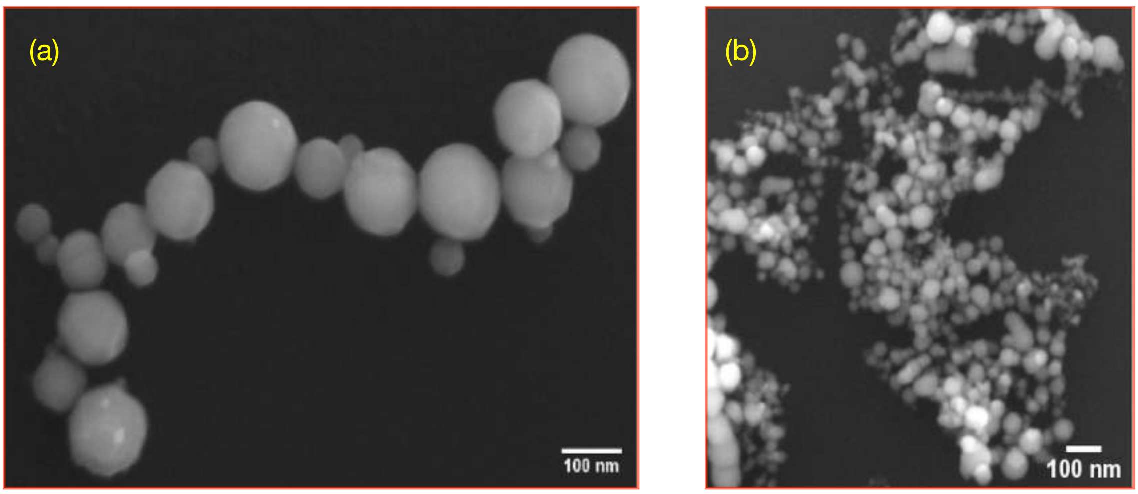

Fig.4: SEM images of nanoparticles synthesised at 100A of arc current in (a) air and (b) helium

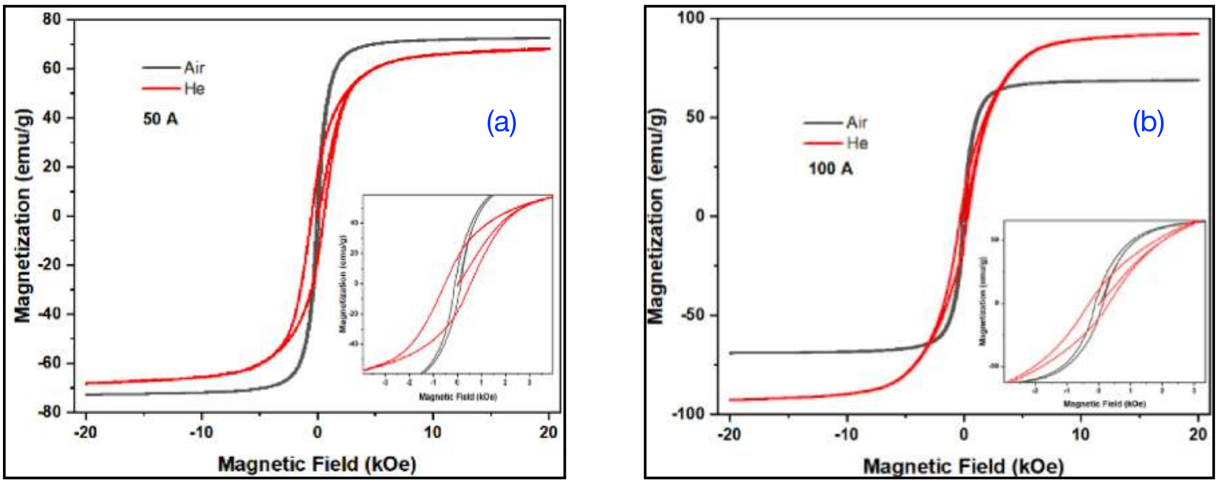

Fig. 5: M-H curves obtained for nanoparticles synthesised at (a) 50A and (b) 100A

In conclusion, it can be said that thermal plasma can be effectively used to prepare magnetic nanoparticles with super paramagnetic properties. The particle sizes are in the order of few tens of nanometers. X-ray diffraction analysis indicates formation of multiphase components which indirectly suggest varying temperature footprints spatially in the nucleation and growth zones of the nanoparticles. These variations in the formation combined with the high temperature plasma associated thermal stresses has resulted in super paramagnetic properties of the nanoparticles formed.

References

1. Wahajuddin and S. Arora, "Superparamagnetic iron oxide nanoparticles: Magnetic nanoplatforms as drug carriers"; International Journal of Nanomedicine; vol. 7. pp. 3445–3471, 2012; doi: 10.2147/IJN.S30320.
2. E. M. Koushika, C. Balasubramanian, P. Saravanan, and G. Shanmugavelayutham, "Influence of He and N2 plasma on in situ surface passivated Fe nanopowders by plasma arc discharge"; J. Phys. Condens. Matter; vol. 31, no. 47, Aug. 2019; doi: 10.1088/1361-648X/ab35aa

RESEARCH ARTICLE

Plasma-based Water Purification: Preliminary Experiments

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Plasma treatment of industrial effluents (Pharma Industry)

The liquid waste that is produced by various industrial processes and disposal methods is referred to as "industrial effluent". This waste may contain pollutants that have potential to affect the aquatic ecosystem and the quality of water. There is a great need for developing advanced technologies to treat industrial effluents in order to meaningfully reuse waste water. Plasma-based water purification is one of these technologies that can help to remove micro pollutants from the industrial effluents. In general, 'atmospheric pressure non-thermal plasmas' are used for water purification. And in this setup, the plasma is generated such that it is either in contact with or immersed in the liquid. The reactive species present in the plasma, come in contact and interact with the contaminants of the impure liquid and purify it.

In the present work, atmospheric pressure plasma jets were used for treating industrial effluents. Figure 1a shows the schematic diagram of plasma jet setup in which four

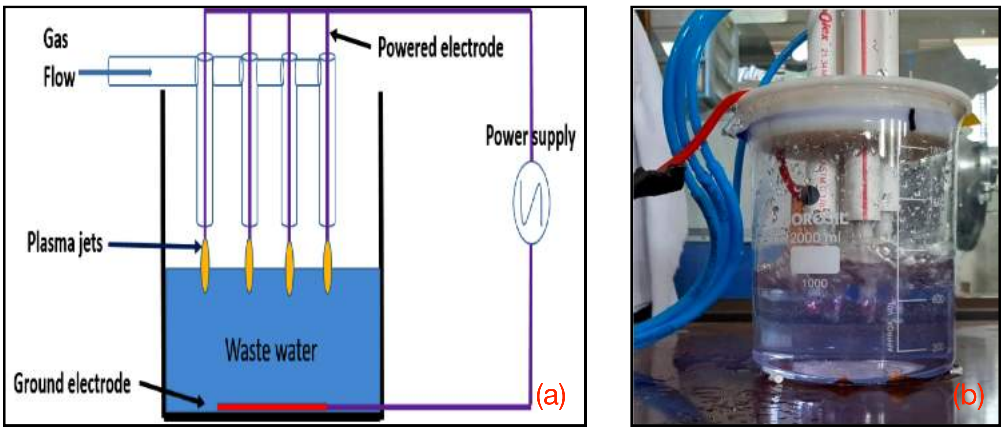

Fig.1: Atmospheric pressure plasma jets (a) schematic of the experimental setup (b) actual plasma jets in contact with water.

plasma jets are in contact with the waste water. Gas breakdown takes place in the gap between the liquid surface and the tip of a powered electrode. The electrons and reactive species generated in the plasma are transported into the liquid and react with the contaminants. The high voltage is applied to the powered electrode using AC power source operating at 10 KHz frequency. A copper plate acting as ground electrode was kept in the liquid. In the present set of experiments, two different types of industrial effluents (sample-1 and sample-2) from a pharmaceutical industry are treated with air plasma for around one hour. Air was allowed to flow through the plasma jets at a flow rate of 50-60 litres per minute (LPM). It was observed that, the Chemical Oxygen Demand (COD) reduces in both the samples after plasma treatment. It was also observed that pH values were decreased, while Oxidation reduction potentials (ORP) were almost doubled for the plasma treated liquid. The total dissolved solids (TDS) of the samples were also increased after plasma treatment. The results are tabulated as below in Table 1.

Degradation of methylene blue after plasma treatment (Textile Industry)

The waste water from textile industries contains a variety of persistent colouring pollutants, synthetic dyes, aromatic compounds and heavy metals etc. Plasma based advanced oxidation processes have been used for the degradation of dyes in water. The degradation of dyes in waste water after plasma treatment was verified with methylene blue (MB) solution as the model wastewater. A 5 gm of methylene blue (MB) powder was mixed in 1 litre of water. Then this solution of MB was dissolved in water for three different concentration (0.1ml/ltr, 0.2ml/ltr and 0.3 ml/ltr). These three solutions were treated

	Sample-1		Sample-2	
Parameter	*Untreated*	*Plasma treated*	*Untreated*	*Plasma treated*
pH	8.50	7.11	-	-
ORP (mV)	100	226	-	-
TDS (ppm)	97940	104124	85442	106352
COD (ppm)	24480	17680	43992	18346

Table 1: Changes in various parameters of Pharma effluents after plasma treatment

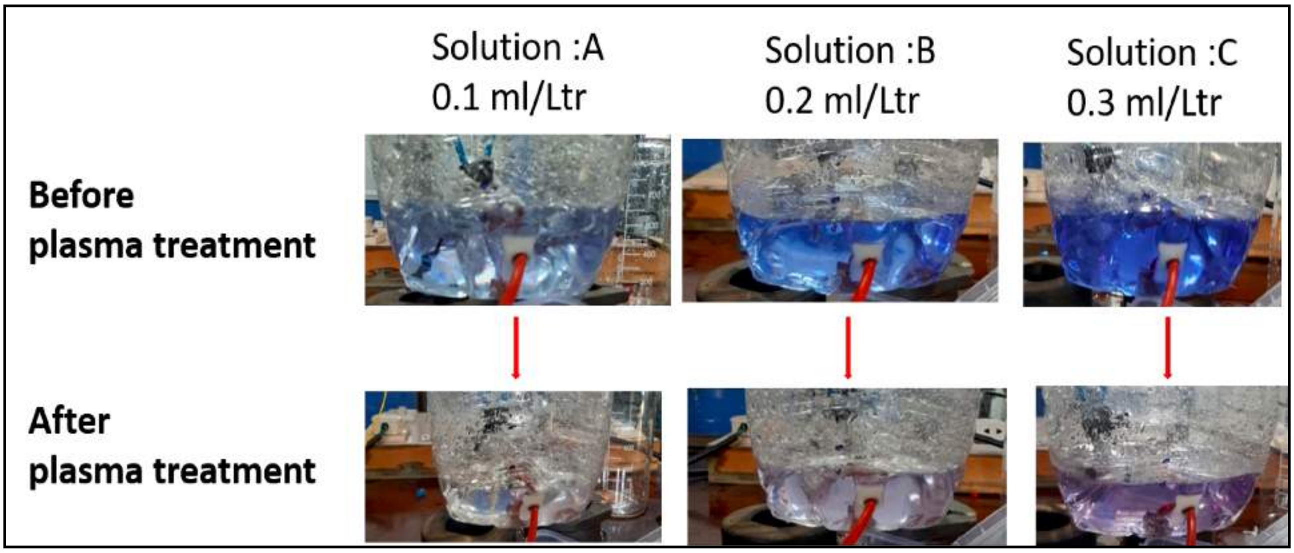

Fig.2: Images of MB solution before and after plasma treatment

with two atmospheric pressure plasma jets for 30 minutes, with the air flow of 50 LPM. Results are shown in Figure 2.

From Figure 2, it is very clear, qualitatively, that the plasma treatment has significantly degraded the MB dye as the colour of the solution has changed. Thirty minutes of plasma treatment was able to almost completely remove the blue colour of the solution-A, where in the concentration of MB was 0.1ml/ltr. Other solution samples with higher concentration of MB dye, are also seen with significant reduction in blue colour. However, more plasma treatment time may be required to achieve complete degradation, and the experiments are in progress to verify the same.

References

1. Plasma-based water purification: Challenges and prospects for the future
   John E. Foster, *Physics of Plasmas,* 24, 055501 (2017).
2. Degradation of Methylene Blue via Dielectric Barrier Discharge Plasma Treatment
   Lihang Wu, Qinglong Xie , Yongbo Lv, Zhenyu Wu, Xiaojiang Liang, Meizhen Lu and Yong Nie, WATER, 11, 1818 (2019).

RESEARCH ARTICLE

Introducing Plasma Washing: The Future of Eco-Friendly Laundry

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Team members

Dr. Vikas Rathore

Dr. S. K. Nema

In an exciting development for sustainable living, recent research has introduced plasma washing as a revolutionary and environmentally friendly method for removing stains from fabrics. Utilising cutting-edge plasma technology, this innovative approach offers an efficient and green alternative to traditional washing techniques, promising to transform the way we do laundry [1,2].

How plasma washing works

Plasma washing leverages a dielectric barrier discharge pencil plasma jet (DBD-PPJ) with air as plasma-forming gas (Figure 1). This advanced method generates reactive species, including oxygen and hydroxyl radicals and ozone, etc. which effectively breaking down complex stain molecules into simpler, water-soluble fragments. The result is not only

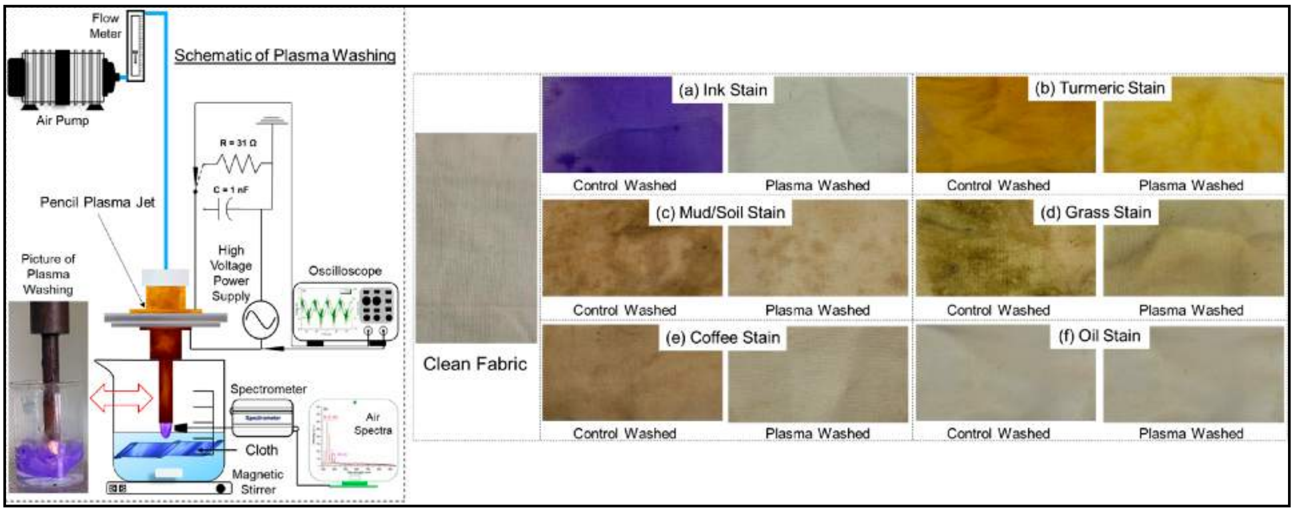


Fig.1: Schematic of plasma washing using dielectric barrier discharge pencil plasma jet. Visual appearance of fabric after control and plasma washing (a) Ink stain, (b) Turmeric stain, (c) Mud/Soil stain, (d) Grass stain, (e) Coffee stain, (f) Oil stain [3]

impressive stain removal (Figure 1) but also purified wastewater, free from dissolved impurities [3].

Impressive stain removal capabilities

The study tested plasma washing on a variety of common stains—ink, turmeric, mud/soil, grass, coffee, and oil—on white cotton fabric. The results were remarkable, with plasma washing significantly improving stain removal compared to control methods (only water washing (control)). Notably, coffee stains achieved the highest detergency, reaching 72.8% after just 15 minutes of treatment. Other stains also showed considerable improvement, with detergency percentages of 48.2% for ink, 47.1% for oil, and lower yet notable improvements for grass, turmeric, and mud/soil [3].

Enhancing fabric sensory properties

Beyond its stain-fighting prowess, plasma washing also retains the sensory properties of fabrics. Participants in the study observed improvements in the smell, touch, and overall appearance of plasma-washed fabrics. Analysis using FTIR (Fourier-transform infrared spectroscopy) and HR-SEM (high-resolution scanning electron microscopy) confirmed that plasma washing does not damage the fabric's surface, preserving its strength and integrity [3].

Environmentally friendly benefits

One of the most compelling features of plasma washing is its environmental impact. The study found that residual wastewater from plasma washing is devoid of dissolved stain residues, thanks to the effective degradation by oxidising species generated during the process. This means that the effluent wastewater is clean and free from pollutants, highlighting plasma washing as a comprehensive solution for both stain removal and wastewater purification [3].

How plasma washing stacks up

The effectiveness of plasma washing was illustrated through various analyses. Visual assessments showed substantial stain removal, particularly for challenging stains like coffee and ink. Colour and detergency analyses indicated a positive correlation between plasma treatment time and stain removal efficacy, with prolonged plasma washing leading to better results. Sensory evaluations rated plasma-washed fabrics highly, except for oil-stained fabrics, which still showed some residual stickiness and odour after treatment [3].

Sustainable and effective laundry care

The study's findings support plasma washing as a promising and sustainable alternative for fabric care. This method not only excels in removing stains but also revitalises fabrics, ensuring that they look, feel, and smell better post-wash. Moreover, the absence of fabric damage, coupled with the successful extraction of stain residues from wastewater, underscores the practicality of integrating plasma washing into conventional laundry practices.

Conclusion

Plasma washing stands out as a groundbreaking innovation in the realm of laundry care. With its impressive stain removal capabilities, preservation of fabric quality, and significant environmental benefits, plasma washing is poised to revolutionise the way we approach laundry. This technology paves the way for a cleaner, greener future, offering a sustainable and efficient solution for everyday fabric care.

To summarise, as we strive towards more sustainable living practices, plasma washing presents an exciting advancement over conventional washing techniques. It not only addresses the practical need for effective stain removal but also aligns with our growing commitment and responsibility towards a better environment. We should keep an eye on this promising technology as it moves closer to mainstream adoption, heralding a new era in eco-friendly laundry solutions.

References

1. Plasma Washing Machine; Patent-CN200910185298A; China2010
2. Plasma atomizing device and method for washing and disinfecting clothes; Patent -CN104480669A; China2016
3. Investigating the Efficacy of Plasma Washing for Stains Removal Rathore V, Nema S.K.; Preprint - https://doi.org/10.21203/rs.3.rs-3680924/v1

ACHIEVEMENTS

J. B. JOSHI RESEARCH FOUNDATION INNOVATION AWARD

Dr. Vikas Rathore was awarded the "J.B. Joshi Research Foundation Innovation Award" for the year 2023 in Engineering Sciences by the Homi Bhabha National Institute for his PhD thesis entitled "*Study of Plasma Activation of Water and its applications in Antimicrobial and Agricultural activities*". He completed his Ph.D. at Institute for Plasma Research (IPR) under the guidance of Dr. S. K. Nema. He is currently a Post-Doctoral Fellow at IPR, working in the field of plasma hydroponics and vertical farming. Congratulations Dr. Vikas.

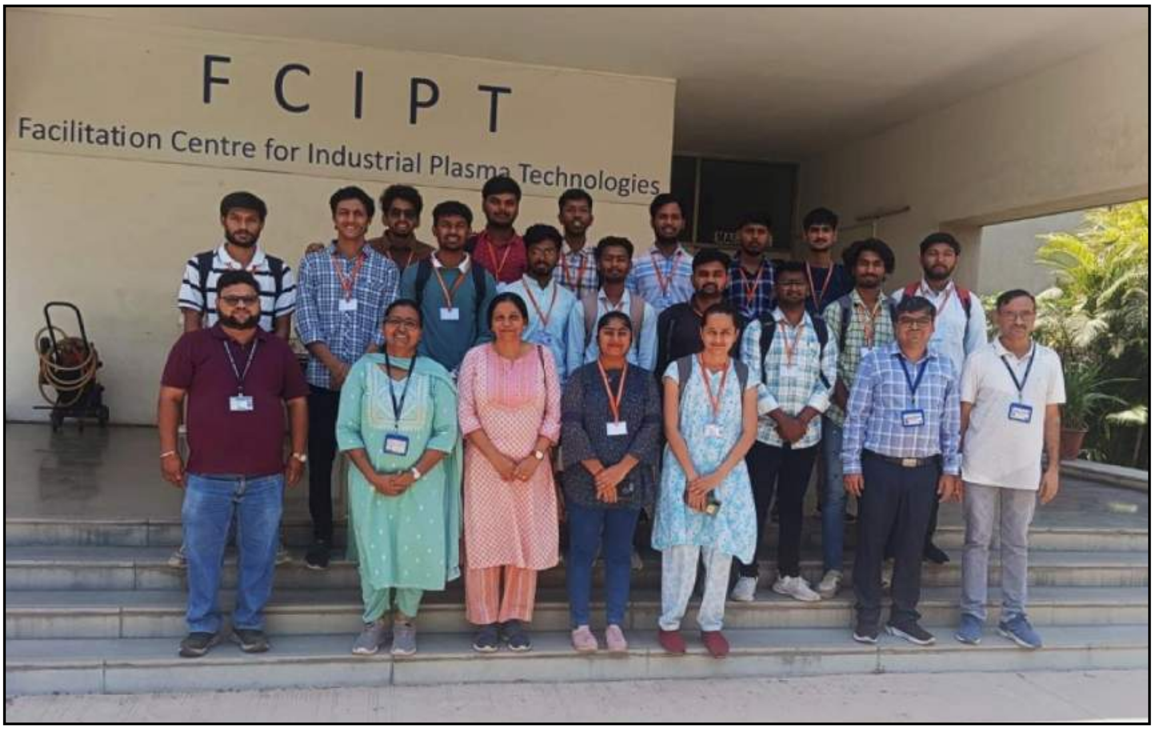
Dr. Vikas Rathore receiving the award from Prof. T. G. Sitharam (Chairman AICTE) on HBNI Foundation Day (03rd of June 2024)

VISITS TO FCIPT

Students' Visit from Government Engineering College, Gandhinagar, Gujarat

As a part of industrial visit, sixth semester students of Metallurgy Department from Government Engineering College (GEC), Gandhinagar, Gujarat; visited FCIPT, IPR on 23rd April. 'Heat Treatment' is an important subject for metallurgical engineering students. Students could get a good practical feel of plasma-based heat treatment processes like plasma carburising and plasma nitriding etc. They had also visited the recently installed industrial scale plasma carburizing system, a first of its kind in India. The students were exposed to both theoretical as well as practical knowledge about this process.

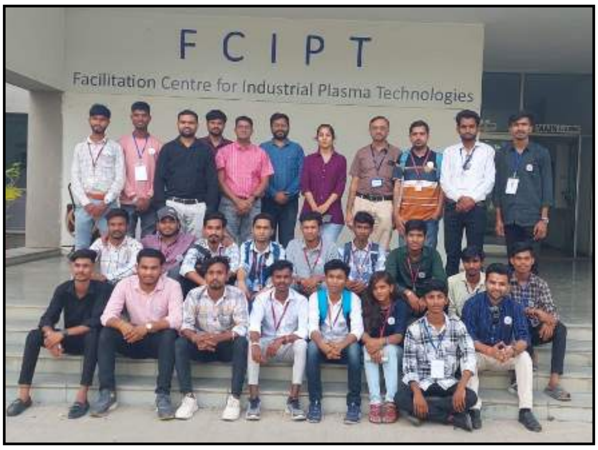
A few pictures during their visit are shown below.



Students from Government Engineering College, Gandhinagar, Gujarat

VISITS TO FCIPT

OTHER VISITS



Students from Shri Govind Guru University, Godhra; and from Navjivan Science College, Dahod; Gujarat visited FCIPT on 05th of April

Students of IPR's Summer School Program, visited FCIPT on 03rd of June

Student of Advanced Physics Summer School Program (APSSP) from St. Xavier's college, Ahmedabad during their visit to FCIPT on 27th of May

STUDENTS' NEWS

THESIS DEFENCE

Mr. Sebin Augustine gave his Ph.D. thesis defence talk on 3rd of June, titled "Development of SERS substrates based on self-organized nanoparticles for the molecular sensing applications". Congratulations Dr. Sebin.

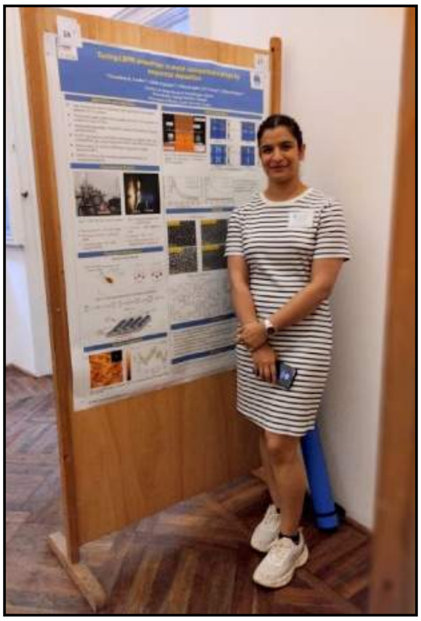
Sebin Augustine delivering Thesis defence talk

Dr. Sebin Augustine with his Doctoral Committee members

STUDENTS' NEWS

INTERNATIONAL VISITS

Ms. Tarundeep Kaur, a Ph.D. scholar at FCIPT, attended an International School on Plasmonics and Nano-optics at Institute of Advanced Studies in Como (Italy), in the first week of June. She had portrayed her work in the form of poster presentation.



OTHER NEWS

VISITS BY OFFICE STAFF

Dr. Mukesh Ranjan paid a visit to Prof. Sudeep Bhattacharjee's lab at IIT-Kanpur, and visited their Plasma & Ion Beam facilities.

PATENTS / PUBLICATIONS / TALKS DELIVERED

PATENTS APPLIED / GRANTED

1. A system and method for preparation of the metal oxide nanoparticles
   Balasubramanian C, Adam Sanghariyat, Chirayu Patil, Subroto Mukherjee
   Patent Granted. Patent Number: 467608

PUBLICATIONS IN PEER REVIEWED JOURNALS

[1] Ion beam-induced nanoripples patterns for SERS based saliva analysis to detect oral cavity cancer
Sebin Augustine, Arti Hole, Sooraj K P, Mahesh Saini, Atul Deshmukh, Vikram Gota, Pankaj Chaturvedi, Mukesh Ranjan, C. Murali Krishna
Radiation Effects and Defects in Solids (2024)

[2] Facile fabrication of Au nanoparticles loaded Ce doped ZnO nanorods for efficient catalytic and photocatalytic decomposition of toxic pollutants in water
Shipra Choudhary, K.P. Sooraj, Mukesh Ranjan, Satyabrata Mohapatra
Inorganic Chemistry Communications 165 (2024) 112482

[3] Enhanced Magnetic Anisotropy and its Thermal Stability in Obliquely Deposited Co-Film on the Nanopatterned Substrate
Sharanjeet Singh, Anup Kumar Bera, Pooja Gupta, Mukesh Ranjan, Varimalla R. Reddy, Andrei Chumakov, Matthias Schwartzkopf, Dileep Kumar
Applied Surface Science 663 (2024) 160154

[4] Sunlight driven photocatalytic degradation of organic pollutants by solvothermally synthesized rGO-BiVO4 nanohybrids
Rosalin Beura, K.P. Sooraj, Pardeep Singh, Mukesh Ranjan, Satyabrata Mohapatra
Chemical Physics Impact 8 (2024) 100595

[5] Investigation of facet evolution on Si surfaces bombarded with Xe ions
Sukriti Hans, Basanta Kumar Parida, Vivek Pachchigar, Sebin Augustine, Sooraj K P, Mukesh Ranjan
Physica Scripta 99(2024) 045954

[6] Influence of In- situ Substrate Temperature on Anisotropic Behaviour of Glancing Angle Grown Nickel Nanocolumns
Rajnarayan De, S. Augustine ,B. Das, M.K. Sikdar , M. Ranjan , P.K. Sahoo , S. Maidul Haque, C. Prathap , K. Divakar Rao
Applied Physics A 130(2024).

TALKS DELIVERED

1. **Dr. Ramkrishna Rane** gave a **keynote talk** on ***Plasma Surface Engineering for Biomedical Applications***, in The 1st global forum and International Workshop in Hybrid mode on Industrial Plasma Processes and Diagnostics (**IPPPD-2024**), **May 9-10**, organised by Department of Energy science and Engineering, **IIT, Delhi**.
2. **Dr. Ramkrishna Rane** gave an **invited talk** on ***Non-Thermal Plasma Assisted Surface Modifications for Biomedical Applications in DAE-BRNS Theme Meeting on Advanced Applications*** in Thermal and Non-Thermal Plasma (**AATNT-2024**), **June-8**, organised by Beam Technology Development Group , **BARC, Mumbai.**

TECHNICAL/RESEARCH REPORTS

1. Underwater In-situ Plasma Treatment of Coarse Wool Fibers for Scouring and Bleaching
   Nisha Chandwani, Himanshu Pandey and Vishal Jain
   IPR/RR-1616/2024
2. Adhesion and Growth of Titanium Nitride coating deposited on AISI 316L using Cylindrical Magnetron Sputtering
   Kunal Trivedi, Ramkrishna Rane, Alphonsa Joseph, Supratik RoyChowdhury
   IPR/RR-1638/ Apr 2024
3. Generation of Dielectric Barrier Discharge Plasma on large area electrode at Atmospheric Pressure for Agriculture Applications
   Anand Visani, Ramkrishna Rane , Akshay Vaid, Rohit Parihar , Parmesh Maila , Alphonsa Joseph
   IPR/RR-1647/May 2024
4. Influence of Plasma Forming Gas (Oxygen/Argon) and Plasma Source Driving Frequency (13.56 MHz/40 kHz) on Surface Properties of Silicone Catheters
   Purvi Dave, Balasubramanian C, Chirayu Patil, R. Rane and S. K. Nema
   RR-1658 IPR/RR-1658/ Jun 2024

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