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RECENT RESEARCH TRENDS ON PHOTO-CATALYSIS FOR CLEAN ENVIRONMENTAL APPLICATIONS AND SINGLE METAL DOPED TIO_2 CATALYST SYNTHESIS & EFFICIENCY ANALYSIS ACROSS CALCINATION TEMPERATURES

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ABSTRACT

There is growing enthusiasm to apply scientific knowledge and methods of green nano-technology to develop "cleaner technologies" so that the natural resources and energy are used efficiently eliminating environmental contaminations. The paper discusses the global publishing trends in one such technology area, photo catalysis and environment applications, during the last five years, in the first part. The total number of publications, major publishing houses, the leading journals publishing on environmental photo catalysis and collaborative research trends etc., a comparative analytical review study based on Specific databases of different publishers is presented. Having a clean environment is a requirement that is not limited by geographical/political boundaries, rather strengthened together over the period. Specific data sources are being used to analyze research collaboration and growing research trends on photo catalysis within and amongst different countries. The comparative study highlights the journals, publishers and regions' interest, involvement and publishing trends in the discipline quantitatively as well as qualitatively amongst all the apex publishers considered. The second part of the paper discusses on synthesis of Ti-Mg based catalysts and evaluates the efficiency of the catalyst across various calcinations temperatures for environmental applications.

Keywords: Environment Remediation & Applications, Magnesium/Titania Catalyst Synthesis and Efficiency, Metal Doping, Nanomaterial, Photo-catalysis Publication Analysis.

I. INTRODUCTION

Degradation of traces of organic substances through photo catalysis reactions has achieved the appeal in the process improvement for complete mineralization of the waste water pollutants into environmentally harmless compounds. The increasing research pattern on photo catalysis and the growth of the discipline lead conception

of its applications like hydrogen fuel generation by water splitting, environmental remediation and chemical synthesis, mainly in the field of green chemistry.

Photo catalyst is defined as a substance which is activated by adsorbing a photon and is capable of accelerating a reaction without being consumed. These substances are invariably semiconductors. Semiconducting oxide photo catalysts have been increasingly focused in recent years due to their potential applications in solar energy conversion and environmental purification. Several semiconductors (TiO_2, ZnO, Fe_2O_3, CdS, ZnS) can act as photo catalysts but TiO_2 has been most commonly studied due to its ability to break down organic pollutants and even achieve complete mineralization. Photo catalytic and hydrophilic properties of TiO_2 make it close to an ideal catalyst due to its high reactivity, reduced toxicity, chemical stability and lower costs.

Solar photo catalytic oxidation processes for degradation of water and air pollutants have recently received increasing attention. Degradation is carried out both under homogeneous and heterogeneous conditions as photo catalysts are more extensively used, because they are cheaper, more robust, easily recovered and reused. However ongoing interests and developments in harnessing solar energy are expected to increase its use in photo catalytic degradation applications in visible light.

In recent years, it has been recognized that both chemical synthesis and chemical degradation are preferably performed using technologies that are more sustainable, less hazardous, less polluting and with less byproduct waste. Among other technologies, photo catalysts have been recognized as desirable. Conversion of water to hydrogen gas by photo catalytic water splitting, solar water disinfection, self-sterilizing photo catalytic coatings, removal & destruction of organic contaminants, Conversion of carbon dioxide into gaseous hydrocarbons, Decomposition of polyaromatic hydrocarbons etc. through photocatalyic reactions demonstrates its significance now a days, as it is performed at ambient pressure, ambient temperature, and at a cheaper cost. Catalyst deactivation, slow kinetics, low photo efficiency, unstable intermediates and unpredictable mechanisms are the main challenges to development of photo catalytic oxidation processes.

TiO_2 is a semiconductor with a number of properties pertinent to photo catalysis such as transparency to visible light, high refractive index and low absorption coefficient. TiO_2 has been used in a wide range of applications including ultraviolet filters for optics and packing materials, environmental remediation, papermaking, ceramics, solar cells, electro chromic displays, anodes for ion batteries, self-cleaning coatings and paints and humidity as well as gas sensors. A large number of prior state of the art references have mentioned using titanium dioxide as a photo catalyst for an assortment of chemical reactions and antimicrobial activity. Many attempts have been made to modify the photo catalytic activity by doping the titanium dioxide with a number of different compounds and using a number of different techniques. However, these attempts have limited stability and efficiency or were active only / primarily under UV light.

A number of attempts have been made to modify TiO_2 to enhance its activity by doping the crystalline structure with a variety of compounds including those with nitrogen, carbon or sulfur atoms. Some attempts have been made to obtain visible light activation of the photo catalysts by the red shift of the adsorption spectrum. Other compounds including alkaline earth metals, noble metals and non-metal species deposited on TiO_2 may show different effects on the photocatalytic activity of TiO_2 under solar and artificial visible light irradiation.

There are several mechanisms that are responsible for such effects: i) dopants enhance the electron-hole separation by acting as electron traps, ii) they extend the light absorption into the visible range and iii) A

number of different metals, especially transition metals, when used as dopants, cause the titanium dioxide to increase adsorption of visible light. The present study describes a photo catalyst synthesis method by dry mixing synthesis of Mg-doped titanium dioxide utilizing mild reaction conditions and benign precursors and avoiding organic solvents. These used in conjunction with the synthesis methods results in a photo catalyst activated by visible light.

Alkaline Earth Metal (Mg^{2+}) doping of TiO_2, has been investigated as a possible way to improve the efficiency of TiO_2 catalysts for the photo splitting of water. This may also improve the adsorption properties of the catalyst and extend the absorption of light to the visible region through dye degradation activity. We have studied the Mg/TiO_2 system which exhibits enhanced photo catalytic effects compared on specific varying calcination temperatures. The efficiency of this catalyst was found to depend on the level of Mg^{2+} doping, homogeneous mixing, calcination temperature and the duration of heating of the sample.

II. METHODOLOGY

Titanium dioxide [TIO_2] is mixed with a doping material Magnesium Nitrate [$Mg(NO_3)_2$] followed by drying at 45ºC forming a dried mixture. This is then calcined at different temperatures viz. 550 ºC, 500 ºC, 450 ºC, 350 ºC & 250 ºC for specific uniform time duration, The resulting material is then used as a catalyst. After calcination, the dopant is then found in the titanium dioxide particle. Calcination may remove part or all of the components of the dopant. This process aids in making the titanium dioxide more porous, a desirable trait, as greater surface area provides for greater catalytic activity. Also, the temperature and time of calcination affects the size and agglomeration of crystalline particles.

In the present experiment, it is desirable to have a very porous product to have a high surface area for catalysis. The calcination period also affects the composition of the dopant and its interaction with the TiO_2. Oxidation and degradation of the dopant and reaction with, formation of, and porosity of titanium dioxide are examples of properties affected by the calcination. The photo catalyst prepared can catalytically react with organic compounds and can be used for degradation of highly acidic dye i.e. Congo Red to see the efficiency of the catalyst. It is of particular value to use the present experiment to kill microorganisms, to degrade allergens and to degrade toxic compounds. The catalysts may also be used to catalyze various chemical reactions, thereby producing a large number of desired chemicals.

2.1 The Energy of a Single Photon Can be Calculated by Using Planck-Einstein Equation

$E = hc/\lambda$,

where E is the energy of a single photon (W s),

h is the Planck's constant (6.626×10^{-34} J s),

c is the speed of light (2.998×10^{8} m s^{-1}) and

λ is the wavelength of the irradiation source (nm).

2.2 Percent Degradation may be Calculated by Using Following Formula

% Degradation/Removal = C0-Cf/C0*100

C0 Initial Concentration

Cf Final Concentration

2.3 Adsorption Capacity May be Calculated as following

Adsorption Capacity = (C0-Cf/w)*(V/1000) mg/gm

C0 Initial Concentration

Cf final concentration

W Weight of the catalyst

V Volume of the Solution Taken

III. RESULTS & DISCUSSION

3.1 Collaboration Between Different Countries

Using Wos (Web of Science)database as the resource, we obtained more than 2500 publications across five years (2000-2014), systematically classified and arranged them using key words.

WoS is an online subscription-based scientific citation indexing service maintained by Thomson Reuters that provides a comprehensive citation search. Sorted, and indexed in seventy nine (79) '.xps' master files, containing 50 Publications each (in 90% files) and 10 Publications each (in 10 % files): each record in the file had briefs details under categories like Title, Author(s), Source, Cited References, Accession Number, Language, Publisher. ISSN, ISO Source Abbrev etc. from 2005-2014.

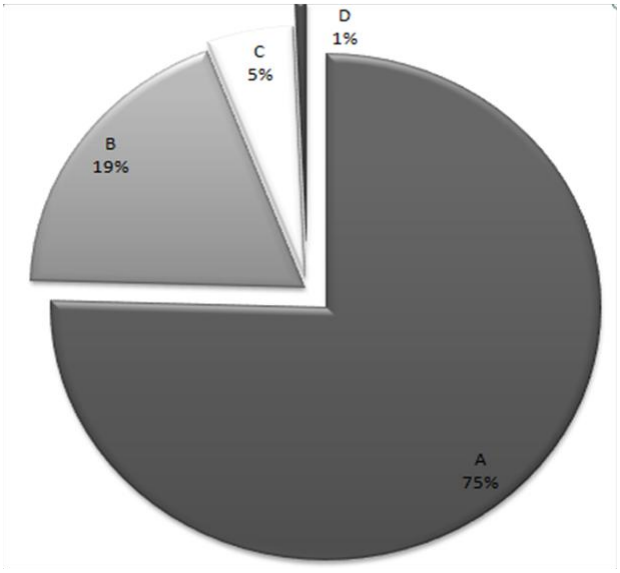

Figure 1 Analysis of collaborative research between different countries (Number of collaborating countries—A: 1, B: 2, C: 3, D: 4) The numbers in the figure represents the number of publications and the % contribution.

A typical example regarding research collaborations across countries during the year 2013, obtained from the data base is presented in the Pi chart given below (Fig. 1).

The Figure shows that about 75% of the publications is done without collaboration with other countries whereas 19% of research output involves two participating countries. Multi-country collaboration involving 3 and 4

participating countries is very small. By doing similar exercise across years, it is possible to analyze the emerging trends in collaborative research in this field.

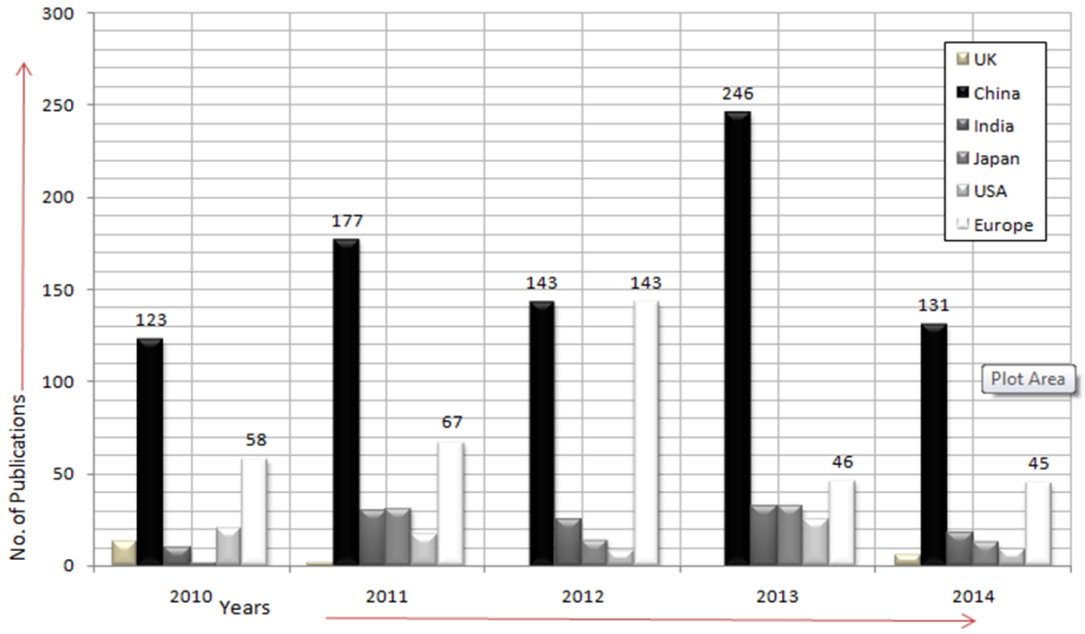

Figure 2 Analysis of research publications by 06 major contributors across five years. The numbers in the figure represents the comparative number of publications within and across the years.

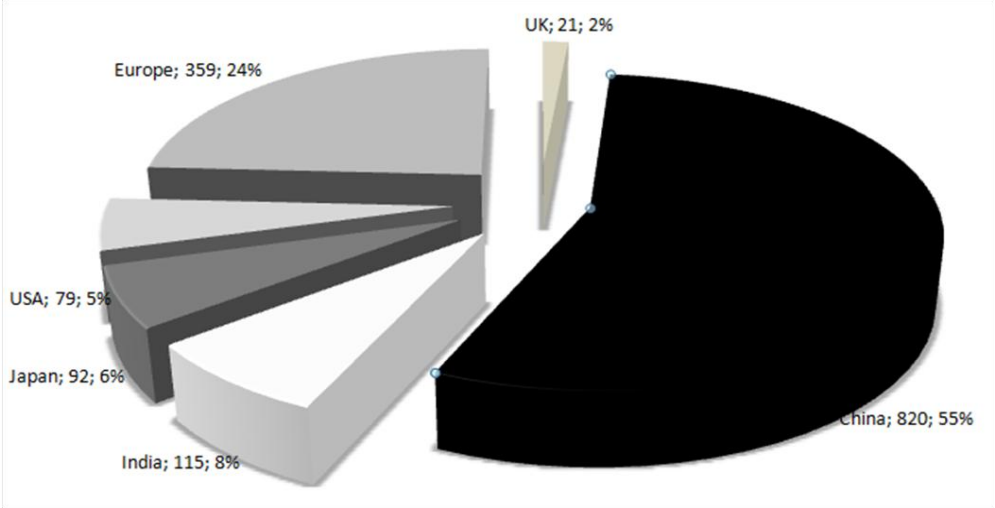

Figure 3 Analysis of Research Publications by 06 Regions Across five years. The Numbers in the Figure Represents the Number of Publications and the % Contribution.

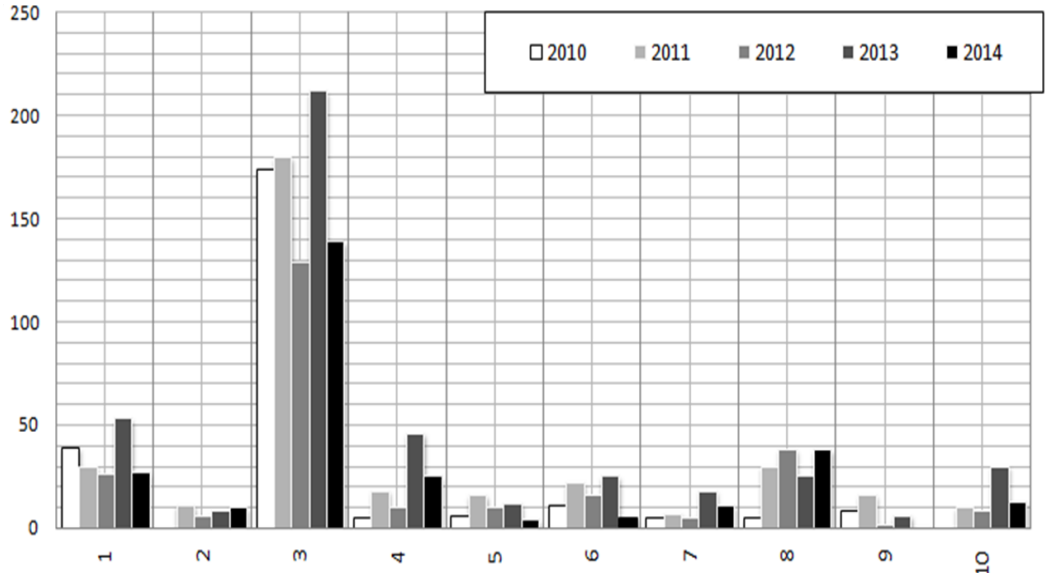

Figure 4 Analysis of research publications by 10 major Publishers across five years. The numbers in the figure represents the number of publications by leading publishers on photo catalysis research.1- ACS, 2- AMER Scientific Publishers, 3- ELSEVIER, 4- RSC, 5- SCIENCE PRESS, 6- SPRINGER, 7- TAYLOR & FRANCIS, 8- TRANS TECH PUBLICATIONS Ltd, 9- WILEY- BLACKWELL, 10 -WILEY V C H VERL AG GMBH

The review narrates the comparative comparison of global countries on research paper contributions on photocatalysis for the five years leading to find leading five regions which have been most involved in area of Photocatalysis & Environment. The review analysis leads to infer that the countries with more than nine 09 publications across the five years served to classify the area specific research contribution prototype significantly amongst all countries as per criteria standard considered.

Considering leading 6 publishers proclivity journal wise across the time span of five years, on photocatalysis for clean environmental applications, helps in reviewing top journals active to publish on the area quantitatively and qualitatively for all the apex six publishers separately. Country Collaboration study says that the comparative percentage contribution by multiple number of global countries on research paper contributions on photocatalysis for the years, showing countries collaboration intensity and leading five Publisher trends, those have been most involved and active together in the respective discipline of research for remediation and clean environment applications.

Compiled yearly data study highlights comparative scrutiny of multiple countries individually and their percentage contribution increasing or decreasing pattern individually across the five years and country collaboration increasing/decreasing/pattern category wise and frequency of collaborations yearwise. It helped to analyze no. of publications published journal wise and year wise for all the six publishers separately.

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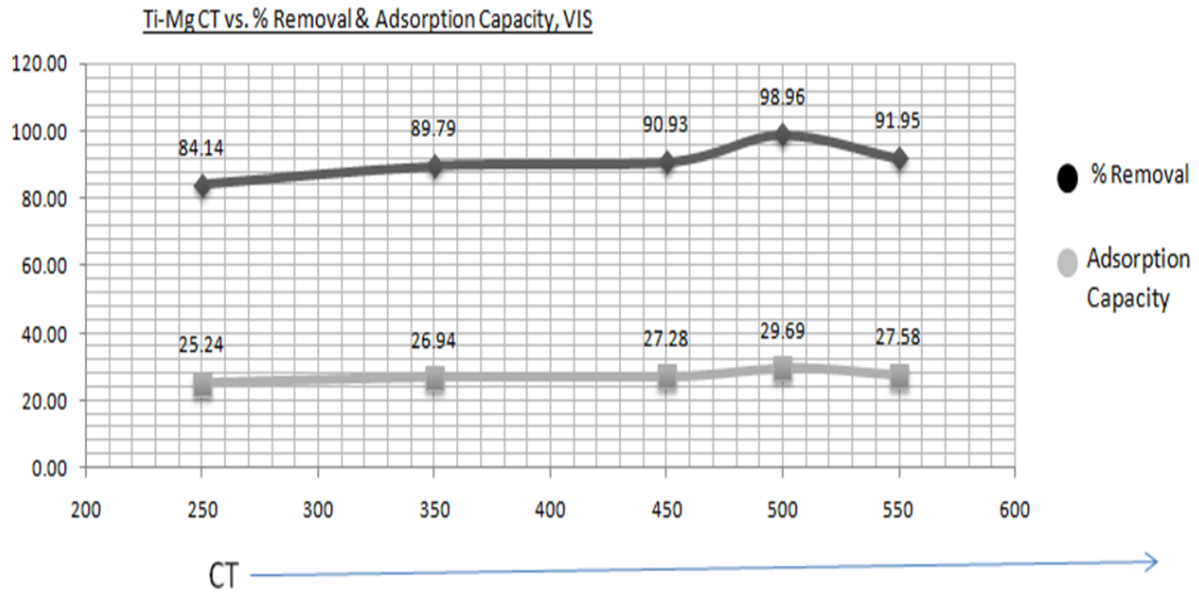

Figure 5 Analysis of Mg Doped TiO2 Catalysts Efficiency in terms of % Removal and Adsorption Capacity with respect to Calcination Temperatures in Visible Region. The numbers in the figure represents the highest efficiency at 500 Degree Celsius in Visible Region.

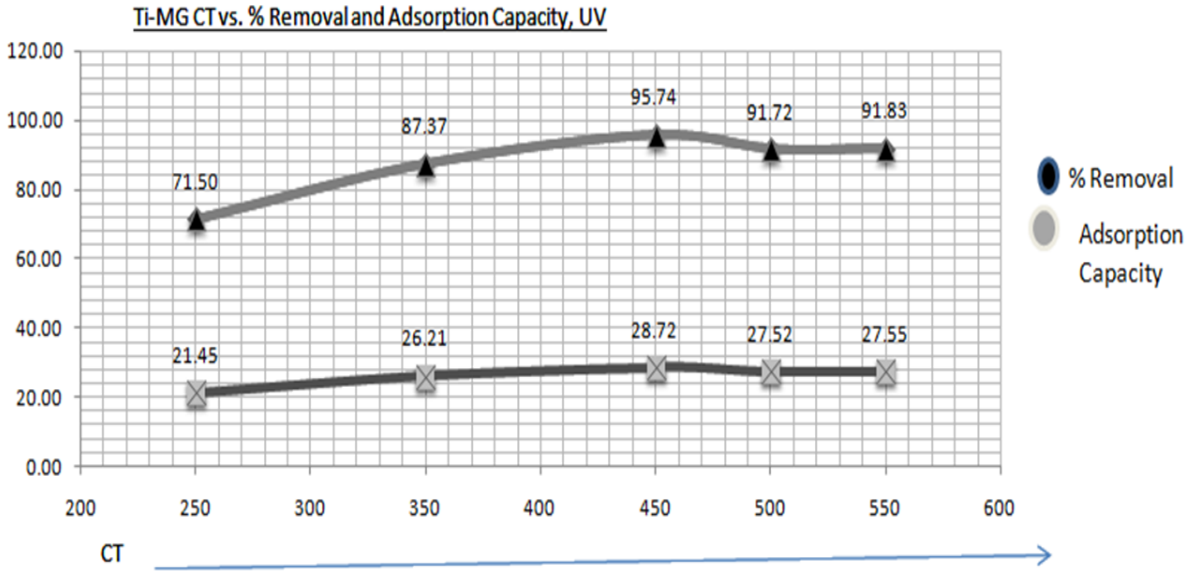

Figure 6 Analysis of Mg Doped TiO2 Catalysts Efficiency in terms of % Removal and Adsorption Capacity with respect to Calcination Temperatures in UV Region. The numbers in the figure represents the highest efficiency at 450 Degree Celsius in UV Region.

In the experiment, it is observed that the efficiency of Mg/TiO_2 Catalyst is been following an increasing trend for both the regions UV and Visible, up to certain increase in Calcination temperature. In Visible region, the above catalyst is showing 98.96% efficiency in terms of Percentage degradation and adsorption capacity at 500ºC CT for Congo Red Dye Degradation. Rather, In UV Region, Mg/TiO_2 Catalysts shows 95.74 % dye degradation at 450ºC CT.

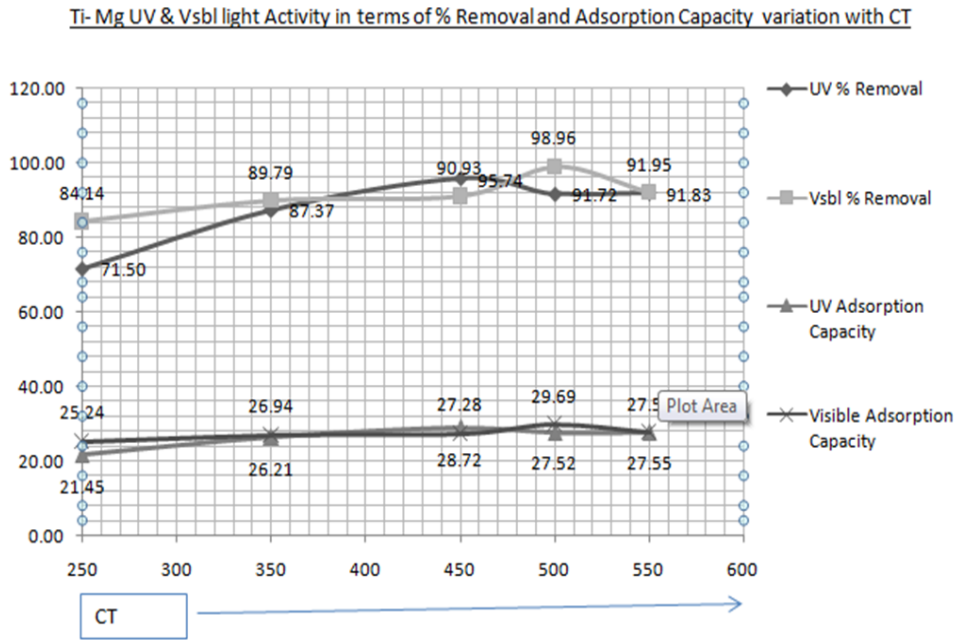

Figure 7 Analysis of Mg Doped TiO2 Catalysts Comparative Efficiency at various calcinations temperatures in terms of % Removal and Adsorption Capacity in UV Region and Visible Region.

IV. CONCLUSION

Primarily growing research interest and collaborative research review is analyzed concluding core areas of research on photo catalysis. It is interesting to note that collaborative research on the various part topics is on the increase. It also looks at the countries that are vibrant on research related to photocatalysis and environment, as reflected from the number of publications, international collaborations obtained based on the country of contributing authors. This is reflected in the increasing number of publications and the journals publishing work in the discipline.

Compiled year wise data analysis amongst leading six (06) countries concluded from above analysis, helped in relative study of multiple countries for the years individually, observing year wise and region wise rising or falling trend on photo catalysis for clean environmental applications. The respective analysis also helps to do the comparative study of global countries on research paper contributions and interest in the area of research for the years from 2010-2014 to find leading countries which have been significant contributors during the analysis.

The surface of TiO_2 consists of rows of Ti atoms, in-plane oxygen atoms and bridging oxygen atoms. Mg Dopants may distort the lattice and substitute for either O^{2-} or Ti^{4+}. Depending on the calcination temperature, Mg atoms can be absorbed onto TiO_2 or substitute either Ti^{4+} or O^{2-}. The photocatalytic degradation is a very complicated process, which is affected by the crystallinity, crystallite size, phase/chemical composition of the catalysts and the morphology of particles. It is assumed that produced radicals ($.O_2^-$, .OH, etc) are the major species responsible for the photocatalytic degradation of organic contaminants.

The hole in the VB can be captured by OH^- or H_2O species adsorbed on the surface of the catalyst to produce radicals, whereas photogenerated electrons in the CB can reduce the adsorbed oxygen into $.O_2^-$, which

contribute to the increased activity of the nanocatalyst. In addition, hole itself can also effectively oxidize target pollutants adsorbed onto the surface of the catalyst. Apparently, the degradation of model pollutants proceeded on the surface of the nanocatalyst by the synergistic effect of holes and produced radicals, and not in the bulk of the solution due to the fact that photogenerated radicals were extremely short lived and tended to recombine to form water.

Additionally, the catalyst can affect a large number of general chemical reactions including affect hydrophilicity/hydrophobicity of a surface exposed to the catalyst. These catalysts may be used prophylacticlly for protection from the same sources of contamination. This may be useful for treating harmful waste and for sterilizing and decontaminating fluids for human use. Congo red is the sodium salt of 3,3'-([1,1'-biphenyl]-4,4'-diyl)bis(4-aminonaphthalene-1-sulfonic acid)(formula: $C_{32}H_{22}N_6Na_2O_6S_2$; molecular weight: 696.66 g/mol). It is a secondary diazo dye. Congo red is water-soluble, yielding a red colloidal solution; its solubility is better in organic solvents such as ethanol.

It has a strong, though apparently noncovalent, affinity to cellulose fibers. However, the use of Congo red in the cellulose industries (cotton textile, wood pulp, and paper) has long been abandoned, primarily because of its toxicity and tendency to run and change color when touched by sweaty fingers. These photocatalysts may degrade Congo red dye and the other organic pollutants efficiently. in presence of ambient or artificial light may be used as a substitute for all applications which required UV light treatment, particularly sterilizations and chemical reactions. The present catalyst activity encompasses degrading a large number of different organic chemicals.

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