PROJECT WORK

USE OF PHOTOCATALYSIS IN 3D PRINTERS

SUBMITTED TO

DEPARTMENT OF CHEMISTRY
SVCR GOVT. DEGREE COLLEGE
PALAMANER

SUBMITTED BY

M VARALAKSHMI
S ARSHIYA
III B.Sc (MPC)
SVCR Govt. Degree College
Palamaner, Andhra Pradesh-517 408

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Topic :-

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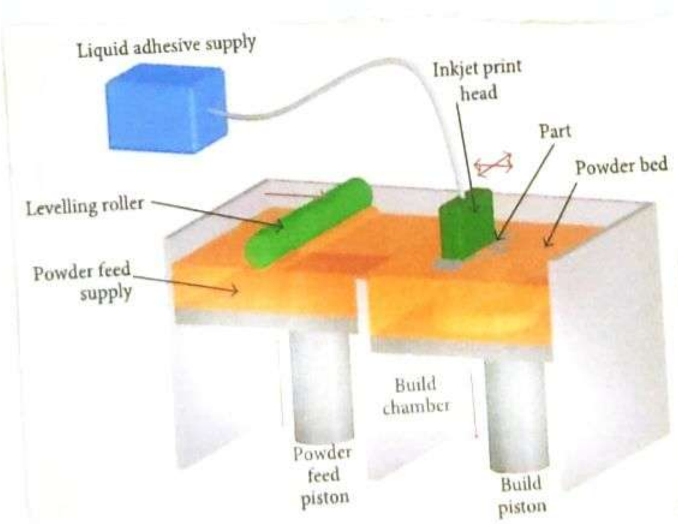

Indirect Inject Print (IIP) is a layer-by-layer process of depositing liquid binder onto thin layers of powder to create a 3D object [17].

Ceramic- Based 3D Printed Supports for Photocatalytic Treatment Of Wastewater

Introduction :-

Global warming, energy crisis, and Pollution are Serious Concerns affecting both the human health and environment. The environmental pollution includes a wide range of hazardous chemicals which are harmful even at extremely low concentrations.

The common treatment of these pollutants involves the use of pyrolytic methods which Consume large amounts of fossil fuels producing elevated levels of CO_2 and thus contributing again to climate change and energy crisis.

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Another Severe issue [1-3] is water pollution from emerging contaminants (ECs) Such as endo-crine disrupting chemicals, pharmaceuticals, and

Personal care products even at trace Levels. Some adverse potential effects caused by ECs are water toxicity, resistance development in pathogenic bacteria, genotoxicity, and endocrine disruption [4-6].

Wastewater treatment plants are not designed to remove low concentration of Synthetic pollutants such as pharmaceuticals and hence alternatives Such as the Advanced Oxidation Technology (AOT) have been used to solve this environmental problems [7,8].

Heterogeneous photocatalytic processes Constitute one of the most important AOTs and are based on the oxidation of polluting com-pounds which can be found in air or water by means of a reaction occuring on a Semi-conductor catalytic surface activated by light with a specific wavelength.

TiO_2 is the most investigated Semiconductor catalyst particulary because of its great potential in the treatment of environmental pollution [9] and it's chemically stable, nontoxic, and inexpensive [10-12].

In this sense, a new exciting approach for the production of structured (3DP) system. Until the past few years, this type of technology has been restricted to medium- and big-sized Companies devoted to the fabrication of prototypes.

A digital model of the object is created in a computer. Using adequate software, the user may control several relevant parameters such as the number of layers which are piled up to generate the full item depending on the resolution required, thickness of the layers, and porosity. In the second step, each digital layer is printed in an appropriate substrate. Different 3D printing techniques can be selected depending on the material required and the way to fuse layers together.

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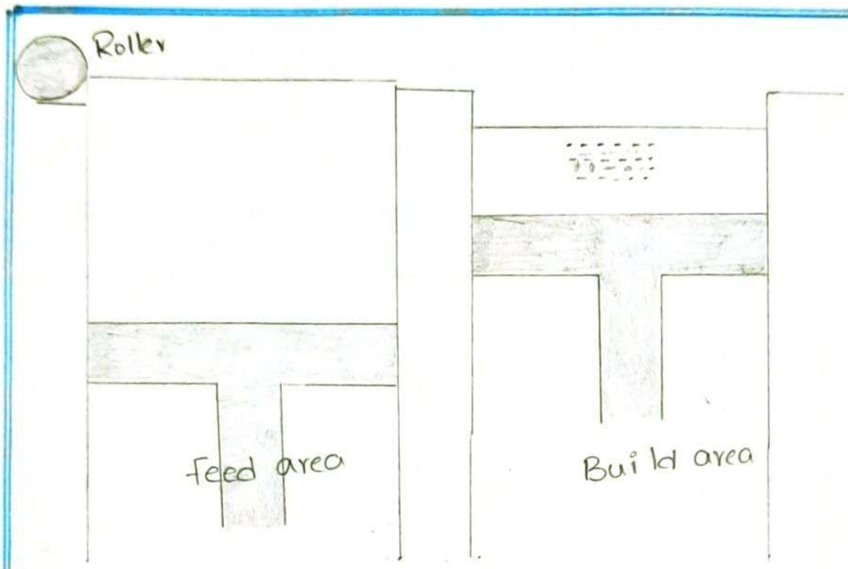
2. Materials and Methods:

The activity of the TiO_2 photocatalyst supported over a 3D printed ceramic structure was studied evaluating the photodegradation of methylene blue as a model molecule for wastewater treatments. The photocatalytically active material, TiO_2, was examined by X-ray diffraction in order to obtain the percentage of anatase and rutile phase. Nitrogen adsorption-desorption porosimetry and mercury porosimetry techniques were used to study its specific surface area and textural properties [20].

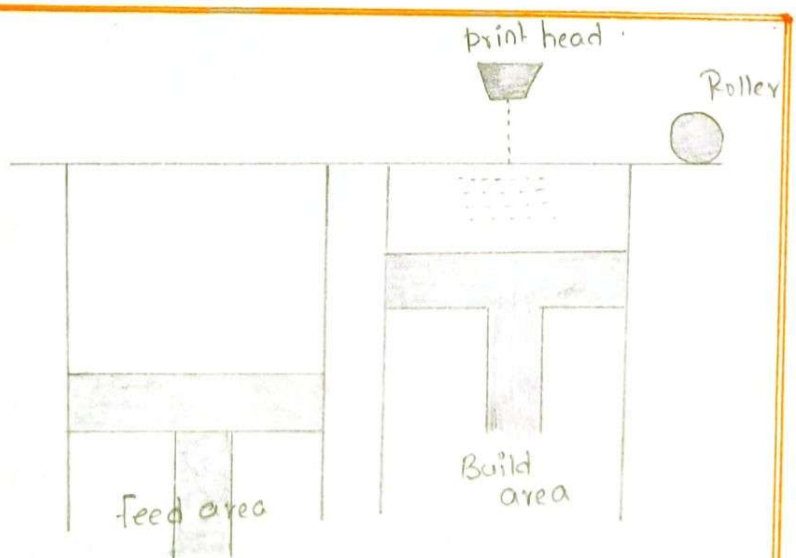
* 3D printing structures:-

The materials used in the 3D printing process were calcium sulphate hemihydrate and a water-based binder clear, from S.A.T. ELITE) These materials were used in a 3D printer, with a 300 x 450 dpi resolution and layer thickness of 0.1 mm.

First, the structure is digitally designed using free software Tinkercad [22] and the corresponding digital model is saved as a stl file and then sent to the 3D printer. During the three printing processes, a roller spread a thin powder layer from the feed area to the build area Journal && chemistry



(a)



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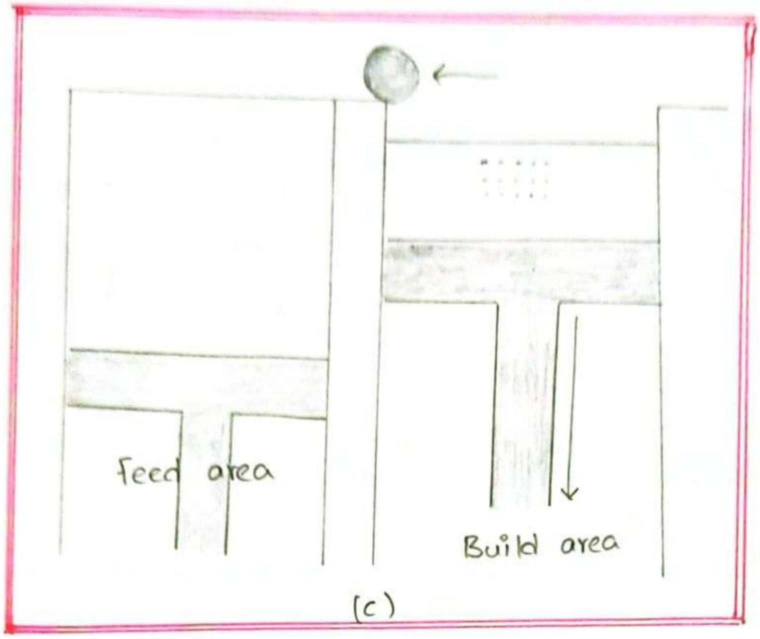
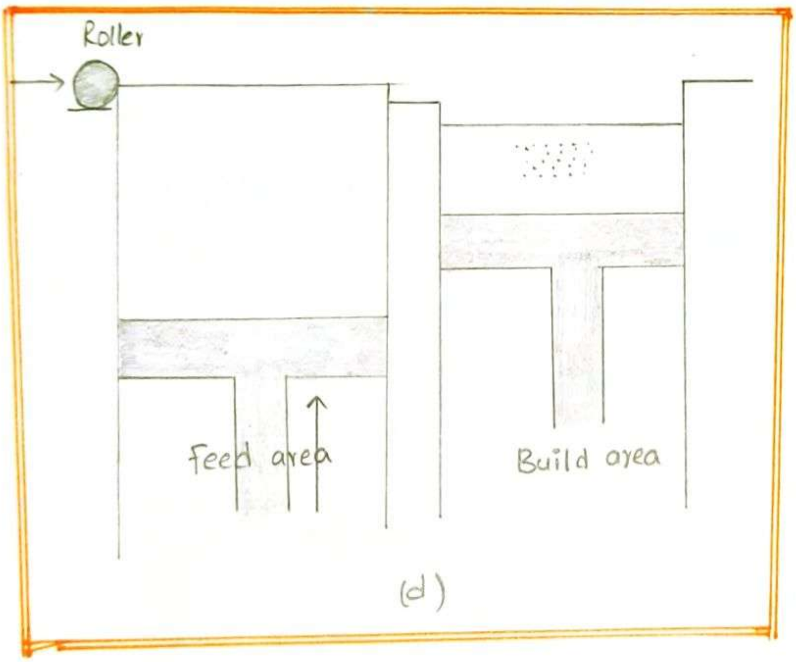




3DP Process Scheme.

(a). The roller spreads a thin layer of powder from the feed area to the build area

(b). The print head injects binder droplets on the powder bed.

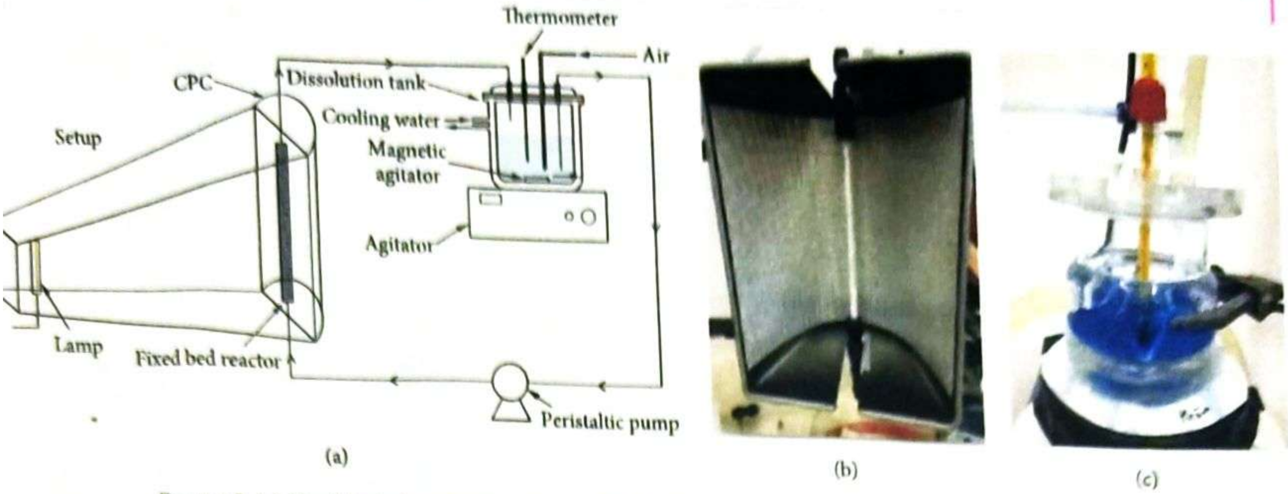


Figure 5: (a) Fixed-bed photoreactor scheme. (b) Fixed-bed reactor. (c) Wastewater photoreactor tank.

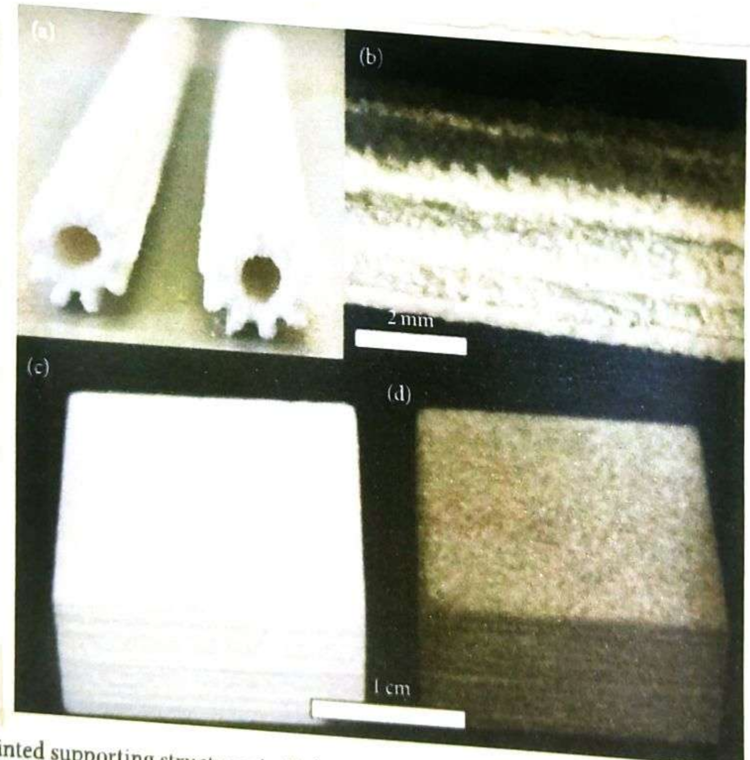


Figure 3: ((a) and (b)) 3D printed supporting structures in $CaSO_4$. (c) 3D printed square testing pieces in the green state and (d) after firing at 250°C for 3 h.

(c). After printing a layer, the roller returns to the feed area

(d). Powder in the feed area is raised, while that in the build area is lowered. The roller then spreads layer of powder [21].

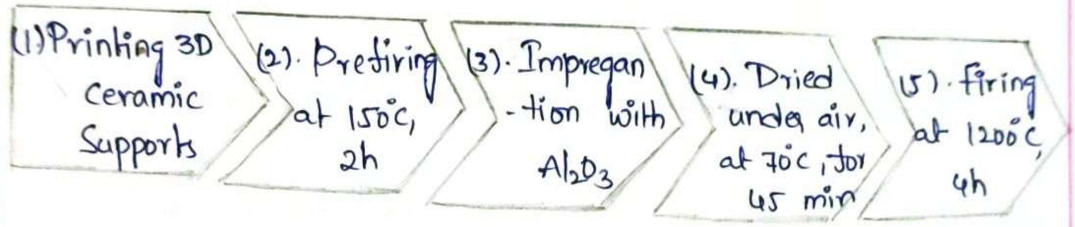
and then the print head deposits binder droplets selectively within the build area. when the first layer is printed, the roller returns to the feed area, spreading another powder layer to the build area. This procedure is repeated until the fabrication of the whole 3D structure is completed [21].

*** Improving the Mechanical stability of the 3D Printed structures :-**

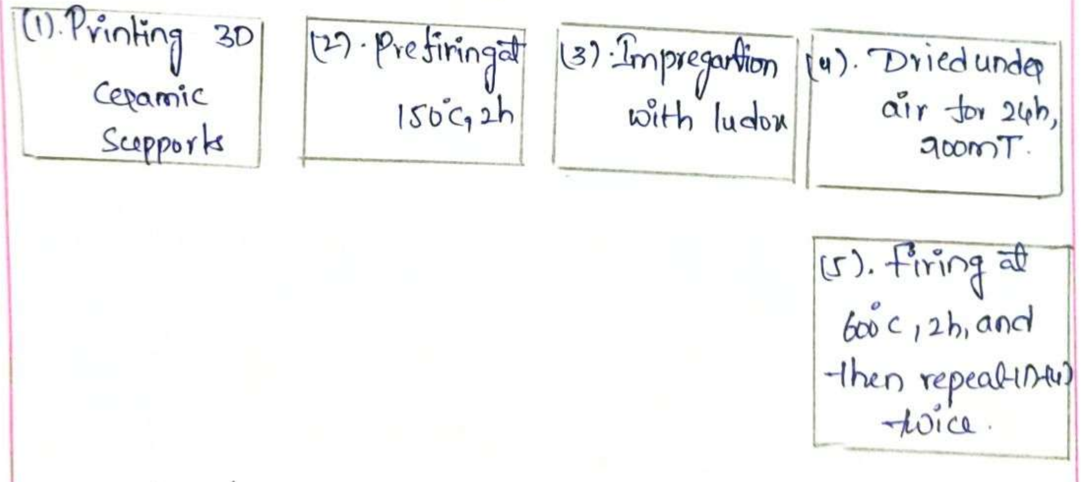
Two routes were followed to impregnate the 3D structures with another inorganic material enhancing the mechanical stability up to 1200°c. The 3D Printed Samples were previously fired at 150°c for 2h to improve the mechanical stability in aqueous solution needed for the impregnation processes.

1. Ratio & Components and impregnation times used in the Optimization & the impregnation process & 3D structures with Al_2O_3.

procedure	Al_2O_3(g)	water (g)	Dolopix(g)	Impregnation times (s)
1	30,0	8,39	0,161	10, 20, 30, 60,
2	30,0	16,2	0,423	300, 600, 1800
3	30,0	33,8	0,644	

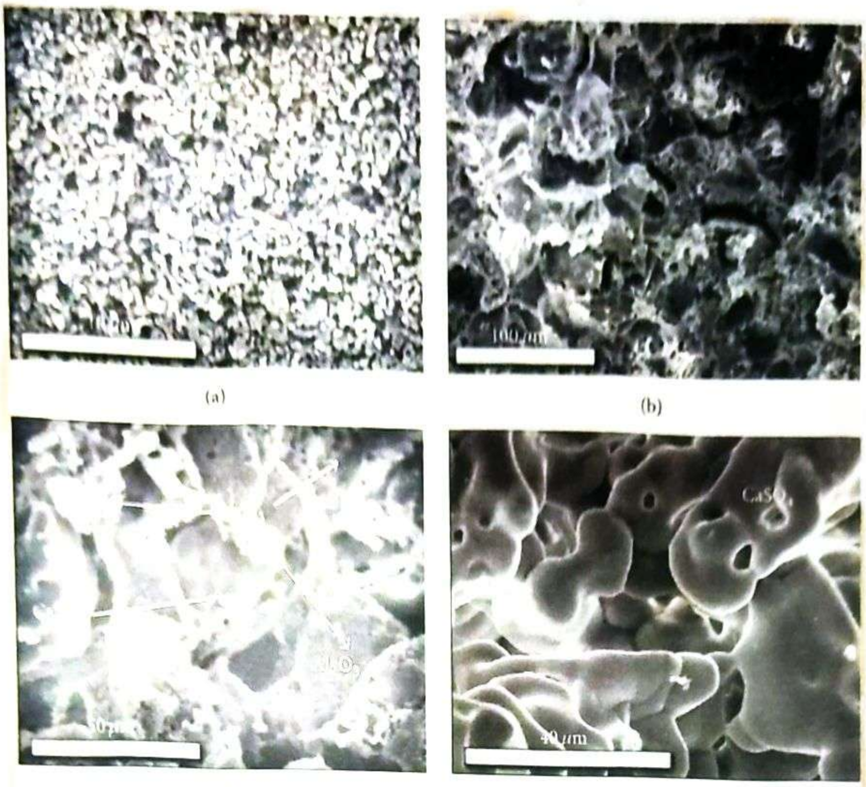


(a).



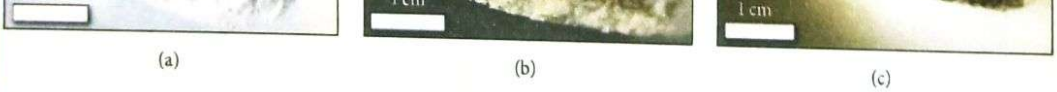
Microstructural Characterization :-

The morphologies of the 3D structured sample in the green and sintered states were examined using a stereomicroscope Leica Zoom 2000



(a) (b) (c) (d)

FIGURE 7: SEM images and EDX data of Al_2O_3-impregnated samples following procedure 2 (Table 1) with 30 s of impregnation time. (a) SEM image of surface of the covered 3D structure. ((b) and (c)) SEM image showing a good distribution of Al_2O_3 inside the porous structure. (d) SEM image of the inner part of the supporting $CaSO_4$ porous structure.



(a) (b) (c)

...URE 6: Optical images of impregnated 3D structures with dispersions of Al_2O_3, using an Al_2O_3 concentration of (a) 0.77 g/ml, (b) 0.65 g/ml, (c) 0.47 g/ml.

and a Scaning electron microscope (Jeol LTD, JSM-6300) combined with energy dispersive Spectroscopy. For SEM studies, all samples were covered with a thin film of Sputtered silver to avoid changing Problems and to obtain better image definition.

Result and Discussion:-

As commented in the text, before the activation of the 3D Supporting structures, the mechanical stability of the structures must be improved and we can use two routes.

* Impregnation with Alumina:-

Several impregnation studies with alumina dispersions were tested. The impregnation time was also optimized and it was concluded that no significant differences were observed b/w Samples impregnated for 30 s or 5 min and, hence, 30s was the time used in all the Procedures tested. Procedure 1 Produces a 0.8 mm thick external covering layer of Al_2O_3 over the 3D structure; however, the porous 3D structure seems to be alumina - free, and hence the inner structure will collapse at hight temparatures.

Procedure 2 :-

Types of covering : an external layer of Al_2O_3, as in the first case, and an additional inner impregnated layer covering about 70% of the 3D porous structure. The combination of both layers is ideal for improved mechanical stability.

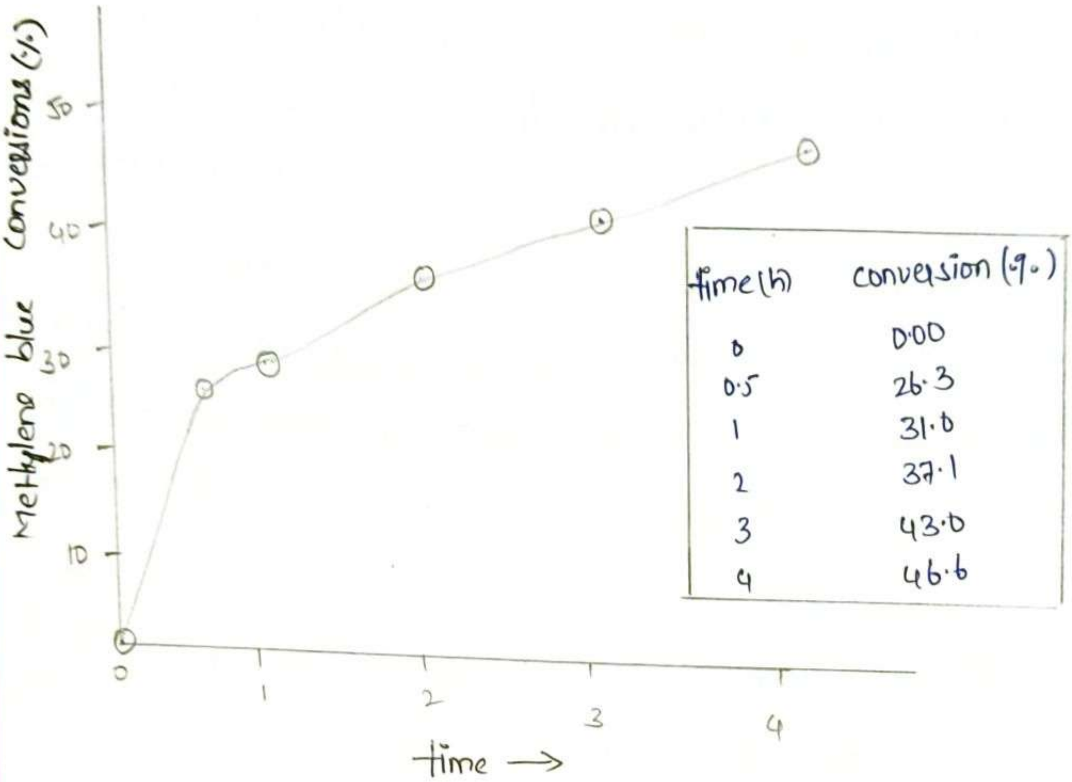
And finally in procedure 3 with a more diluted dispersion, only the internal layer was observed, which is not enough to provide mechanical stability at high temparatures and hence procedure 2 was used to test all the 3D printed structures.

From the SEM images, It is possible to observe a good distribution of 1um Al_2O_3 particles in the surface of the covered 3D structure and also a good distribution inside of the porous structure. The presence of Al_2O_3 is negligible in the inner part of the 3D porous structure, with a value of 0.6%.

Figure 10: Several 3D printed square pieces of $CaSO_4$ were used to optimize the infiltration process with Ludox. All the samples were infiltrated with a solution of Ludox : water with a ratio of 1 : 5 (wt) for 30 s and then dried for 10 min at 70°C and finally they were fired at the temperatures shown in the images for 2 h.

Figure 9: Simple 3D models of two types of geometrical surfaces printed to verify how the surface design can modify the photocatalytic experiments.

of Al showns in the EDX studies compared to 25,1 % of Al obtained in the structures impregnated shown in figures



time (h)	conversion (%)
0	0.00
0.5	26.3
1	31.0
2	37.1
3	43.0
4	46.6

Temporal evalution of MB removal during photocatalytic experiments under UV light irradiation using 3DAS fabricated with the first route.

Shows the result of the photocatalytic performance under UV light radiation. The temporal evalution of the concentration of the MB as contaminant model showed that MB acheives 46.6 % of conversion with the irradiation time after 4h. This value proves that the 3D supporting structure can be effectively used as a support for photocatalytic materials; however, the degree of conversion can be considered relatively how and hence a more optimized structure, possibly with geometries maximizing illumination of the active area and improvement of the active area should be fabricated.

Indeed, just modifying the geometrical surface from plain surface to twisted one produces an enhancement of more than 6% in the conversion of MB, that is, from 46.6 to 52.6%.

Conclusion :-

3D printing technology has been successfully used to create 3D supporting structure of $CaSO_4$ which can be activated with TiO_2 showing photocatalytic activity.

Two approaches have been proposed and optimized to enhance the mechanical stability of the 3D supports up to 1200°C. In one of them, Al_2O_3 is used as a binder of the whole 3D structure; in the other method, a dispersion of nanoparticles of SiO_2

acts as a binder.

In both cases, the A3DS show photocatalytic activity for the MB removal from wastewater, reaching more than 50% of conversion in just 1h of irradiation when using ludox in the activation process. This approach reaches a high photodegradation rate of about 90% after 5h.

The A3DS offer clear advantages for the industrial treatment of wastewater given that the photocatalytic materials remain confined to the packed bed avoiding the need of separating the catalyst from the decontaminated water effluent.