ISSN 2394-3777 (Print)
ISSN 2394-3785 (Online)
Available online at www.ijartet.com

International Journal of Advanced Research Trends in Engineering and Technology (IJARTET)
Vol. 4, Special Issue 22, December 2017

Synthesis and Characterisation of Activated carbon coated with Nano Zinc oxide – Photocatalyst from Paper Sludge

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Abstract: In paper and pulp industries, management and disposal of sludge produced from wastewater treatment plants is a laborious task. Sludge disposal into land is a commonly adopted method in paper and pulp industries. In the study, Sludge Based Photocatalyst (SBP) was prepared from paper mill Secondary Sludge and characterized for photocatalytic activity. The Secondary Sludge collected from the local paper industry was converted into Activated Carbon (AC) by chemical activation [1] using $ZnCl_2$ and NaOH in different, sludge to chemical ratios (1:1 - 1:3) separately producing six samples of Activated Carbon(AC). Nano Zinc Oxide (ZnO) was synthesized in sol gel method using Zinc Acetate dihydrate as precursor[2]. SBP was prepared by coating nano ZnO on Activated Carbon under heating with ethanol as solvent .The Prepared (SBP) was characterized using PSD,SEM, EDAX, FTIR, BET and UV-DRS spectroscopy. Particle Size Distribution showed the average size of coated nano ZnO in 30-70nm. The morphology of AC and SBP was studied from SEM and it confirmed the porosity of AC and coating of ZnO on SBP.EDAX analysis was used to determine the composition of AC and SBP. The FTIR spectra used to find the presence of carbon bond in AC and coating of ZnO on AC in SBP. BET analysis showed the increase in surface area from $0.9m^2/g$ (raw sludge) to 40 m^2/g (SBP). The UV-DRS spectra showed the absorbance of the UV-VIS wavelength (200-800nm) by the prepared photocatalyst from paper sludge. The photocatalytic activity of the SBP was tested using decoloration of a dye solution.

Keywords: Paper sludge, Sludge Based Activated Carbon, Zinc Oxide nanoparticle

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I. INTRODUCTION

Paper mill sludge is a major economic and environmental problem for the paper and pulp industries. The management and disposal of sludge produced from effluent treatment plants in environmental friendly manner is a laborious task. Landfilling, landspreading, vermicomposting and incineration are the common methods for management and disposal of paper sludge. Paper mill produces primary and secondary sludge from primary and secondary clarifiers respectively during the wastewater treatment process. In recent days, legislation has laid restriction of sludge disposal into landfill sites since it undergoes both aerobic and anaerobic decay releasing CO2 and CH4 into the atmosphere [1]. Also Paper Mill Sludge (PMS) is clayey in nature with high organic content and low permeability. Thus disposal of sludge into landfill, over years the soil becomes consolidated stopping the surface water infiltration. Land spreading of sludge into agricultural and forest land is hazardous since the sludge contain heavy metals because of deinking process in recycled paper industries. Compounds that can be found in mill sludge at concentrations above 10 mg/kg of dry sludge include naphthalene, phthalates, chloroform, PCBs, wood extractives or derivates and chlorinated lignin derivates[2]. In vermicomposting, decay of PMS in a controlled manner is possible but the C:N ratio is 930:1, so it is not appropriate for plant growth[2][3]. In practice approx, 19% of PMS is incinerated on the sites due to energy recovery but the economics of incineration is questionable because PMS contains 30% to 50% of water and cellulosic fibers calculated on dry solids. Some other methods of disposal for paper sludge are utilizing it in brick and aggregate production . After the year 2000, studies were made in converting the sludge into adsorbent since it has good sorbent property [4] and the same is used in adsorption of oil and heavy metals.. The PMS can be converted into Activated Carbon(AC) by physical activation, chemical activation and combination of both[5].The chemical activation is found to be efficient than physical activation since the carbon development takes place at lower temperature with higher yield[6] The commonly used chemicals for activation are ZnCl2, KOH, NaOH, Phosphoric acid, etc,. The Activated Carbon was proved to be good adsorbent because of its high surface area and pore volume. The micro and mesoporous activated carbon can be produced from PMS by chemical activation process [4]. Thus produced activated carbon can be used as a photocatalyst by coating it with nano Zinc oxide(ZnO) .

At present in the field of photocatalysis, ZnO emerged as efficient and promising candidate in Green Environmental Management system because of its unique characteristics, such as direct and wide band gap (3.2 - 3.7eV) in the near-UV spectral region, strong oxidation ability, good photocatalytic property, and a large free-exciton binding energy. Synthesis of nano ZnO is possible in many methods such as Sol-gel method, Hydrothermal method, Emulsion, microemulsion methods, precipitation method with and without surfactant, etc,.

Although there are many studies in literature for the preparation of activated carbon from PMS and synthesis of ZnO /AC nano composite, very studies are reported for the preparation of the Sludge Based Photocatalyst (SBP) coated with nano ZnO .Hence an attempt was made in synthesis and characterization of Sludge Based Photocatalyst as a effective method of sludge disposal in paper industry with the help of nanotechnology .

II. METHODOLOGY

A. *Materials*

The secondary paper mill sludge from secondary clarifier was periodically collected from the Effluent Treatment plant of local recycle paper industry "ITC paperboards and speciality papers division PVT Ltd, Karamadai, Coimbatore". All Chemicals and reagents are procured from Merck Lifescience of laboratory grade..

B. *Preparation of Sludge Based Photocatalyst*

Preparation of Activated Carbon from Paper Mill Sludge

As cited by Khalili, et al,.[5] the collected PMS was washed and dried in hot air oven at 110ºC for 24 hrs to remove moisture content followed by mechanically crushing to powder the sludge. Using $ZnCl_2$ and NaOH, chemical activation was performed separately for the powdered sludge of size less 600μm with different sludge to chemical ratios (1:1 - 1:3). Chemical activation was done at 80ºC for 8 hrs with continuous stirring using a magnetic stirrer (REMI 5MLH PLUS). The Slurry produced after stirring was heated at 110ºC followed by sun drying for 24 hrs to activate good pore formation. Finally, chemically activated sludge is converted into Activated Carbon by pyrolysis at 500ºC for 3 hrs in a closed container. The Prepared Activated Carbon is washed in 1.2 M HCl and distilled water to remove excess $ZnCl_2$ and NaOH

Preparation of Nano Zinc Oxide

Zinc acetate dihydrate ($Zn(CH_3COO)_2.2H_2O$) was used as precursor. ZnO nanoparticles were prepared by dissolving 0.2 M zinc acetate dihydrate in ethanol at room temperature with continuous stirring at 25^{o}C for 2 hrs. Clear and transparent sol with no precipitate and turbidity was obtained. 0.02 M of NaOH (0.1N NaOH) was then added to the sol and stirred continuously for 1 hr. The sol was kept undisturbed till white precipitates settles down. After precipitation, the precipitates were collected by centrifuging and washed with excess ethanol to remove impurities. Precipitates were dried at 80^{o}C for 15 min on hot plate. Precipitates were calcined at 400°C for 30 min [9]

Coating of Nano Zinc Oxide on Activated Carbon

All six samples of prepared Activated Carbon were subjected to BET Surface Area Analysis and it was observed AC obtained with 1:1 $ZnCl_2$ sludge to chemical ratio to have comparatively good surface area and pore volume. Hence it was taken for further study of coating nano Zinc Oxide on Activated Carbon. The synthesised nano Zinc Oxide and sludge based AC was taken in the ratio 1:2 . The nano zinc oxide was dispersed in 40 ml of ethanol using sonicator (LABMAN) for 10 min .Under magnetic stirring at 80ºC the sludge based activated carbon was added slowly and stirred for few hours until the ethanol evaporates. Then it is dried in hot air oven to get moisture free Sludge Based Photocatalyst . FinallySBPwas powdered using mortar &pestle and stored in air tight container .

III. CHARACTERISATION OF SLUDGE BASED PHOTOCATALYST

Sludge Based Photocatalyst was characterized using Brunauer Emmett Teller Analysis (BET), Fourier transform infrared spectroscopy (FTIR), Particle Size Analysis (PSA),Field Emission Scanning Electron Microscopy (FESEM). Energy Dispersive Spectroscopy (EDAX) and UV-Diffuse Reflectance Spectroscopy(UV-DRS). The surface area, total pore volume and average pore diameter of the samples were determined from the adsorption isotherms of nitrogen at 77 K by using surface area analyser (BELSORP Mini-II).The FTIR analysis was done using spectrophotometer (PERKIN ELMER Model No L160000Espectrum) to find the presence of functional groups in Sludge Based Activated Carbon,SBP and the bonding interaction in SBP after coating with nano Zinc Oxide. The average particle size of nano Zinc Oxide was determined using Particle Size Analyser (MALVERN Zetasizer) using the principle of Dynamic Light Scattering. The surface morphology of raw sludge ,SBP and coating of Nano Zinc Oxide over AC were studied using FESEM analysis (CARL ZEISS, Sigma Version). The EDAX (BRUKER QUANTAX) was used to study the composition of AC and SBP. The UV-DRS (PERKIN ELMER, Lambda 35) helped in understanding the absorbance of UV-VIS wavelength by the material and the coating of nano zinc oxide over sludge based AC .

Photocatalytic activities of SBP was evaluated by decolorization of Methylene Blue (MB) dye in aqueous solution. The experiments were carried out in the presence of UV irradiation without any catalyst, with catalyst in dark and in the presence of SBP photocatalyst. The photocatalytic reactor was used for the batch study consisting of magnetic stirrer ,glass beaker and UV light source. Reaction was set up by adding 5g of the as-prepared SBP into 1000 ml of MB solution (25 mg/L) in the Pyrex glass beaker volume of 1000 ml and the suspension was magnetically stirred in dark for 30 min to obtain adsorption/desorption equilibrium before irradiating the light in the beaker. Before illumination of the samples by visible radiations, air/oxygen was purged into the solution with the help of a porous tube at hand purging in order to keep the suspension of the reaction homogenous. Thus photocatalytic activity of the SBP was observed and it was confirmed by colour removal of MB

IV. RESULTS AND DISCUSSION

BET Analysis

The Brunauer Emmett Teller Analysis gave BET surface area, average pore size and pore volume of the samples .The table 1 shows the BET surface area results of different samples.

From the BET results it is evident that all the samples are mesoporous in nature with mean pore dia greater than 2nm and the surface area of the raw sludge has increased when converted into AC. Sludge to Chemical ratio $ZnCl_2$ (1:1) gives the AC of higher surface area than other sludge to chemical ratios. Also the surface area and pore volume has further increased to 40.6 m^2/g and 0.0064 (cm^3/g) after coating with nano Zinc Oxide. It shows the coating of nano Zinc Oxide is on the surface of the AC and only partial filling of pores of AC with nano Z inc Oxide

TABLE I. SURFACE AREA, MEAN PORE DIAMETER AND TOTAL PORE VOLUME OF DIFFERENT SAMPLES

Sl. No	Sample	Surface Area(m^2/g)	Mean pore Diameter (nm)	Total Pore Volume (cm^3/g)
1	Raw Paper Sludge	0.900	5.98	0.0014
2	AC (ZnCl2 1:1)	26.90	6.27	0.0042
3	AC (ZnCl2 1:2)	10.74	13.28	0.0035
4	AC (ZnCl2 1:3)	11.07	6.09	0.0016
5	AC (NaOH 1:1)	16.80	9.60	0.0032
6	AC (NaOH 1:2)	20.26	7.69	0.0039
7	AC (NaOH 1:3)	17.53	8.80	0.0029
8	Sludge Based Photocatalyst (SBP)	40.66	6.33	0.0064

FTIR Analysis

FTIR spectra in figure 1 shows the FTIR spectra of SBAC (Sludge Based Activated Carbon), nano Zinc Oxide and SBP. The interaction of nano Zinc Oxide with Sludge Based AC is clear from the spectra. The transmission IR in the range 1620 cm^{-1} - 1680 cm^{-1} shows the C=C is observed in SBAC and SBP. Metal Oxides like ZnO gives absorbance below 1000 cm^{-1} and it is also observed in the obtained spectra. The peak observed above the wave number 2000 cm^{-1} indicates the O-H

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bond stretching. [8] presented an Elaborate Study On Electronic Devices & Circuits to acquaint the students with the construction, theory and operation of the basic electronic devices such as PN junction diode, Bipolar and Field effect Transistors, Power control devices, LED, LCD and other Opto-electronic devices.

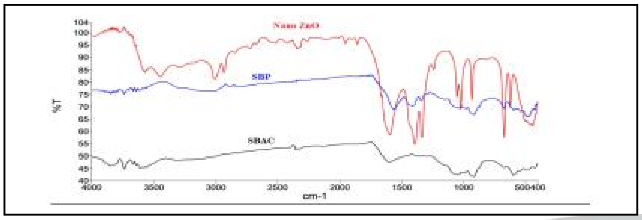

Fig. 1. FTIR spectra

DLS Spectra

Figure 2 depicts the Dynamic Light Scattering (DLS) results of ZnO. From the result it was observed that the PDI value lies within the range (0.08 – 0.7) which reveals the monodispersity nature of the particle. The Z-average value of ZnO was determined as 32-35 nm.

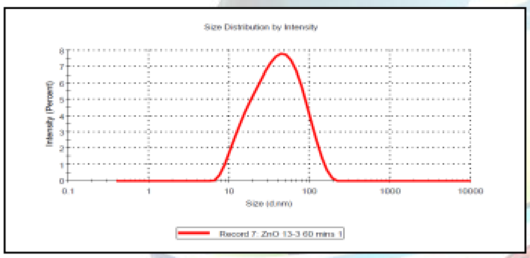

Fig. 2. FTIR spectra

FESEM with EDAX Analysis

FESEM image as in figure 3 depits the increase in porosity of sludge based Activated carbon after chemical activation and the coating of hexagonal shaped nano zinc oxide over SBAC. The EDAX analysis was done for Sludge Based Activated Carbon and SBP. From the figure 4,it was understood that there is the percentage increase in Zinc and Oxygen elements on SBP confirms the coating of Zinc Oxide over AC.

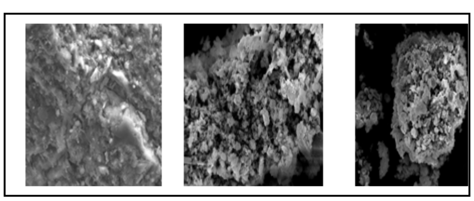

Fig. 3. FESEM Images

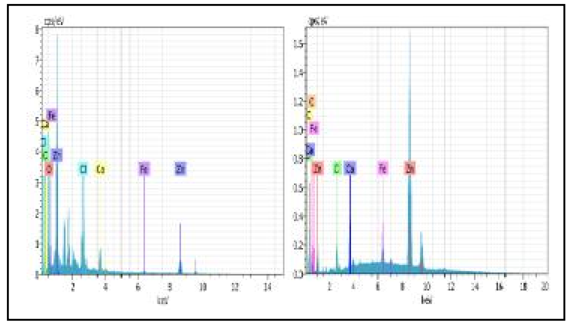

Fig. 4. EDAX result of SBAC and SBP

UV-DRS Analysis

DRS spectra using UV-DRS spectrophotometer as shown in figure 5 confirms the absorbance of UV light irradiation by the prepared sludge photocatalyst in the UV-VIS range of 200-800nm and also the interaction of nano Zinc Oxide over SBAC.

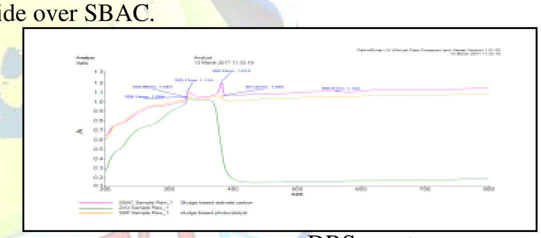

Fig. 5. DRS spectra

Dye Decolourisation Test

Decolourisation of methylene Blue dye using the prepared SBP was studied under UV irradiation using photocatalytic reactors with 25ppm aqueous solution with Photocatalyst dosage of 5g/l and its found that colour removal at 30 minutes of time.

V. CONCLUSION

The results of this study shows that the Secondary Sludge from paper industry can be converted into Sludge Based Photocatalyst(SBP) with combined process of chemical activation and nanotechnology application. This study could be a better alternative for sludge management and disposal in paper and pulp industries.

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