

# Synthesis and Characterization of Aluminium Oxide ( $\text{Al}_2\text{O}_3$ ) Nanoparticles and its Application in Azodye Decolourisation

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**Abstract:** The adsorption behaviour of an azodye Methylene Blue (MB) over aluminum oxide nano particles (AONP) generated by sol-gel method has been studied to investigate the physicochemical process involved and explore the potential use of AONP in wastewater treatment. The variables incorporated in the present study are concentration of dye, dosage of adsorbent and contact time. The characterizations of AONPs were carried out using X-ray diffractometry (XRD), Scanning Electron Microscopy (SEM), Fourier Transform Infrared Spectroscopy (FTIR), Energy Dispersive Analysis of X-rays (EDAX) and Raman spectroscopy. SEM image showed the distribution pattern of nanoparticles. FTIR spectra revealed that functional groups (O-Al-O) are present. Raman spectra showed the crystalline nature of nanoparticles. Average size of  $\text{Al}_2\text{O}_3$  nanoparticle from XRD peak was found to be 25 nm having rhombohedral structure. Chemical composition of AONPs was confirmed from EDAX spectroscopy measurement. The smaller dosage of AONP was tested for the photocatalytic degradation.

**Keywords:** Colour Pigment, Adsorbent, Adsorption, Decolourisation, Sol-gel Method

## 1. Introduction

In recent years, the use of nanotechnology has gained significant attention in environmental applications for wastewater treatment [1]. Nanoparticles in water treatment have been effectively utilized due to their unique characteristics such as high surface area to volume ratio, small size, availability of large number of reactive sites, and high capacity for regeneration [2]. The current water pollution problems, including water quality, can be improved using nano adsorbents, nanocatalysts, nanostructured catalytic membranes, and many other products and processes resulting from the advancement of nanotechnology [3]. During the last few years a large number of nanomaterials have been synthesized and used as adsorbent to remove the pollutants from the wastewater [4]. Inorganic nanomaterials such as iron and aluminium based nano adsorbents were firstly investigated which may be due to low manufacturing cost

and high decontamination efficiency [5-9]. AONP is one of the most important and extensively used ceramic materials as adsorbent for water and wastewater treatment, catalysts or catalyst supports for chemical reactions, electrical insulators, structural composites for spacecraft, abrasive, thermal wear coatings and membrane applications [10-13]. Aluminium oxide nanoparticle is reported to exist in several phases [14].

It is well known fact that presence of dyes in wastewater is the most undesirable. Dyes are water soluble in nature and most suited in their action in aqueous medium. Nowadays industrial wastewater is the major environmental problem. Many industries like plastics, pharmaceuticals, textiles, leather, cosmetics, paints and varnishes etc. make use of dyes to colour their final products. Subsequently, the wastewater effluents generated from these industries are highly coloured and its disposal in water bodies causes damage to aquatic flora and fauna. These dyes reduce penetration of sunlight which affects the photosynthetic activities of aquatic flora. Number of dyes are xenobiotic and non-biodegradable in

nature [15]. The traditional technologies for wastewater treatment effectively work upon the removal of biological oxygen demand (BOD), but reduction of BOD is ineffective against colour removal. The combination of technologies like adsorption and dye degradation can provide solution to this problem despite these processes are in laboratory stage of development [16]. Chemical oxidation of dyes is very successful for azo dyes as it can initiate the cleavage of azo bond. The problem of secondary pollution due to formation of oxidized amines and chlorine, in case of NaOCl, is incredible [17]. Advanced non-noble metal catalyst for the oxygen reduction reaction (ORR) is Ni/Co-MOF nanoflakes because of its excellent oxygen reduction catalytic activity, good methanol tolerance and good durability [18].

Due to special properties of the nanomaterials, it attracts much more attention. It is a new functional material and most of atoms on the surface of the nanoparticles are unsaturated, therefore can easily bind with other atoms. Nanoparticles have high adsorption capacity, also the adsorption process rapid and the operation is simple. So, interest is growing in the application of nanoparticles as adsorbents [19]. Adsorption is a conventional technology of dye removal having very high efficiency and simple process. Activated carbon is a very efficient adsorbent used mainly for cationic and anionic dyes. The use of carbon as adsorbent in wastewater treatment have become impractical due to competitive adsorption of other organic molecules along with dye molecules, therefore it can be used at end of the treatment process mainly for colour removal. The non-conventional adsorbents are in application due to their easy availability. Adsorption technology is a non-destructive technology involving phase change from aqueous phase to solid surface immobilization. Some techniques involving adsorption along with the catalytic degradation of dye found to be more advantageous [20]. The application of nanoparticles as adsorbents has become as an interesting area of research because of their small particle size and high surface area. The more active sites are also capable of interacting with pollutant species [21]. The application of AONP has been evaluated for the removal of hexavalent chromium from aqueous medium [22]. Also study indicates that adsorption capacity remains unchanged after regeneration of nanosized adsorbent [23].

Methylene blue (MB) is one of the most commonly used dyes in different industries such as textiles, printing and rubber [24-26]. The effluents from these industries are a major source of environmental pollution. Not only the water bodies become coloured, but there is decrease in the dissolved oxygen of water and blocking of the sunlight, thereby disturbing the natural growth activity of aquatic life. Therefore, treatment of effluents containing dyes is one of the challenging problems in the field of environmental chemistry [27-31].

In the present study aluminium oxide nanoparticles (AONPs) were prepared by sol-gel method and used for the adsorptive removal of azo dye Methylene Blue (MB) from aqueous medium using batch adsorption technique.

## 2. Experimental

### 2.1. Synthesis of Aluminium Oxide Nanoparticles

The nanoparticles were prepared by the sol-gel technology. All chemicals used were analytical grade. aluminium chloride, AlCl<sub>3</sub> (Molychem), 25% NH<sub>3</sub> solution (Qualigen Fine Chemicals) and polyvinyl alcohol (PVA) (Modern Industries) were used as raw materials for the synthesis of aluminium oxide nanoparticles.

0.1 M alcoholic AlCl<sub>3</sub> solution was prepared, followed by addition of 25% ammonia solution. The resulting solution turned to a white sol. This was followed by the addition of PVA (0.5M). The solution was stirred continuously using a magnetic stirrer until it became a transparent sticky gel. The gel was allowed to mature for 24 hours at room temperature. The resultant gel was heat treated at 100°C for 24 hours which led to the formation of light weight porous materials due to the enormous gas evolution. The dried gel was, then calcined at 1200°C for 4 hours and finally, the calcined powders were crushed using mortar and pestle to get the fine homogeneous dense powder [32]. Figure 1 shows chemical structure of methylene blue (MB).

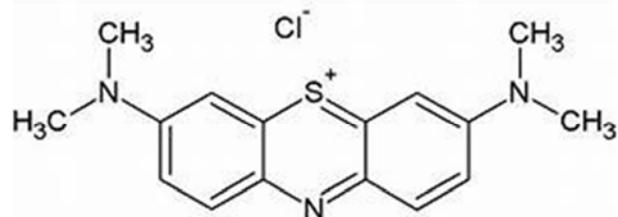


Figure 1. Chemical structure of methylene blue (MB).

### 2.2. Photocatalytic Degradation Studies

Photocatalytic activities of the as-synthesized powder were evaluated by depolarization of Methylene blue dye in aqueous solution. The experiments were carried out in the presence of UV light irradiation without any adsorbent (blank), with adsorbent in daylight and in the presence of UV light with adsorbent. The photocatalytic reactor consists of a glass chamber with an inlet tube for provision of dye solution purging during photo catalysis and outlet tube for the collection of samples. Experimental arrangement is shown in figure 2.

Distilled water was used to prepare all stock solution and stored in dark bottles. From a stock solution of 1000 mg/L of the dye, different concentrations were made. Reaction was set up by adding different dose of the as-synthesized aluminium oxide nanopowder (10, 20, 30 mg) into 1000 mL of MB solution of varying concentration (10, 15, 20, 25mg/L) in the glass chamber. The solution was magnetically stirred in with and without nanoparticle addition into dye solution for 180 minute to obtain adsorption equilibrium after irradiating the internal and external UV light sources in the chamber of the reactor. Sample was withdrawn at 60 minute time interval over contact time for 180 minute. The solution was centrifuged at 3000 rpm for 10 minute and filtered

through Whatman filter paper to remove the nano particles before measuring absorbance.



Figure 2. Experimental arrangement.

The absorbance of sample was measured at 580 nm using visible double beam spectrophotometer (Systronics, Model 1203). For quantitative analysis percentage degradation of MB dye was calculated using the following formula: % decolourisation =  $(A_0 - A_t) / A_0 * 100$ .

Where  $A_0$  is absorbance of dye at initial stage,  $A_t$  is absorbance of dye at time  $t$ .

$$q_e = ((A_0 - A_t) / W) * V$$

where  $q_e$  is the amount of dye adsorbed at the time of equilibrium (mg/g),  $A_0$  and  $A_t$  are initial and final concentration of dye (mg/L),  $V$  (L) is the volume of sample, and  $W$  (g) is the mass of adsorbent [33, 41].

### 3. Results and Discussion

#### 3.1. Photocatalytic Degradation Study

The photocatalytic activity of as-synthesized nanomaterial was evaluated by the degradation of MB dye in aqueous solution. The decolourisation of the MB dye was examined under three different conditions (treatments): daylight irradiation with and without nanopowder (blank), in presence of UV light irradiation without nanopowder (in dark) and in the presence of Al<sub>2</sub>O<sub>3</sub> nanopowder as adsorbent under UV light irradiation, respectively. For dark experiments (in the absence of the adsorbent) under UV light irradiation, almost insignificant degradation of the dye was observed.

In the absence of adsorbent (AONP), but in presence of UV light irradiation, average 10% decolourisation efficiency was observed throughout the 180 min reaction time. This result confirms that degradation of MB in the absence of the adsorbent, but presence of UV light irradiation is insignificant. Further, the experimental results showed that when the dye solution is exposed to UV light irradiation for 180 min in the presence of AONP as adsorbent, significant degradation of MB dye was observed. The corresponding plots of percentage removal of MB dye as function of time under UV irradiation in the presence and absence of AONP

adsorbent are as shown in figure 3 to figure 6. Accordingly, the degradation efficiency of MB dye under the UV light was found to be much larger than the degradation efficiency as compared to dark treatment.

The degradation efficiency of AONP in the presence of UV light increased due to the fact that the Al<sub>2</sub>O<sub>3</sub> nanoparticles prepared by the sol gel method has a high specific surface area, that could give more active surface sites to absorb water molecules and to form active HOO and OH radicals by trapping the photo generated holes.

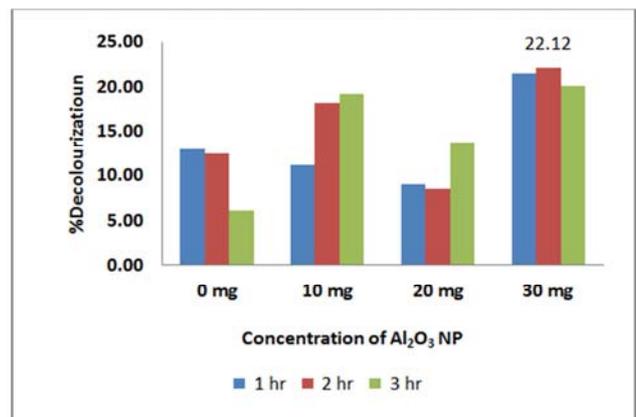


Figure 3. Decolourization of methylene blue Dye (10 mg) using Al<sub>2</sub>O<sub>3</sub> Nanoparticles.

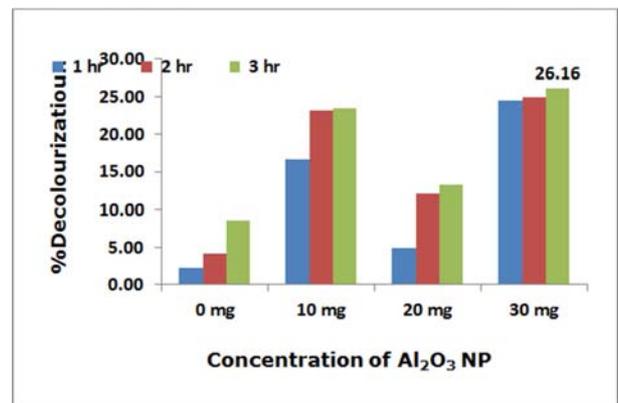


Figure 4. Decolourization of methylene blue dye (15 mg) using Al<sub>2</sub>O<sub>3</sub> Nanoparticles.

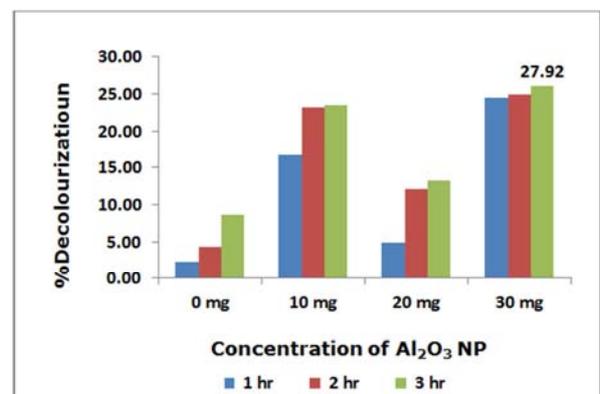
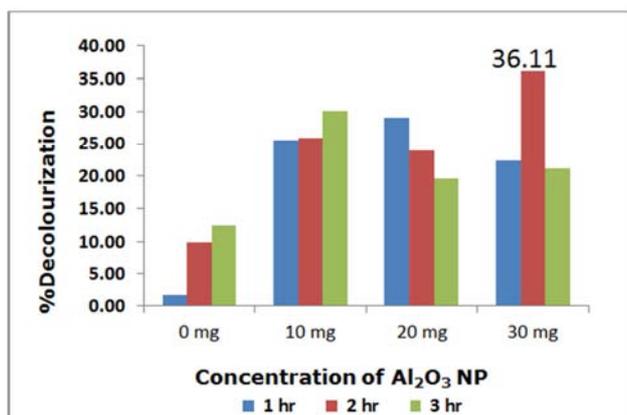


Figure 5. Decolourization of methylene blue dye (20 mg) using Al<sub>2</sub>O<sub>3</sub> Nanoparticles.



**Figure 6.** Decolourization of methylene blue dye (25 mg) using Al<sub>2</sub>O<sub>3</sub> Nanoparticles.

Furthermore, these free active radicals drive the photo degradation reactions and leads to the decomposition of

organic pollutants in the aqueous solution [31]. High surface area also facilitates the absorption of dye molecules on the surface of AONP. Under UV light irradiation, MB molecules get absorbed on the surface of nanoparticles and produce electrons. These electrons are captured by the surface adsorbed O<sub>2</sub> molecules to yield HO<sub>2</sub>• and O<sub>2</sub>•<sup>-</sup> radicals, which gets more chance to come in contact with dye molecules and thus increasing the reaction speed.

The MB molecules thus could be mineralized in time by the super oxide radical ions. Thus it can be said that the smaller crystalline size of nanoparticle are favorable for the reduction of O<sub>2</sub> and oxidation of H<sub>2</sub>O molecules by trapping electrons and holes, which improves the photocatalytic activity of the adsorbent under UV light. The average amount of dye absorbed (%qe) in batch experiment is 23.9 mg/g after 3 hours (Table 1).

**Table 1.** Amount of dye absorbed (%qe) in batch experiment.

Amount of adsorbent (AONP)	Concentration of Methylene Blue (MB) Dye			
	10 mg	15 mg	20 mg	25 mg
10 mg	18.7	34.2	35.4	69.9
20 mg	5.7	7.8	26.1	31.1
30 mg	9.0	14.1	12.8	22.0
Total amount of dye absorbed at each concentration of dye after 3 hours	33.4	56	74.3	122.9
Average amount of dye absorbed after 3 hours (%qe) in Batch Experiment				23.9

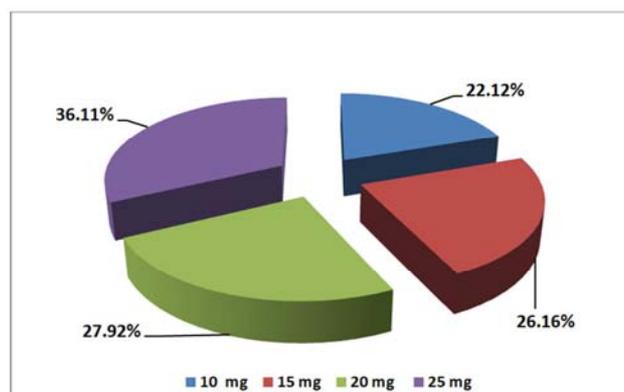
### 3.2. Effect of Initial Methylene Blue (MB) Concentrations

Effect of initial dye concentration on the degradation efficiency was investigated by varying initial dye concentration. The photo catalytic activity of the AONP is as shown in figure 3 to figure 7. It was found that, photo degradation efficiency increased with increased concentration of MB dye and the adsorbent after 180 minute contact time.

### 3.3. Effect of Amount of Adsorbent

The amount of adsorbent also affects photo degradation efficiency of the adsorbent. Different amounts of adsorbent were used (10 mg to 30 mg) for degradation of MB dye under UV light irradiation and the results are as shown in figure 3 to figure 7. It was observed that, as the quantity of adsorbent increased, the rate of photo degradation of dye also increased. This may be due to the fact that, as the amount of adsorbent increases, the number of active sites on the adsorbent and the available surface area also increases. It should be noted that when the concentration of the adsorbent increases above the optimum value, the degradation rate decreases due to the interception of the light by the suspension [34, 35]. The excess adsorbent prevent the illumination thereby a primary oxidant, OH radical, in the adsorbent system also decreases and the efficiency of the degradation reduces accordingly [36]. Also, the

increase of adsorbent concentration beyond the optimum value may result in the agglomeration of adsorbent particles.



**Figure 7.** % Decolourisation of Methylene Blue Dye at Various Concentrations Using Al<sub>2</sub>O<sub>3</sub> Nanoparticles.

Therefore more adsorbent surface become unavailable for photo absorption, thus resulting decrease in the degradation rate of adsorbent [37]. Beyond a certain limit of adsorbent amount, the solution becomes turbid which blocks UV radiation for the reaction to proceed and therefore percentage degradation starts decreasing [38, 39]. For all these above reasons optimization of factors affecting the degradation process becomes necessary.

### 3.4. Effect of Contact Time

The effect of contact time was investigated in the batch experiment at 10, 15, 20 and 25mg/L dye concentration. The adsorption capacity of dye showed varying results with increasing contact time. The rate of dye removal was initially high due to high concentration gradient and more availability of adsorption sites. The rapid transport of dye molecules from aqueous solution to the bulk makes the adsorption fast. The surface of AONPs is charged and the net charge at the surface at a particular pH governs the adsorptive removal of dye from the solution [15].

### 3.5. Characterization

The characterization of aluminium oxide nanoparticles were carried out using XRD, SEM, EDAX, FTIR, and Raman spectroscopy. SEM image gives the distribution pattern and size of the nanoparticles (Figure 8). The FTIR spectra revealed that, there are 410.84, 420.48, 445.56, 491.85, 501.49, 588.29, 636.51, 709.80 (O-Al-O) functional groups (Figure 9). Raman spectra shows the crystalline nature of the nanoparticles. In an amorphous state, the Raman bands are quite broad but often can be derived from one of the crystalline forms of the same material.

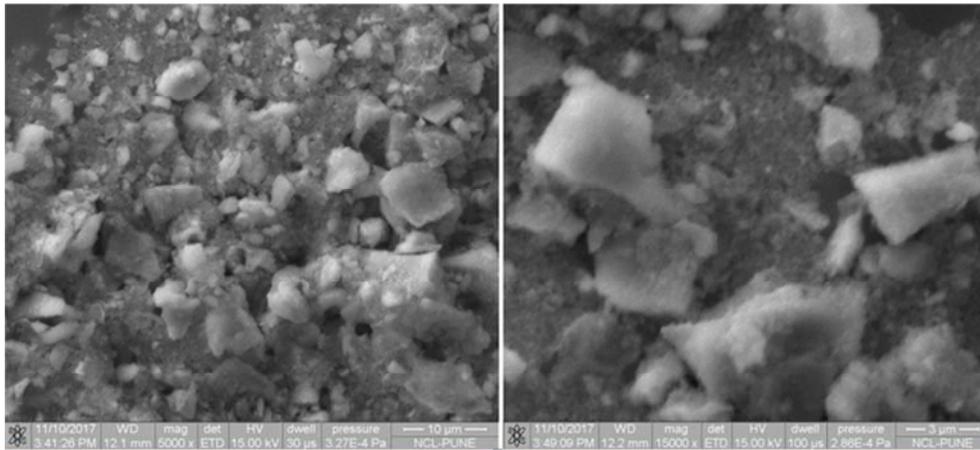


Figure 8. SEM of  $\text{Al}_2\text{O}_3$  Nanoparticles.

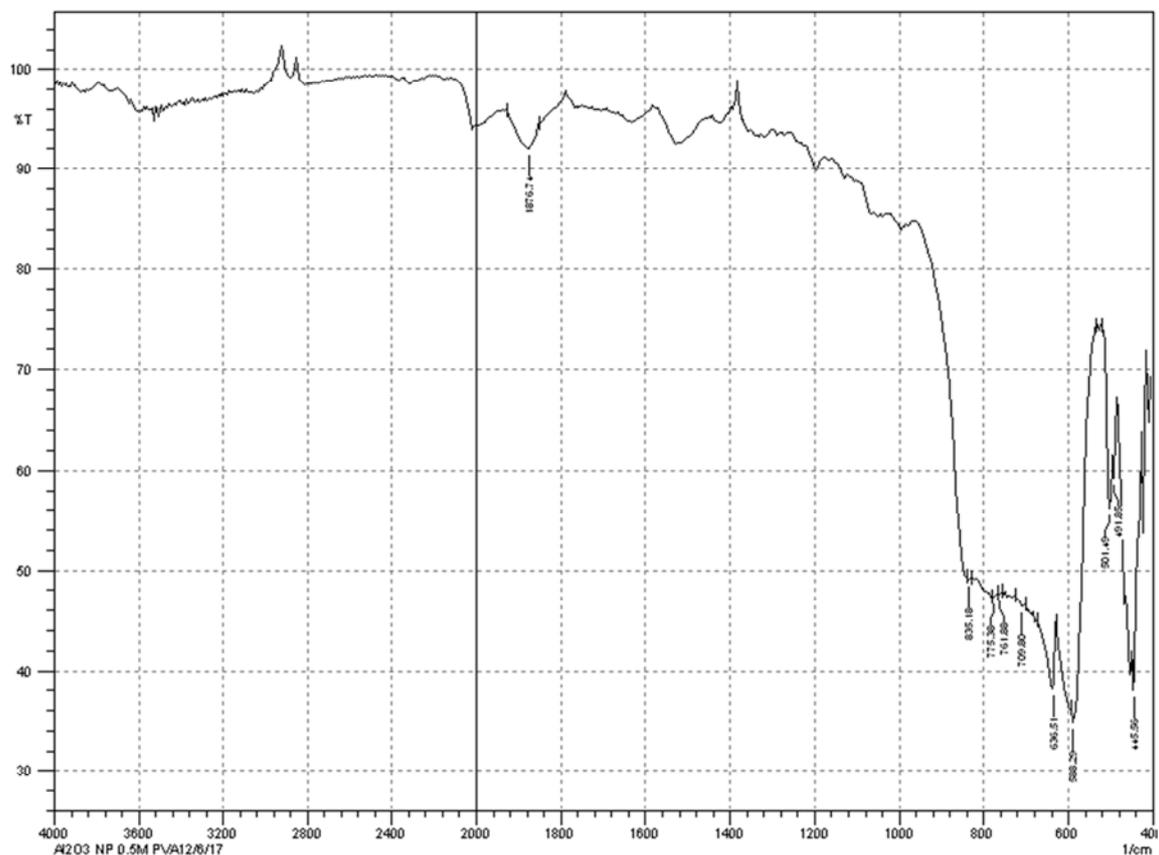


Figure 9. FTIR of  $\text{Al}_2\text{O}_3$  Nanoparticles.

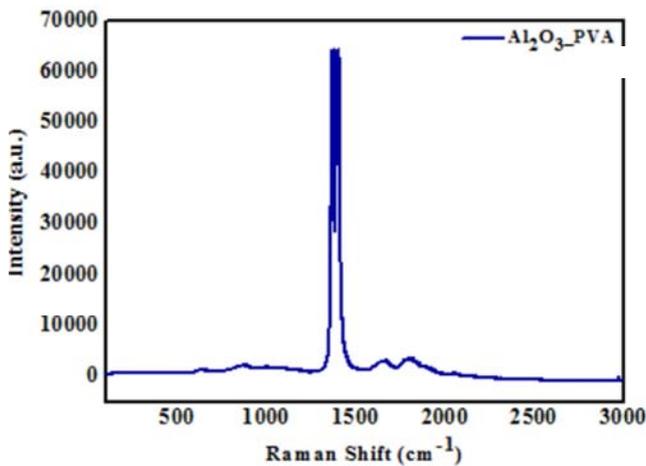


Figure 10. Raman Spectra of  $Al_2O_3$  Nanoparticles.

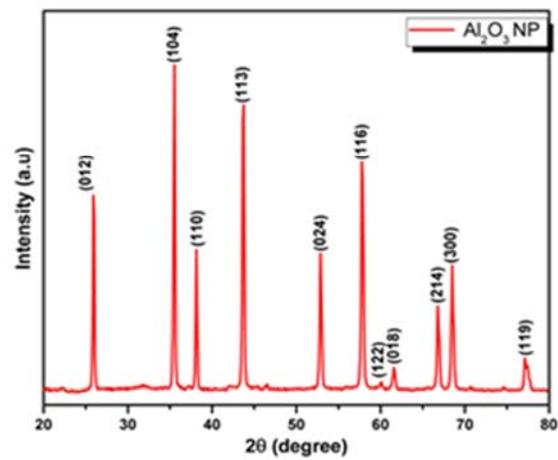


Figure 11. XRD of  $Al_2O_3$  Nanoparticles.

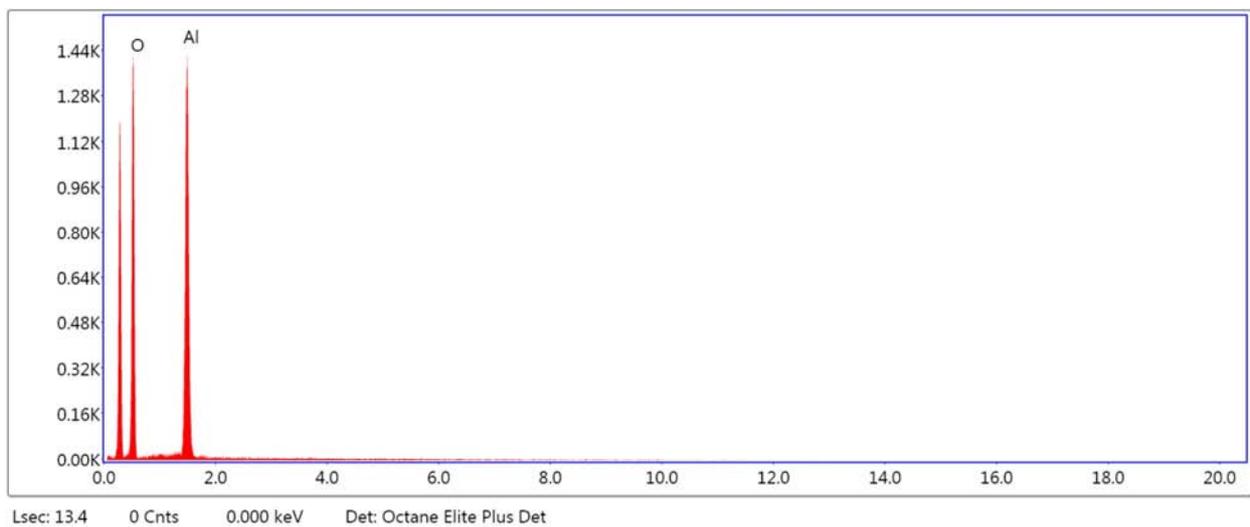


Figure 12. EDAX of  $Al_2O_3$  Nanoparticles.

In fact, in the case of ceramics, the transition from the amorphous to crystalline form (devitrification) can be an important phenomenon in terms of the performance of the ceramic.

The assumption is that in the amorphous form there is a distortion of interatomic bond angles. Long-range order is lost, but nearest neighbour interactions are affected so as to shift a particular vibrational frequency; because there is a population of such distortions, the observed band will be broad (Figure 10). Similar results have been obtained by others also [40]. The peaks in the XRD pattern significantly supported formation of nanosized  $Al_2O_3$  nanoparticles from JCPDS file (71-1683) having rhombohedral structure. Nine reflections were observed at  $2\theta$  angles around  $25^\circ(012)$ ,  $35^\circ(104)$ ,  $43^\circ(113)$ ,  $52^\circ(024)$ ,  $57^\circ(116)$ ,  $61^\circ(122)$ ,  $66^\circ(214)$ ,  $68^\circ(300)$  and  $70^\circ(119)$ . Average particle size was calculated from all peaks and was found to be 25 nm, whereas, the lattice constant 0.614 using Debye Scherrer formula,  $D=0.9\lambda/\beta\cos\theta$  where,  $D$  is the crystalline size,  $\lambda$  is the wavelength of  $CuK\alpha$  radiation,  $\beta$  is full width half maximum (FWHM) of the diffraction peak and  $\theta$  is Bragg's angle of X-

ray diffraction peak (Figure 11). The quantitative analysis of the  $Al_2O_3$  nanoparticle was done using EDAX spectroscopy measurement and it shows Al and O as the major components of aluminium oxide nanoparticles in the heads as shown in figure 12.

## 4. Conclusions

Aluminium oxide nanoparticles ( $Al_2O_3$ ) were successfully synthesized via sol gel technique and the average particle size was found to be 25 nm having rhombohedral structure. FTIR spectra of aluminium oxide nanoparticles indicated the formation of aluminium oxide nanoparticles ( $Al_2O_3$ ). X-Ray diffraction patterns confirm the formation of aluminium oxide ( $Al_2O_3$ ) nanoparticles. The formation of aluminium oxide ( $Al_2O_3$ ) nanoparticles was validated from Raman spectra, XRD, SEM and EDAX analysis.

Maximum decolourisation was found to be 36% for 25 mg methylene blue (MB) dye concentration and 30 mg dose of aluminium oxide (AONP) nanoparticles. The average amount of dye adsorbed in the batch experiment was 23.9 mg/g. Thus,

the above results support the recommendation that aluminium oxide nanoparticles offer new dimension towards reliable and economically affordable water treatment of coloured industrial effluents. The nanomaterial is very promising and can be effectively used for the removal of azodyes from the aqueous solutions.

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