Indian Journal of Chemical Technology
Vol. 31, November 2024, pp. 921-928
DOI: 10.56042/ijct.v31i6.9831

Performance evaluation of chitosan-zinc oxide nanocomposite thin films in refinery wastewater treatment

M. Geetha Devi*, G. Chandra Sekhar[2]& Patrick Isibor[3]

[1]Department of Mechanical & Industrial Engineering, College of Engineering, National University of Science & Technology, Oman

[2]Department of Chemical Engineering, Pondicherry University, Pillaichavadi, Pondicherry, India

[3]Department of Biological Sciences, College of Science and Technology, Covenant University, Ota, Ogun State, Nigeria

*E-mail: geethadevi@nu.edu.om

Received 23 March 2024; accepted 4 October 2024

The current research aims to develop a natural polymer based nanocomposite film using low molecular weight chitosan and zinc oxide nanoparticles (ZnO NPs) for the removal of pollutants from refinery wastewater. The ZnO NPs have been synthesised by modified sol gel technique. The nanocomposite thin films have been fabricated using dip coating method by immersing a glass substrate into the chitosan -nanoparticle composite. The refinery wastewater treatment is carried out using the fabricated composite film by altering the processing conditions of wastewater pH, exposure time, speed of agitation and the number of deposition layers and the best treatment conditions are established. The SEM micrographs of composite thin films exhibited excellent surface morphological behaviour of the nanocomposite. The AFM topographic image demonstrated the nanoscale formation of thin films. From the experimental studies performed with the composite thin films for the treatment of refinery wastewater, the best performance was achieved at pH 8.0, 60 min of contact time with 10 layers of thin-film deposition, and a stirring speed of 100 rpm. The outcome of the study demonstrates that the nanocomposite thin films developed from chitosan and ZnO NPs has a promising pollutant removal capacity in the refinery wastewater treatment.

Keywords: Dip coating, Oil refinery, Thin films, Wastewater, Zinc oxide nanoparticles

Introduction

Most of the industrial operations results in the discharge of huge quantity of inorganic and organic pollutants that are accumulated in water bodies and destroy the habitat for animals and plants. This environmental concern is to be addressed by the effective treatment of wastewater and utilization of water resources through appropriate recycling and reuse techniques. Intensification in industrial and domestic activities results in the deterioration of water quality. This imposes the pressing need and essential requirement for the elimination of impurities from industrial and domestic wastewater. Regardless of the widespread technological advancement in the manufacturing sectors, the uninterrupted discharge of polluted water from various industrial activities leads to environmental and human health risks. Nanomaterial based wastewater treatment techniques are found to be effective and recommended due to their attractive surface properties, better thermo chemical stability, and environmental friendly nature, high oxidation potential and prospective applications in solar energy systems [1-5]. Different categories of nanoparticles have been broadly considered due to their flexible and tuneable properties such as antimicrobial activity, bio sensing, cytotoxicity, photo catalytic, and corrosion inhibition[6, 7].

Several studies have been focussed on the removal of toxic chemicals, microorganisms and pathogens present in water bodies[8-10]. Majority of the chemical and manufacturing industries produces extensive amount of highly toxic wastewater, which causes serious health issues[11-13]. The petroleum oil refining operations generates billions of wastewater and it disturbs communities across the world particularly in the Gulf region[4,15]. The major contaminants present in the refinery wastewater are mainly phenols, sulfides, chlorides, oil, ammonia, and mercaptans. Crude oil contains high levels of sulfur, salts and metals[16-18]. The conventional treatment processes such as chemical precipitation, coagulation, sono-oxidation, flocculation, photo catalysis, electrochemical precipitation; ozonation, adsorption etc. have several limitations in removing colour, dissolved solids, suspended solids, turbidity, and also require additional treatment techniques[19-23].

Different types of nanoparticles such as titanium dioxide, mesoporous silica, iron oxide, ZnO etc. are extensively employed in the treatment of industrial effluents. ZnO NPs are preferred in biomedical, optics, and electronics applications due to their low-cost, effectiveness, simple preparation method, and eco-friendly behavior[24-26]. The synthesis techniques employed in the ZnO NPs preparation includes chemical, physical, and biological methods[27-29]. Green synthesis of ZnO nanoparticles from leaf extract are used in wastewater treatment, antibacterial and cosmetic applications[30]. Owing to the high specific surface area and excellent biocompatibility, ZnO NPs are extensively used in the fields of electrochemistry, medical devices, cosmetics, textile industry[31,32]. Ultra-thin Film Membranes (UFM) derived from Graphene Oxide (GO), chitosan and polyvinyl alcohols have been investigated in industrial wastewater treatment[33]. Majority of the treatment processes are either expensive or creates environmental issues through the discharge of huge volume of solid wastes, which require enhanced purification by series of processing stages and thereby incur high cost[34, 35]. In the past few decades, nanothin film technology is gaining great attention owing to their facile fabrication techniques, eco-friendly nature and cost effectiveness, minimum utilization of resources, and discharge of less sludge volume. ZnO/chitosan nanocomposite was successfully employed as a promising adsorbent for the removal of Congo red from aqueous solutions[36]. Another study focused on the in situ fabrication of ZnO@chitosan nanocomposite (ZOCS) to remove Pb(II), Cd(II) and Cu(II) ions from polluted water[37]. Anna et al. reviewed the application of sustainable biopolymeric nanocomposites highlighting its advantages and disadvantages in wastewater remediation. Also, the study outlined the reusability and current challenges of the polymeric nanocomposites for environmental applications[38]. However, the treatment of refinery wastewater using nanocomposite thin films using biopolymers has been studied to a lesser extent; particularly the removal of pollutants from refinery wastewater using the biopolymer chitosan and nanoparticles are studied to a lesser extent. Therefore, the present study attempted the in-house synthesis ZnO NPs for the fabrication of chitosan-ZnO nanocomposite thin films, and to study its effectiveness in the treatment of refinery wastewater.

Experimental Section

Zinc acetate dihydrate [Zn $(CH_3COO)_2$ $2H_2O$] and sodium hydroxide (NaOH) was chosen as the raw material for the synthesis of ZnO NPs using modified sol-gel method. The development of nanocomposite thin film was prepared by dip-coating technique. Low molecular weight Chitosan (MW: 20 kDa) with a degree of deacetylation of 80% was used for the development of thin film. The functional group, particle size distribution, phase identification, surface morphology and elemental analysis are performed using Fourier Transform Infrared Spectroscopy (FTIR - Perkin Elmer Frontier), Dynamic Light Scattering (DLS), X-ray Diffraction (Rigaku, Mini Flex 600), Field emission Scanning Electron Microscope (SEM-JEOL JSM-7600F), and Energy Dispersive X-Ray Analysis (EDX) respectively. The surface topology of the fabricated thin film was analysed by Atomic Force Microscopy (AFM). COD test was conducted using Thermo Reactor (AQ 400, thermo Scientific Orion and Thermo Reactor Orion COD 125) and turbidity measurements using digital Turbidity meter (WTW Turb 550). The raw and treated refinery wastewater parameters were tested as per APHA standards[39]. The raw wastewater sample was collected from Petroleum Development Oman (PDO), and the characteristics are shown in Table 1.

Synthesis of ZnO NPs

The ZnO NPs were synthesized at room temperature by modified sol-gel process at room temperature[40]. The synthesis was performed by mixing equal volumes of Zn $(CH_3COO)_2$ $2H_2O$ (0.05 M) and NaOH (0.1 M) for 24 h at a stirring speed of 200 RPM and the resulting mixture was centrifuged at 5000 RPM for 20 min. The ZnO NPs particles are washed five times with ethanol to remove the impurities followed by drying at 400°C for 2 h in a furnace and then powdered using a mortar and a pestle to obtain the desired size range. The reaction involved in the formation of ZnO NPs is indicated in Eq. 1.

Table 1 — Characteristics of refinery wastewater

Parameters	Average values
pH	6.8
TSS (mg/L)	398
TDS (mg/L)	1400
Turbidity (NTU)	10
COD (mg/L)	1100
DO (mg/L)	20

$$Zn[CH_3COO]_2.2H_2O + 2NaOH \rightarrow ZnO + 2NaCH_3COO + H_2O \quad \ldots(1)$$

Nanocomposite thin film fabrication and characterization

A desired quantity (5.0 g) of low molecular weight chitosan was mixed with 100 mL of acetic acid (1% by wt) and kept under vigorous stirring at the rate of 1500 RPM for 3 h followed by slow addition of 0.4 g of ZnO NPs and then sonicated in an ultrasonic bath for 24 h to form a uniform dispersion of the NPs with required consistency. The layer deposition was performed by placing the glass substrate vertically into the coating solution for 15 min under gentle stirring. After layer deposition, the coated glass substrates are rinsed with Millipore water to remove the excess solution followed by drying at ambient temperature for 24 h. The layer deposition was continued till the required layers are deposited on the glass plate. Finally, the coated substrates are used for the refinery wastewater treatment.

Refinery wastewater treatment

The wastewater treatment was carried out using coated glass substrates in batch mode by studying the influence of wastewater pH, contact time, agitation speed and the number of deposition cycles and the ideal processing conditions were established. The coated glass substrates were placed vertically along the sides of a beaker containing 1000 mL of refinery wastewater under shaking. The treated wastewater samples were collected at definite time intervals and tested for measurement of TDS, COD, TSS, turbidity and dissolved oxygen values. All experiments were repeated, and the mean value of three data sets was taken for the determination of treatment efficiency. The efficiency of wastewater treatment using the fabricated thin films are calculated using the Eq. (2)

$$\% \text{ Reduction in parameters} = \frac{C - D}{C} \times 100 \quad \ldots(2)$$

Where, ‘C’ and ‘D’ are the initial and final values.

Results and Discussion

The SEM image of the ZnO NPs was used to analyse the surface characteristics of the nanoparticles. The SEM micrograph depicted in Fig. 1 describes the microstructural characterization, grain boundaries and surface morphology of the ZnO NPs displaying the actual shape. Fig. 1 validates the spread of nanoparticles. Fig. 2 shows the EDS spectrum of ZnO NPs with major peaks demonstrating the elemental composition of 61.6% Zn, 21.8% O_2, 12.9% C and 3.7% Al.

The FTIR characterization studies were performed for the identification of varied peaks present in the sample. The spectrum shown in Fig. 3 reveals the characteristic functional groups of ZnO NPs. The ZnO stretching vibrations are observed from a significant peak identified at a wavenumber corresponding to 563 cm^{-1}. The broad bands at

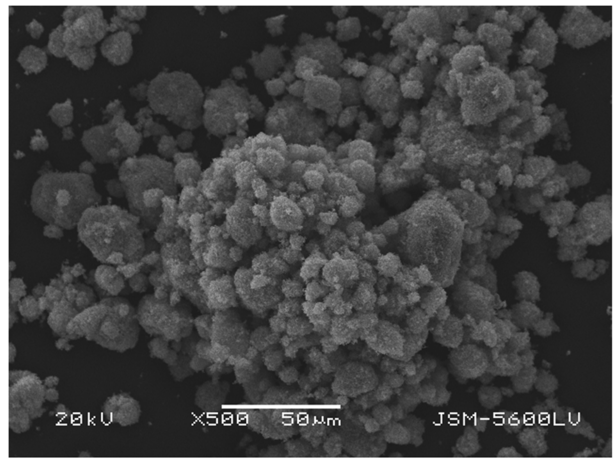

Fig. 1 — SEM micrograph of ZnONPs

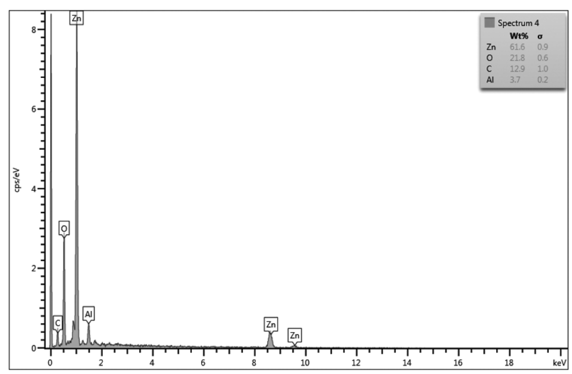

Fig. 2 — EDS spectrum of ZnONPs

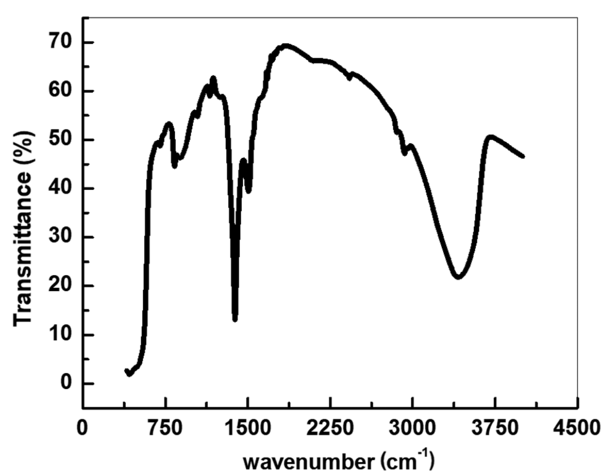

Fig. 3 — FTIR spectrum of ZnO NPs

3478 cm^{-1} and 889 cm^{-1} were attributed to the O-H stretching vibration and deformation. Another significant peak observed at 1003 cm^{-1} is mainly due to the C-N bond conforming to the presence of primary amine and the stretching vibration of the C-O bond of the primary alcohol. Additionally, the C-H stretching vibration of alkane group is observed at wavenumbers between 2800 cm^{-1} and 3000 cm^{-1} (Ref.41).

The powder X-ray diffraction patterns of the ZnO NPs with hexagonal unit cell structure are represented in Fig. 4. The diffractogram and inter planar spacings are well matched with the standard diffraction pattern of wurtzite ZnO, demonstrating the formation of ZnO nanocrystals[42]. ZnO NPs shown in Fig. 4 exhibited a single phase and free from any impurities confirming the crystallinity of the sample. A variety of peaks observed at different Bragg's diffraction angles of 31.87°, 34.58°, 36.43°, 47.73°, 56.81°, 62.94°, 68.11°, and 69.12° are strongly indexed as hexagonal wurtzite phase of ZnO [43].

The particle size distribution of ZnO NPs depicts the average diameters as well as the purity of the sample. The size analysis of ZnO NPs demonstrated in Fig. 5 shows the average size of particles (about 60 nm) which clearly shows the homogeneous distribution of the nanoparticles. A single peak in the Fig. 5 confirms the uniform size distribution of particles, which is one of the essential requirements in wastewater treatment applications.

Preparation of composite thin films

The SEM micrograph of the nanocomposite film shown in Fig. 6, revealed a uniform distribution of ZnO NPs with slight accumulation of particles on the chitosan surface[44]. Additionally, the atomic level surface topology of the chitosan-ZnO composite thin film was examined through AFM. The Fig. 7 (a) and Fig. 7(b) illustrate the 2-D and 3-D images of the thin film using AFM. It has been realized that during the process of nanocomposite layer formation; ZnO NPs are spread over the thin film surface with even distribution[45].

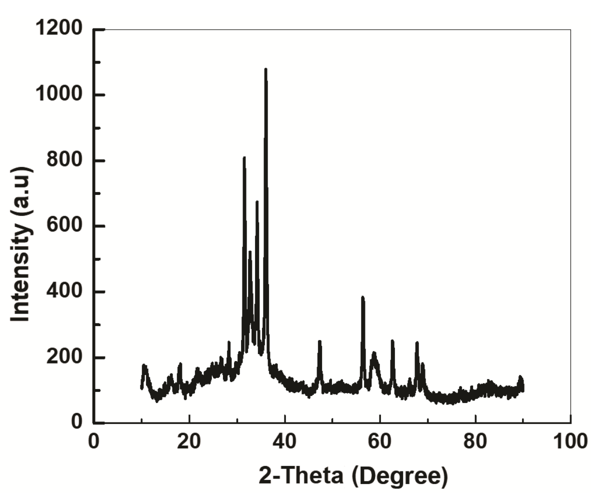

Fig. 4 — XRD pattern of ZnO NPs

Refinery wastewater treatment using chitosan-ZnO nanothin film

The efficacy of refinery wastewater treatment using the fabricated chitosan-ZnO nanothin film was appraised by altering the processing conditions of wastewater pH, duration of mixing, agitation speed and number of deposition cycles on reduction of COD, DO, TSS, TDS and turbidity.

The pH of oily wastewater is one of the crucial parameters affecting the treatment efficiency. The impact of variation in wastewater pH with parameter

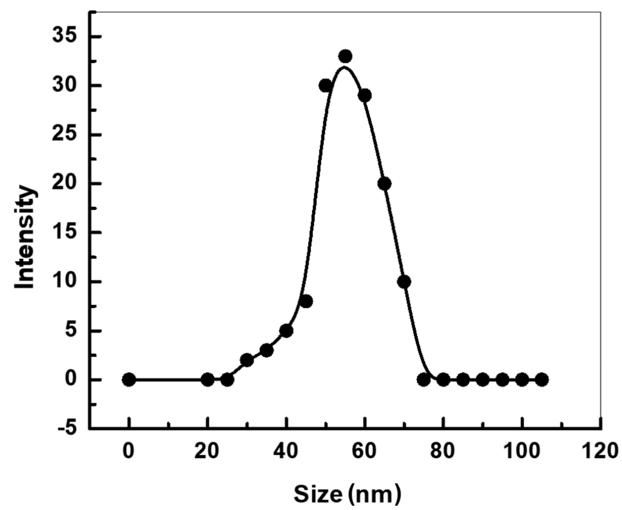

Fig. 5 — Size distribution of ZnO NPs using DLS

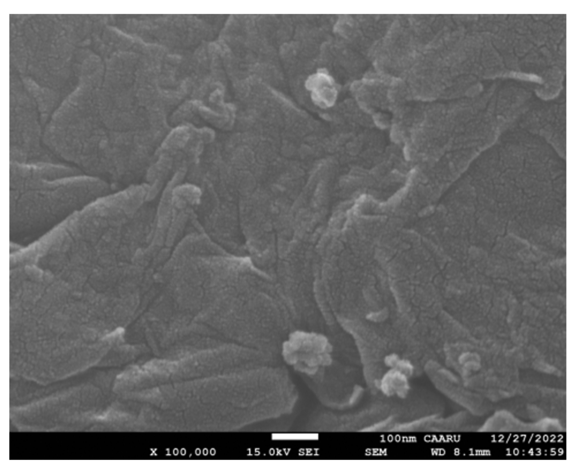

Fig. 6 — SEM micrograph of ZnO-NP thin film

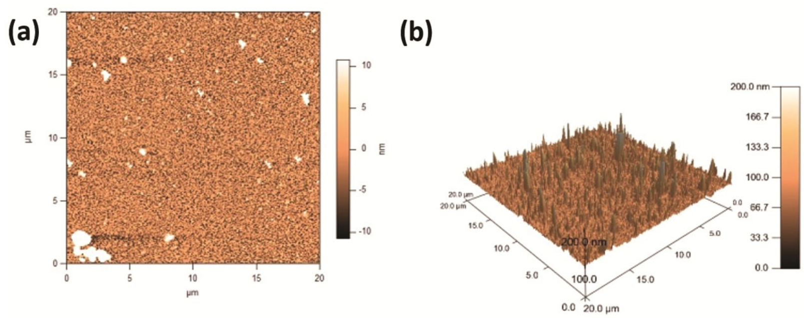

Fig. 7 — (a) 2-D image and (b) 3-D images of chitosan - ZnO thin film using AFM

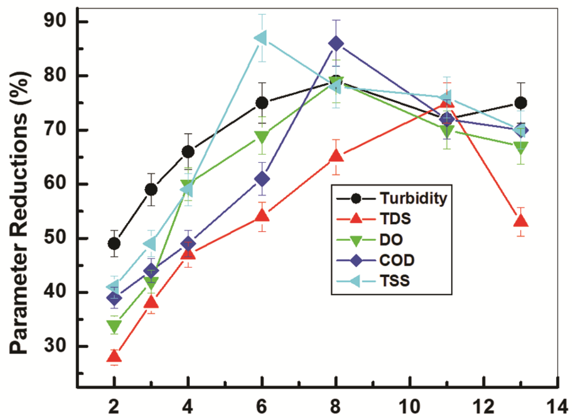

Fig. 8 — Effect of variation of wastewater pH

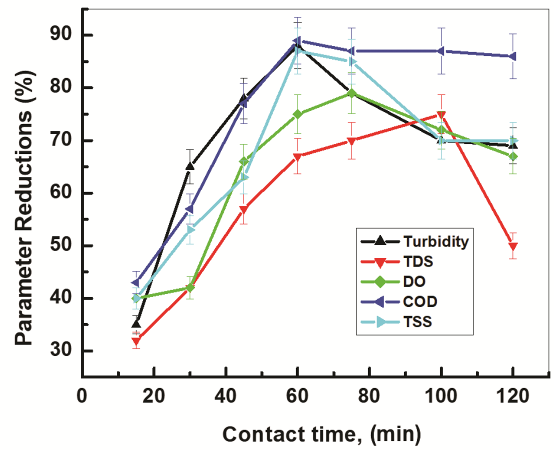

Fig. 9 — Effect of variation of stirring time

reductions are demonstrated in Fig. 8. As observed in the Fig. 8, considerable numbers of protons are available on the thin film surface at lower pH values, which results in the enhanced adsorption rate. The refinery wastewater solution pH was altered from acidic to alkaline range and the best COD removal efficiency (86%) was achieved at pH 8.0 and this pH was reflected as the ideal pH for the subsequent experiments. The highest COD reduction at pH 8.0 was due to the availability of maximum number of adsorption sites on the thin film surface and hence greater transfer of pollutants on to the vacant sites.

Contact time play a significant role in the adsorption process, as the contact time influences the diffusion and transfer of pollutants from bulk solution to the adsorbate surface. Fig. 9 depicted the graphical representation of the influence of contact time on percent reductions. The increase in the contact time enhances the removal efficiency and maximum parameter reductions are observed at 60 min of stirring time. This is due to the availability of significant number of active sites on the surface of the composite at the early contact and pollutants occupied sites near the equilibrium. The percentage reduction increased with increase in contact time till it reached equilibrium adsorption time. As shown in Fig. 9, the best performance was witnessed at 60 min of stirring time, and there experience a dip in performance above 60 min of contact time.

The influence of number of deposition layers is a key factor determining the best pollutant removal. The best performance was accomplished with 10 numbers of deposition layers and a little drop in COD reduction was observed when the number of deposition layers is increased from 10 to 12 as indicated in Fig. 10. As the number of deposition layers is increased, the treatment efficiency also increased with a maximum COD amounts to 87%. This result clearly shows that more ZnO is getting immobilized on to the coated layers of glass substrate which in turn increase the contaminant removal efficiency.

The influence of agitation speed variation with pollutant removal efficiency is shown in Fig. 11. It is observed that the parameter reductions are greater at a stirring speed of with 87% reduction in COD at 8.0 pH and 75 min contact time with 10 deposition layers. Considerable reduction in the pollutant removal are observed with increased stirring speed up to a

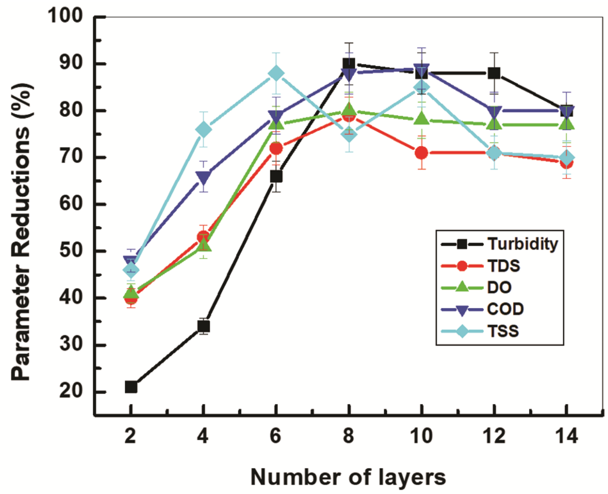

Fig. 10 — Influence of number of deposition layers

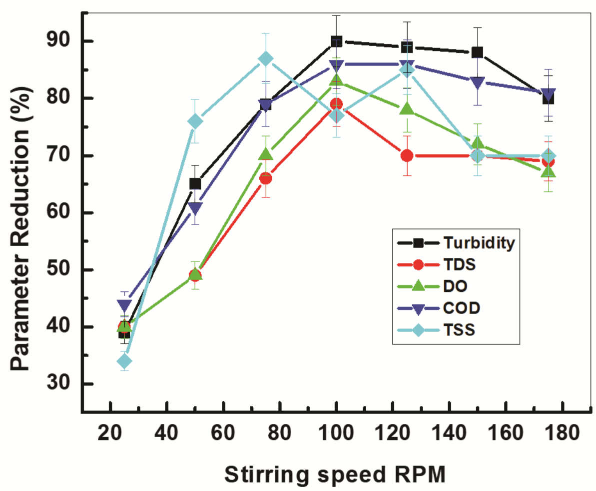

Fig. 11 — Effect of variation of stirring speed

maximum agitation speed of 100 RPM, beyond this a dip in percentage reduction was observed. The morphological characteristics of the composite film after the treatment process are shown in Fig. 12. The surface of the film looks very thick along with the appearance of dark spots confirms the successful deposition of pollutants on the composite film showing the accomplishment of treatment process.

The nanocomposite film after one cycle of treatment process was again reused for another 3 cycles of operation. It was observed that the nanocomposite film showed excellent pollutant removal efficiency. The percentage pollutant removal efficiency after third treatment cycle was 70%. Reusability of the film is gauged as the measure of nanocomposite film stability. Another advantage of using nanocomposite film in the treatment is the

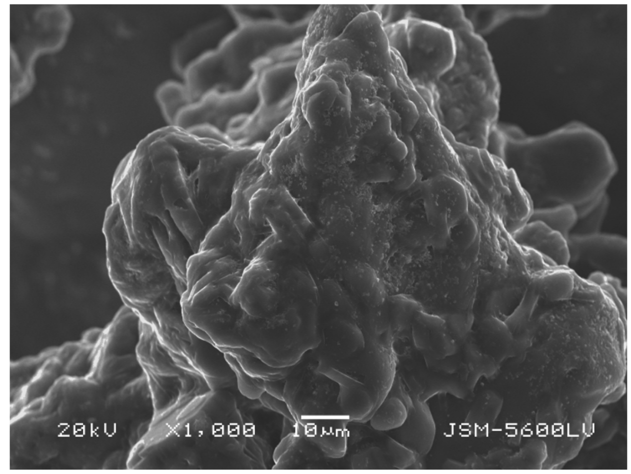

Fig. 12 — SEM of nanocomposite film after treatment

generation of fewer amounts of solids after treatment. Hence, this eco-friendly and cost-effective treatment method using chitosan-ZnO nanocomposites shows great potential in addressing the challenges in refinery wastewater treatment. The nanocomposite thin film represents a promising avenue for environmental pollution remediation strategies.

Conclusion

In this work, chitosan-ZnO nano thin films were developed by dip coating technique for the refinery wastewater treatment applications. The ZnO NPs of size around 60 nm were successfully synthesized using modified Sol-gel method. The effectiveness of chitosan-ZnO nanocomposite thin films in the treatment of refinery wastewater was investigated at different experimental parameters by varying the pH, contact time, agitation speed, and number of coating layers. The optimum processing conditions were established at pH 8.0, contact time 60 min, 10 numbers of layers of chitosan-ZnO and 100 RPM stirring speed. The experimental results validate that chitosan-ZnO nanocomposite thin films demonstrated excellent pollutant removal from refinery wastewater. The outcome of the study reveals an easy and simple way to immobilize ZnO NPs in chitosan thin films and offers a promising alternative to the conventional methods in the treatment of refinery wastewater. This novel research ensures a sustainable water management system aligning with the goals and targets of the 2030 agenda of United Nations Sustainable Development Goals (SDG – 6 i.e., clean water and sanitation for all) and also supports the objectives of Oman Vision 2040. Currently, the research team is investigating the performance of chitosan–ZnO nanothin films for textile and diary wastewater treatment.

Acknowledgement

The authors greatly acknowledge National University of Science & Technology for providing the infrastructure facilities to perform the experiments. Also sincere thanks to Ms. Bushra Nasser Ahmed Al Sabahi, Instructor, College of Pharmacy, National University of Science & Technology for the support in FTIR analysis.

References

1 Ramos A P, Cruz M A E, Tovani C B & Ciancaglini P, Biomedical applications of nanotechnology, *Biophys Rev*, 9 (2017) 79.

2 Hussein A K, Applications of nanotechnology in renewable energies: A comprehensive overview and understanding, *Renew Sust Energy Rev*, 42 (2015) 460.

3 Nandita D, Ranjan S & Ramalingam C, Applications of nanotechnology in agriculture and water quality management, *Environ Chem Lett*, 15 (2017) 591.

4 Ismail I, Balachandran S & Devi M G, Synthesis, characterization and application of nanoparticles in wastewater treatment, *Ind Chem Eng*, 61 (2018) 77.

5 Abdullah A Rasbi A W Y, Devi M G & Chandrasekhar G, Synthesis and application of silica and calcium carbonate nanoparticles in the reduction of organics from refinery wastewater, *J Ind Chem Soc*, 99 (2022) 100519.

6 Sangeetha M, Devi M G & Dutta S, Fabrication, characterisation and application of poly allyl amine hydrochloride/poly styrene sulphonate/zinc oxide (PAH/(PSS/ZnO)n bilayers in the removal of pollutants from oil refinery waste water, *Int J Environ Anal Chem*, 103 (2021) 1.

7 Fatima F, Siddiqui S & Khan W A, Nanoparticles as novel emerging therapeutic antibacterial agents in the antibiotics resistant era, *Biol Trace Elem Res*, 199 (2021) 2552.

8 Immanuel P, Senguttuvan G & Mohanraj K, Enhanced activity of chemically synthesized nanorod Mn_3O_4 thin films for high performance supercapacitors, *Int J Thin Film Sci Tec*, 9 (2020) 57.

9 Wang Y, Pan C, Chu W, Vipin A K & Sun L, Environmental remediation applications of carbon nanotubes and graphene oxide: Adsorption and catalysis, *Nanomaterials*, 9 (2019) 439.

10 Taghizadeh M T, Siyahi V, Ashassi-Sorkhabi H & Zarrini G, ZnO, AgCl and AgCl/ZnO nanocomposites incorporated chitosan in the form of hydrogel beads for photocatalytic degradation of MB, E. coli and S. aureus, *Int J Biol Macromol*, 147 (2020) 1018.

11 Iqbal J, Synthesis of nitrogen-doped ceria nanoparticles in deep eutectic solvent for the degradation of sulfamethaxazole under solar irradiation and additional antibacterial activities, Chem *Eng J*, 394 (2020) 124869.

12 Padmaja P & Bhatt R, Environmental applications of chitosan and its derivatives, *Encycl Mar Biotechnol*, 2 (2020) 1065.

13 Al-Moharbi S S, Devi M G, Sangeetha B M & Jahan S, Studies on the removal of copper ions from industrial efuent by Azadirachtaindica powder, *Appl Wat Sci*, 10 (2020).

14 Rahi M N, Treatment of petroleum refinery effluents and wastewater in Iraq: A mini review, *IOP Conf Ser: Mater Sci Eng*, 1058 (2021) 012072.

15 Devi M G, Al-Moshrafi S M K, Hudaifi A A & AlAisari B H, Treatment of refinery waste water using environmental friendly adsorbent, *J Inst Eng India Ser E*, 98 (2017) 1.

16 Sangeetha B M, Al-Balushi N A M, Devi M G, Dutta S, Anjali K P & Abri M A, Fabrication, characterization and application of polymer based nanomaterials in the removal of pollutants from industrial effluents, *Environ Tech Innov*, 23 (2021) 101748.

17 Radelyuk I, Tussupova K, Kleme J J & Persson K M, Oil refinery and water pollution in the context of sustainable development: Developing and developed countries, *J Clean Prod*, 302 (2021) 126987.

18 Tsani S, Koundouri P & Akinsete E, Resource management and sustainable development: A review of the european water policies in accordance with the United Nations' sustainable development goals, *Environ Sci Pollut*, 114 (2020) e570.

19 Arsalani N, Bazazi S, Abuali M & Jodeyri S, A new method for preparing ZnO/CNT nanocomposites with enhanced photocatalytic degradation of malachite green under visible light, *J Photochem Photobiol A Chem*, 389 (2020) 112207.

20 Phin H Y, Ong Y T & Sin J C, Effect of carbon nanotubes loading on the photocatalytic activity of BiSI/BiOI as a novel photocatalyst, *J Environ Chem Eng*, 8 (2020) 103222.

21 Rouhi M, Babamoradi M, Hajizadeh Z, Maleki A & Maleki S T, Preparation of heterojunction PPy/Fe3O4/ Halloysitenano-clay Ag/Co nanocomposite for photocatalytic degradation of methylene blue under visible light irradiation, *Optik Int Light Elect Optics*, 212 (2020) 164721.

22 Gryta M, Separation of saline oily wastewater by membrane distillation, *Chem Papers*, 74 (2020) 2277.

23 Han M, Zhang J, Chu W, Chen J & Zhou G, Research progress and prospects of marine oily wastewater treatment: A review, *Water*, 11 (2019) 2517.

24 Chauhan A, Kumari R V, Sharma A, Shandilya P & Li X, Photocatalytic dye degradation and antimicrobial activities of pure and Ag-doped ZnO using Cannabis sativa leaf extract, *Sci Rep*, 10 (2020) 7881.

25 Bhushan B, Jahan K, Verma V, Murty B & Mondal K, Photodegradation of methylene blue dye by powders of Ni–ZnO floweret consisting of petals of ZnO nanorod around Ni-rich core, *Mater Chem Phys*, 253 (2020) 123394.

26 Abdulrahman A F, The effect of different substrate-inclined angles on the characteristic properties of ZnO nanorods for UV photodetectors applications, *J Mater Sci Mater Electron*, 31 (2020) 14357.

27 Abdulrahman A F, The influence of various reactants in the growth solution on the morphological and structural properties of ZnO Nanorods, *Passer J Basic Appl Sci*, 2 (2020) 69.

28 Heinlaan M, Ivask A, Blinova I, Dubourguier H C & Kahru A,Toxicity of nanosized and bulk ZnO, CuO and TiO_2 to bacteria vibrio fischeri and crustaceans daphnia magna and thamnocephalusplatyurus, *Chemosphere*, 71 (2008) 1308.

29 Aldeen T S, Mohamed H E A & Maaza M, ZnO nanoparticles prepared via a green synthesis approach: Physical properties, photocatalytic and antibacterial activity, *J Phys Chem Solids*, 160 (2022) 110313.
30 Barzinjy A A, Hamad S M, Abdulrahman A F & Biro-Ghafor S J, Biosynthesis, characterization and mechanism of formation of ZnO nanoparticles using petroselinum crispum leaf extract, *Curr Org Synth*, 17 (2020) 558.
31 Saif S, Tahir A, Asim T, Chen Y, Khan M & Adil S F, Green synthesis of ZnO hierarchical microstructures by Cordiamyxa and their antibacterial activity, *J Biol Sci*, 26 (2019) 1364.
32 Ahmed S, Annu S & Chaudhry S A, A review on biogenic synthesis of ZnO nanoparticles using plant extracts and microbes: A prospect towards green chemistry, *J Photochem Photobiol B: Biol*, 166 (2017) 272.
33 Zahid M, Rashid A, Akram S, Rehan Z A & Razzaq W, A comprehensive review on polymeric nano-composite membranes for Water Treatment, *J Membrane Sci Technol*, 8 (2018) 1.
34 Bruno P, Campo R, Giustra M G, Marchis M D & Di-Bella G, Bench scale continuous coagulation-flocculation of saline industrial wastewater contaminated by hydrocarbons, *J Water Process Eng*, 8 (2020) 179.
35 Dakroury G A, El‑Shazly E A A & Hassan H S, Preparation and characterization of ZnO/Chitosan nanocomposites for Cs(I) and Sr(II) sorption from aqueous solutions, *J Radioanal Nucl Chem*, 3 (2021) 1.
36 Nguyen N T, Nguyen N T & Nguyen V A, In situ synthesis and characterization of ZnO/chitosan nanocomposite as an adsorbent for removal of congo red from aqueous solution, *Adv Polym Technol*, 2 (2020) 1.
37 Abdel-Halim A S, Ahmed M A, Shaima T E W, Bayaumy B M & Mona B A, Removal of toxic metal ions from wastewater using ZnO@Chitosan core shell nanocomposite, *Environ Nanotechnol Monit Manag*, 9 (2018) 67.
38 Annu, Mittal M, Tripathi S & Shin D K, Biopolymeric nanocomposites for wastewater remediation: An overview on recent progress and challenges, *Polymers*, 16 (2024) 294.
39 American Public Health Association (APHA-AWWAWPCH), Standard Methods for the Examination of Water and Waste Water, 20th Edn, (APHA, Washington DC, (1998) 1270.
40 Narmadha A A S, Deepapriya P, John D R, Grace I S, Reena R S, Chamundeeswari A, Jose M & Jerome D S, Synthesis and characterization of ZnO nanoparticles by novel sol gel technique, *AIP Conf Proc*, 2244 (2020) 070013.
41 Maah A H A & Hassan A A, Green synthesis of AC/ZnO nanocomposites for adsorptive removal of organic dyes from aqueous solution, *Inorg Chem Comm*, 157 (2023)111415.
42 Zhou J, Zhao F, Wang Y, Zhang Y & Yang L, Size-controlled synthesis of ZnO nanoparticles and their photoluminescence properties**,** *J Lumin*, 122 (2007) 195.
43 Khoshhesab Z M, Sarfaraz M & Asadabad M A, Preparation of ZnO nanostructures by chemical precipitation method, *Met Org Nano Met Chem*, 41 (2011) 814.
44 Abarna B, Preethi T & Rajarajeswari G, Single-pot solid-state synthesis of ZnO/chitosan composite for photocatalytic and antitumour applications, *J Mater Sci Mater Electron*, 30 (2019) 21355.
45 Nithya A & Jothivenkatachalam K, Chitosan assisted synthesis of ZnO nanoparticles: An efficient solar light driven photocatalyst and evaluation of antibacterial activity, *J Mat Sci Mater Elect*, 26 (2015) 1.