



Photocatalytic degradation of methylene blue by nanocomposites synthesised from Zn (II) complex and polyvinyl alcohol

Aliyu D. Mohammed* and Maryam Dodo Abubakar

Department of Chemistry, Umaru Musa Yar'adua University, PMB 2218, Katsina, Katsina state, Nigeria
aly27moh27@gmail.com

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Abstract

ZnS nanoparticles were obtained by the pyrolysis of Zinc (II) complex at 280°C to generate ZnS nanoparticles. The as-prepared Zn nanoparticles were further incorporated into the polymer matrices of polyvinyl alcohol (PVA) to generate ZnS/PVA nanocomposites via electrospinning technique. The electrospun fibre (ZnS/PVA) was employed as a catalyst in photocatalytic degradation of methylene blue. The nanofiber was observed to have an impressive ability on photodegradation of methylene blue; as the methylene blue solution became completely colourless when ZnS/PVA was used as catalyst. Fourier transform infrared (FTIR), scanning electron microscope (SEM), and UV-vis spectroscopy were used to characterise the ZnS nanoparticles and ZnS/PVA nanocomposites.

Keywords: Ligand, methylene blue, nanofibers, nanoparticles, polymer.

Introduction

Monoanionic chelating ligands have a remarkable property of forming stable complexes with most metals in actinide and lanthanide groups and all the transition metals¹. The nature of complexation determines the overall properties of the metal complexes. Thus, the versatile property of the ligands to form monodentate, bidentate chelating or bidentate bridging molecules is responsible for their varying properties²⁻⁴.

Polymers are remarkably used in the synthesis and modification of nanoparticles. The properties of most polymers such as being lightweight constituents which allow easy processing and could be shaped into thin layers by numerous techniques have made them suitable for the application.

Incorporation of polymers into nanoparticles either as capping agents or as properties' enhancers has been a common trend in nanoscience. The combined properties of both the polymer and the inorganic nanoparticles leads to a more developed functions of the nanocomposites produced^{5,6}. For instance, Mohammed *et al.*⁷ have reported the use of polyacryloylated starch as capping agent in the production of nanoparticles from CdS. In such case the functional groups of the polymeric material is very important because they determine some important properties of the nanoparticles such as stability, solubility, strong luminescence and even electronic properties of the nanoparticle.

Another factor that affects the physical and chemical properties of nanoparticles is the surface modification of the particles. The surface nature of composites produced from nanoparticles of transition metal salts and polymer matrices is dependent on the nature and structure of the surface ligand layer, which determine

the interaction between the inorganic core and polymer ligand layer and the structure of inorganic nanoparticles^{8,9}.

The applications of nanoparticles in different industries such as pharmaceutical, electronics, agricultural, energy and cosmetics have been reported. Furthermore, their application in environment and health care researches is one of the most interesting today⁹⁻¹¹.

Incorporation of inorganic nanoparticles to polymer matrices yields a product that is affordable, available, and environmentally friendly. Moreover, the desirable physicochemical properties of the nanocomposite such as light weight, mechanical elasticity and stability have made the nanocomposites a promising product in different industries. The versatile applications of nanofibers range from nanosensors, tissue engineering, filtration media, to drug delivery in pharmaceutical industry¹¹. The common techniques used in the synthesis of nanofibers include electrospinning, interfacial polymerization, electrostatic spinning and melt processing¹².

Water being one of the requirements of life has become one of the greatest media through which pollution gets its way into our environment. Several approaches have been considered in limiting the effects of these harmful materials to the environment. However, most of the techniques being used are met with some limitations which include operational costs or the high cost of the materials¹³. Efficient and more affordable approaches are readily approved to produce a safe and portable drinking water¹⁴.

The remarkable features of nanofibers such as small pore sizes, high specific surface areas, high porosity and photocatalytic

properties have made nanofibers a suitable option for waste water treatment¹⁵.

In this study, the production of nanocomposites from ZnS and PVA using electrospinning process and application of the spun fiber as a catalyst in the purification of waste water containing methylene blue has been reported.

Materials and methods

Materials: Polyvinyl alcohol, n-butanol, polyacrylonitrile, carbondisulfide, dimethyl formamide, methylene blue, zinc chloride, ethanol were all purchased from Sigma-Aldrich.

The structure and morphology of the nanofibers were studied using SEM machines. FTIR spectra were recorded on ATR mode, while UV spectrophotometer was used to obtain the absorption spectra.

Synthesis of potassium butyl xanthate (KBX): The ligand (KBX) was synthesised using the procedure reported by Mohammed *et al.*¹⁶. KOH (1.12g) was suspended in an oven-dried Schlenk flask containing n-butanol (50mL), the mixture was stirred vigorously with nitrogen gas blown to keep an inert atmosphere. Carbon disulfide (1.2mL) was added gradually to the mixture for a period of 30 min. The solution became yellow and later cloudy with more CS₂ in the reaction mixture. After 2 h, the mixture was filtered and washed with n-butanol and put in a vacuum oven to dry overnight.

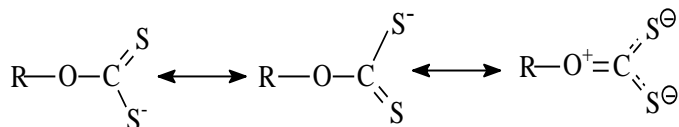


Figure-1: Resonance forms of alkyl xanthate moiety.

Synthesis of the complex, (Zn(L¹))₂: 20mL of aqueous solution of ZnCl₂ (5mmol) was slowly added to 50mL of aqueous solution containing 1.88g of KL¹ (10mmol) with constant stirring. Precipitates began to form immediately. The mixture was continuously stirred for further 45 min, filtered, washed with water and dried at room temperature under vacuum¹⁷.

Synthesis of ZnS nanoparticles: Typically, 7.50g of hexadecylamine was added into a three-necked round bottomed flask equipped with a condenser. Nitrogen was slowly purged into the flask while the temperature is slowly raised to 280°C. 0.50g of the zinc complex dispersed in tri-n-octylphosphine was injected into the hot hexadecylamine. The solution turned to a bright yellow color with a drop in the temperature. The temperature was gradually raised to 280°C and maintained for an 1h. The mixture was allowed to cool to 70°C. Methanol was added to the solution which resulted in the formation of the capped nanoparticles. The colloidal mixture was separated using centrifugation followed by dispersion in toluene. The process was repeated three times to remove excess hexadecylamine¹⁷.

Synthesis of nanofibers: Polyacrylonitrile (1g) was dissolved in dimethylformamide (2mL) and stirred for 1h. ZnS nanoparticles (10mg) were added to the mixture with continuous stirring until homogeneity was achieved after 12h (Equivalent to 13% w/w of the colloidal solution). The solution was loaded in a syringe equipped with a capillary wire needle. 20kV of voltage was connected to the needle tip. A tip collector (20cm) covered with aluminium foil was connected to a ground electrode. Under this high voltage the polymer jet produced fibers that are collected on the aluminium foil. The collector is further heated to 50°C for the solvent to evaporate¹⁸.

Degradation of methylene blue: The nanocomposite (ZnS-PVA) and ZnS nanoparticles were tested on waste water containing methylene blue 10mg/L. PVA was used as a control in the experiment. 20mg of each of PVA, ZnS/PVA and ZnS nanoparticles were separately mixed with the waste water in a beaker followed by agitation using a magnetic stirrer until a uniform dispersion of the catalysts was achieved. 2mL of the aliquot of each sample was taken after 1h. The catalysts (PVA, ZnS/PVA and ZnS nanoparticles) were separated using a centrifuge at 3500rpm for 10min. A UV source (250-W Xe) discharge lamp with a circulating water source in the reactor vessel was used for the study¹¹.

Results and discussion

FTIR analysis: The FT-IR spectrum of KBX, Zn(L¹)₂, ZnS/PVA and PVA are shown in Table-1. The absorption peaks at 2957cm⁻¹ and 2869cm⁻¹ correspond to asymmetric and symmetric stretching of C-H bond in terminal CH₃ group. The absorption bands at 1460cm⁻¹ and 1375 corresponds to asymmetric and symmetric deformation of C-H bond in CH₃ group. The peak at 1061cm⁻¹ is due to C=S stretching vibration, while at 1173cm⁻¹ and 1102 are attributed to -C-O-C-symmetric stretching vibration. The spectra of the xanthate complex shows a characteristic peak at around about 1000–1200 cm⁻¹ which is a characteristic of xanthate group, and another peak at 2929cm⁻¹ due to C-H stretching mode. The virgin PVA and ZnS/PVA show absorption band at 3301cm⁻¹ due to OH stretching vibration, 2927 and 2926cm⁻¹ due to C-H vibrations for the pure PVA and the nanocomposite respectively. There is also a noticeable shift in the peak assigned to C=C stretching vibrations from 1582cm⁻¹ in PVA to 1566cm⁻¹ in the ZnS/PVA nanocomposite. This observed changes in the characteristic band shows that there is an interaction between the ZnS nanoparticles and the polymer.

UV analysis of the ZnS nanoparticle: Optical properties of nanomaterials was observed using Ultraviolet-visible spectroscopy. Figure-2 shows the UV absorption spectrum of the ZnS nanoparticles. It shows a maximum absorption band at 240nm consisting of a long wavelength tail which decreases with time. This shift (blue-shift) in the absorption wavelength compared to a bulk ZnS molecules shows that the particles are formed at quantum confinement size regime. Moreover, time increase doesn't affect the position of maximum absorption¹⁷.

SEM analysis of the particles: The SEM images of the samples are shown in Figure-3a, b. There is noticeable change in morphological feature of the pure PVA and the ZnS/PVA nanocomposite. The long-hairy rod-like fibrous nature of the PVA polymer in Figure-2 (a) has now changed to a slightly more clustered and longer fiber after the incorporation of ZnS nanoparticles from 86µm to 90µm. This show the nanoparticles affects the shape, width and length of the PVA surface.

Photodegradation of methylene blue: The efficacy of the samples on degradation of the dye solution was studied using UV-Vis machine at 666nm which corresponds to the maximum absorption of methylene blue^{19,20}. From Figure-4, there is a noticeable reduction in the absorption peak in both the control (PVA) and ZnS/PVA nanocomposite. Moreover, the nanocomposite showed the highest reduction in the absorption peak. In addition there was decolourisation of the dye solution when the nanocomposite was used.

Table-1: FTIR spectroscopic result of the samples.

Compound IR (cm ⁻¹)	v(O-H)	v(C=S)	v(O-C-O)	v(C=C)	v(C-H)
PVA	3301	–	–	1582	2927
KBX (L1)	–	1061	1173, 1102	–	2957, 2869
Zn(L1)2	–	1065	1201	–	2929
ZnS/PVA	3301	–	–	1566	2926

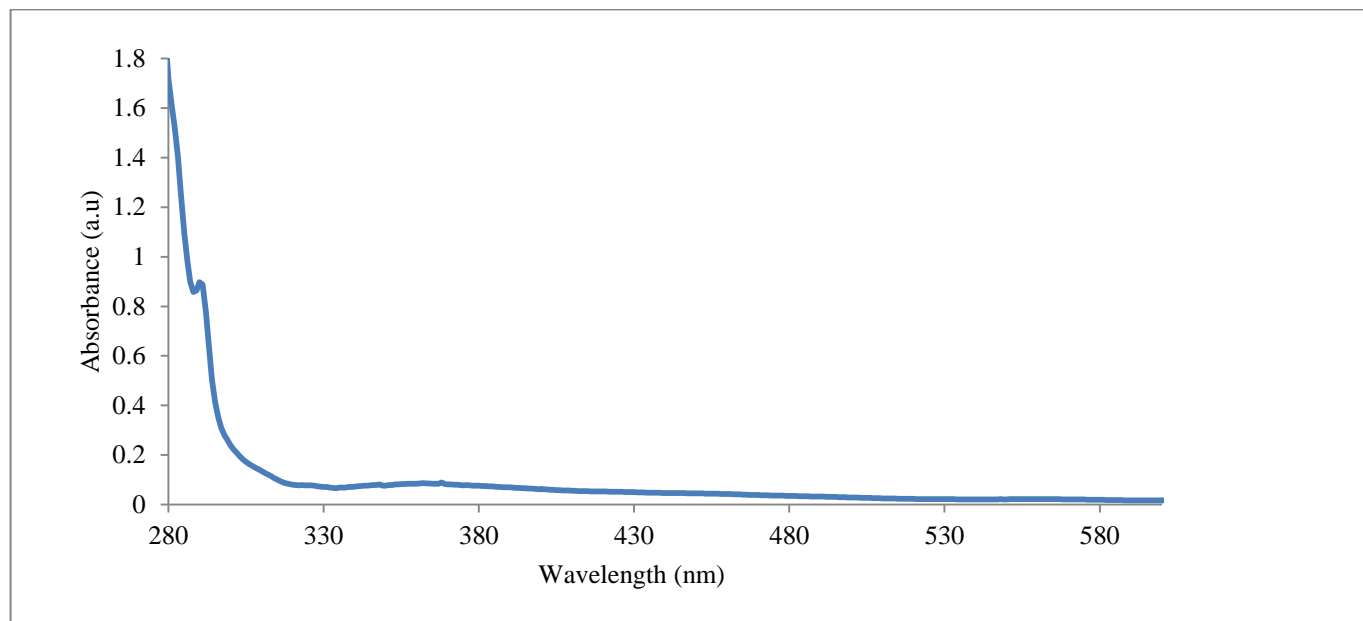


Figure-2: UV-VIS spectrum of ZnS nanoparticles.

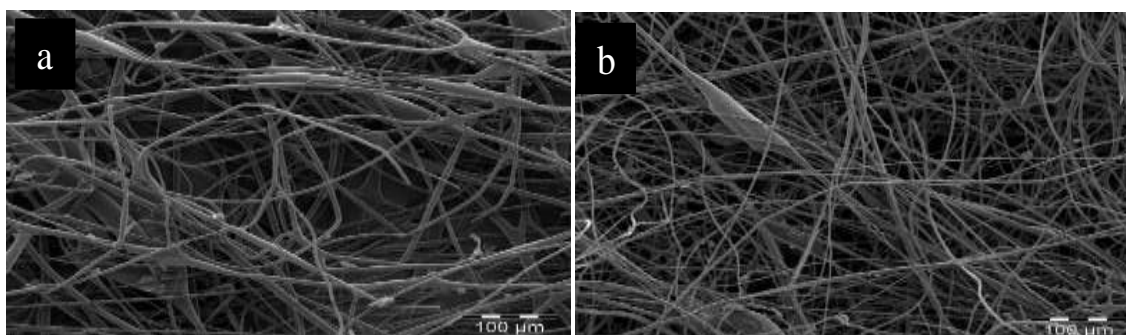


Figure-3: SEM images of (a) PVA and (b) PVA/ZnS nanocomposite.

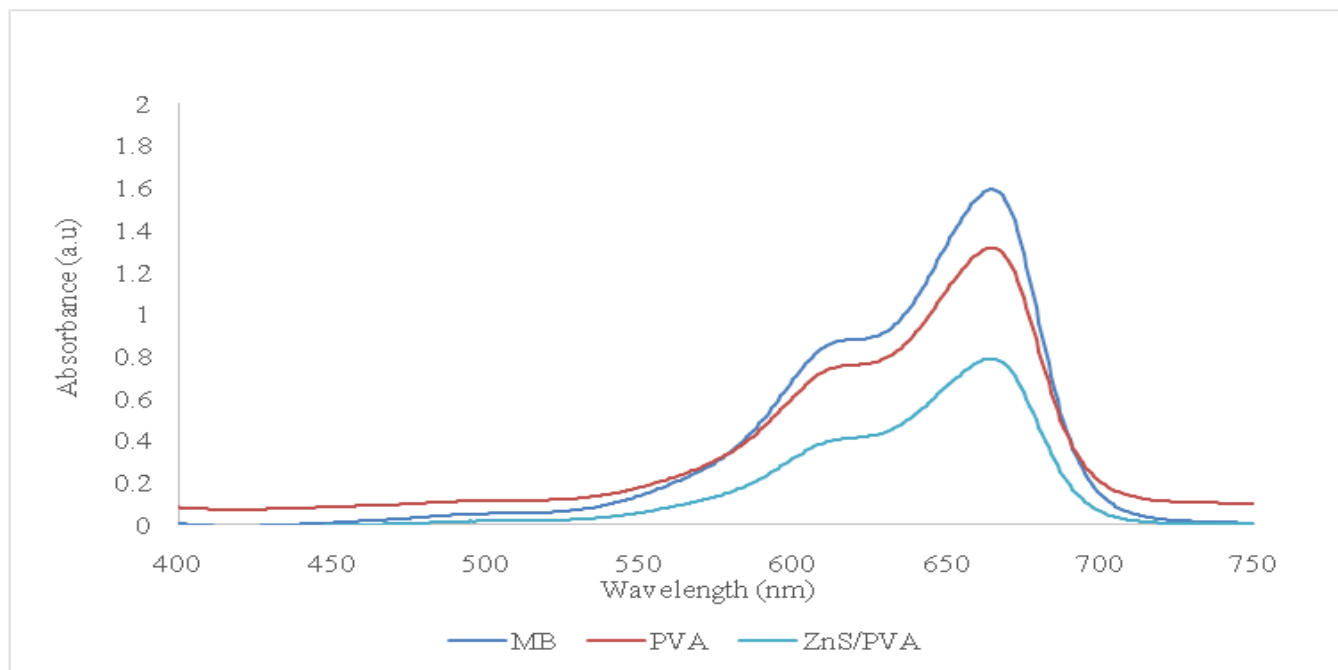


Figure-4: Photodegradation of methylene blue, PVA and ZnS/PVA nanocomposite.

Conclusion

Nanocomposite from Zn (II) complex and PVA showed a promising performance in waste water treatment containing methylene blue. UV-visible spectroscopy confirmed the blue shift in the absorption band as well the effect of the nanocomposite on the dye molecule in the aqueous media. ZnS/PVA showed a more decrease in the intensity of the absorption peak compared to the pure PVA. Scanning electron microscopy showed that there is a change in the surface morphology of the polymer surface before and after the impregnation with ZnS nanoparticles. FTIR analysis showed further evidence of nanocomposite formation from the precursor compounds.

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