

Development and Enhancement of Composites Based on Polyamide 12 Reinforced with Zinc Oxide Nanoparticles

O. Chelil^{1,2*}, D. Lakhdari¹, N. Houas³, A. Remichi¹, L. Sellai¹

¹Department of Petrochemistry, 20 August 1955 University, Skikda, Algeria; ²Department of Process Engineering, Ferhat Abbas University, Setif, Algeria; ³Department of Chemistry, University of Setif-1, Setif, Algeria

ABSTRACT

The study aims to create nanocomposites composed of Polyamide 12 (PA 12) reinforced with Zinc Oxide (ZnO) nanoparticles at various concentrations (1.5%, 3%, 5%, 10%, 15% and 20%) as well as composites composed of polyamide 12 and to use them to adsorb Methylene Blue (MB). According to adsorption experiments, it has been shown that the adsorption rate varies depending on various factors such as the initial concentration of the solution, contact period and pH. The various prepared samples were subjected to different analyses such as Atomic Force Microscopy (AFM), optical microscopy and structural modifications obtained through Ultraviolet-Visible (UV) and Fourier-Transform Infrared (FTIR) spectroscopies. According to the results, it was observed that the PA 12 film becomes less homogeneous and rougher as the amount of ZnO nanoparticles in the PA 12 matrix increases.

The dye (methylene blue) was absorbed by the polyamide 12 film alone in 20 minutes (pH=10) and in 5 min (pH=12) for the nanocomposite PA 12/ZnO (15%). The increase in the rate and amount adsorbed is due to the strong affinity between the adsorbate and the adsorbent as well as the availability of free adsorption sites on the surface of the bioadsorbent from the first contact.

Keywords: Polyamide 12; ZnO nanoparticles; Arginine methylation; Nanocomposites; Adsorption

INTRODUCTION

In recent years, various environmental scientists and engineers have paid extensive attention to detecting and analyzing the Environmental Concern scale (ECs) to set regulatory measures for minimizing their impact on living beings. Some contaminants among these classes are frequently detected in surface water and groundwater and research findings indicated that they exhibit toxicity in aquatic organisms. The water bodies receive these contaminants from various sources such as wastewater treatment plants, sewerage systems, landfill leachate, accidental leakage, agricultural and street runoff [1].

Wastewater generated in industrial processes requires the use of pretreatment methods and processes to reduce and/or eliminate all types of pollutants, before discharging the effluent into nature [2].

The elimination of these pollutants is still possible given the availability of numerous treatment processes [3]. There are a multitude of physicochemical and biological processes for

depolluting contaminated water, in particular using dyes, which are widely used in printing, food, cosmetic and clinical products, but in particular in the textile industries for their stability. Chemical and the ease of their synthesis and their variety of colors. However, these dyes cause pollution once released into the environment.

In many industrial sectors, including the textile textile, paper and leather dyes in the food and cosmetic industries. dyes are widely used. Large volumes of wastewater from these industries are dumped into streams untreated. Their emissions pose a risk to human and environmental health as a source of pollution. In recent years, there has been concern over how treating these industrial effluents can protect the environment and improve the quality of the water. A synthetic dye known as Methylene Blue (MB) is thought to be carcinogenic. Because it can result in skin irritation, allergic dermatitis, nausea and vomiting [4].

There are several physical, chemical and biological methods for treating and decolorizing polluted effluents such as coagulation and flocculation, biodegradation, membrane filtration, chemical

Correspondence to: O. Chelil, Department of Petrochemistry, 20 August 1955 University, Skikda, Algeria, E-mail: o.chelil@univ-skikda.dz

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oxidation, ozonation, ion exchange, electrochemical methods and adsorption etc. [5-8]. Adsorption has been proven to be an excellent method for the removal of dyes in wastewater, due to its significant advantages such as low cost, cost-effectiveness, simplicity, easy use and completion, efficiency compared to conventional methods from an economic and environmental point of view [9,10].

Various kinds of competent adsorbents have been reported. Activated carbon is the most widely used adsorbent to remove contaminants from wastewater because of its extended surface area, microporous structure, high adsorption capacity and a high degree of surface reactivity [11]. In general, it is expensive and the regeneration of the adsorbent for several steps may cause difficulties because of the loss of the textural properties. Consequently, this problem has led to a search for cheap and efficient alternate material such as sawdust, zeolite, chitosan, bentonite and clay [12].

The vibrant and diverse colors associated with dyes may be visually appealing, but their environmental impact is a cause for concern. Many dyes utilized across diverse industries exhibit a concerning characteristic persistence and resistance to degradation. These pose substantial challenges for wastewater treatment plants and significantly heighten the risk of bioaccumulation in aquatic organisms. Among the myriad of persistent dyes, several notable examples underline the severity of this issue.

Methylene blue (3,7-bis (dimethylamino)-phenothiazin⁵⁻-iumchloride) (Figure 1) is a heterocyclic aromatic azo dye progressively utilized in textile industries and more quantity during the manufacturing of paint. The dye was also used to find out the minute amount of sulphides in aquaculture. Is the most commonly used dye in the dyeing of cotton, wood and silk. The cationic methylene blue dye is considered less toxic and used to treat malaria and cancer in the aquaculture industry [13].

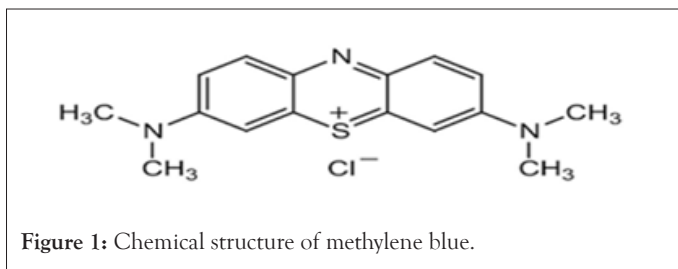


Figure 1: Chemical structure of methylene blue.

Both humans and animals may sustain permanent eye injuries from eye burns. Breathing problems may arise from inhaling it and consuming it by mouth results in burning, nausea, vomiting, sweating and frequent cold sweats. It is highly interesting to treat industrial waste that contains this kind of dye. Numerous physical, chemical and biological methods have been created and evaluated for the purpose of treating effluents that contain dyes [14].

Because of their opened-porous structure and moderate-to-large specific surface area, nanomaterials have been used extensively recently as adsorbents to remove organic substances from wastewater. They have shown great potential in the field of environmental remediation [15]. Several studies address the use of polyamides as material for preparing polymeric membrane using the Phase Inversion (PI) method [16,17].

The work carried out during this work consisted of highlighting the development of nanocomposites based on Polyamide 12 with zinc oxide nanoparticles (PA 12/ZnO) at different concentrations and characterize their physicochemical properties through

various techniques, for example: Atomic force microscopy, optical microscopy, ultra-visible and fourier transform infrared and evaluate their adsorption capacity of methylene blue and optimize the adsorption conditions such as pH, concentration and quantity of adsorbent and finally propose recommendations for the practical use of these materials in the treatment of industrial wastewater containing dyes, taking into account economic and environmental constraints.

The choice of ZnO reinforcement is justified by its very interesting properties allowing it very potential applications, particularly in optoelectronics, agriculture, wastewater treatment and catalysis as a vulcanization activator for rubbers, a hardener or a crosslinking agent for elastomers and in the production of electrically conductive carbon materials, it is also used in the cosmetics, medicine and biotechnology industries, including its use in the elaboration of biodegradable antibacterial packaging and photovoltaic solar cells for green energy.

MATERIALS AND METHODS

A polyamide 12 (RILSAN LMNO) is a semi-crystalline thermoplastic polymer from the polyamide family, supplied by RAKEMA, with a melting temperature of 176°C and a density of 1,01 to 1,02 was used, dichloromethane supplied by biochem chemopharma (density=1,33), formic acid produced by fisher chemical (density=1,22), hydrochloric acid (supplied by RANKEM) and sodium hydroxide were used as solutions. Methylene blue (density=1,01) is a chemical compound used as a dye and zinc oxide (density=5,606) a naturally occurring material known as zincite. It appears in the form of crystals of varying colors between yellow and red depending on the level of impurities in the crystals (mainly magnesium). When synthesized, zinc oxide is white. It is a chemical compound made up of zinc and oxygen.

Preparation of polyamide 12 films

The PA 12 layer was synthesized using the phase inversion approach, as shown by the work of Wandenkolken Lim and col [17]. The PA 12 granule was dried in vacuum drying chamber at 80°C for 24 h. This step was important for remove water adsorbed on the surface of the polyamide granule during its storage. Formic acid (67,5 ml) and dichloromethane (67,5 ml) and PA 12 (3,375 g) were mixed and kept closed in pyrex glass containers (25 ml capacity) for 24 h. This step allows the polymer to swell by the solvent. After that, the system was mixed using a magnetic stirrer at 120°C for 30 min. The reaction mixture is poured into petri dishes to obtain thin films.

Preparation of nanocomposite based on polyamide 12 reinforced by the nanoparticle (ZnO) in solution

To prepare the PA 12/ZnO films, two solutions must be prepared: Formic acid (45 ml) and Dichloromethane (45 ml) and PA 12 (3,375 g) were mixed and kept closed in Pyrex glass containers (25 mL capacity) for 24 hours; the ZnO nanoparticle was dissolved in a mixture of 22,5 ml of formic acid and 22,5 ml of dichloromethane acid, the concentration range of the Zinc Oxide (ZnO) used in the preparation of membranes is (1.5; 3; 5; 10; 15; 20) wt%, then this solution is added to the first solution, after that, the reaction was carried out in a flask fitted with a reflux condenser and equipped with a stirrer and a thermometer is placed on a hot plate and set to the desired temperature (120°C) and the stirring speed is chosen so as to obtain complete dispersion of PA 12 with ZnO. The temperature in the flask is

maintained at 30°C for 3 h. The reaction mixture is poured into petri dishes to obtain thin films (PA 12/ZnO).

Preparation of solutions at different pH

The adsorption experiments were carried out at different pH values from 2 to 13 by introducing a precisely weighed quantity of adsorbent 0,014 g into beakers containing a volume of methylene blue dye solution (10^{-5} M) for 2 h at a speed of 150 rpm, the pH is adjusted by adding Hydrochloric acid (HCl) and Sodium Hydroxide (NaOH). The absorbance of the solution in the presence of the adsorbent was measured using a spectrometer (AGILENT 60 CARY UV-Vis).

Physico-chemical characterization of samples

Atomic Force Microscopy (AFM): Surface topography and roughness of nanoparticles was determined using Asylum Research-Model MFP-3D atomic force microscope at room temperature and resonance frequency of 1.5 Hz, image analysis was performed using Argyle image processing software. The measurements were carried on the surface of samples.

Ultraviolet-visible spectroscopy: Samples at a concentration of 10^{-5} M were analyzed using an Agilent Cary 60 UV-Vis spectrometer, managed by a computer equipped with processing software, in the range of 210 to 800 nm. The analysis is carried out on samples in solution.

Fourier transform infrared spectroscopy: To carry out the spectroscopic analyses, the films obtained are characterized qualitatively and quantitatively by Fourier Transform Infrared (FTIR) spectroscopy, using a Quality Assessment and Test Results-Single Reflection (QATR-S) type device controlled by a computer, with a resolution of 2 cm^{-1} and a number of scans equal to 16

scans. The range of wave frequencies studied extended from 400 cm^{-1} to 4000 cm^{-1} . The analyzes were carried out in transmission mode.

RESULTS AND DISCUSSION

Atomic force microscopy

Atomic Force Microscopy (AFM) was used to further examine the surface morphology, as well as the period and depth of the grooves. The polyamide 12 layer alone has an irregular topographic surface (2D) characterized by the presence of a ridge and valley surface morphology (3D) as shown in Figure 2.

After incorporating Zinc Oxide (ZnO), polyamide films still possess peak and valley surface morphologies. ZnO nanoparticles can act as nucleation sites (formation of a new phase), which results in the increase in the degree of crystallinity of the polymer. Topographic images of the surface of PA 12/ZnO nanocomposites at different concentrations (10, 15 and 20) wt%, reveal aggregate formation on the surface as shown in Figures 2 and the roughness increases with increasing increase in ZnO concentration as shown in Table 1.

According to Table 1 and in comparison with the PA 12 film, the roughness parameter of the nanocomposites first decreased (10 and 15) wt%, then increased (20 wt%). The decrease in surface roughness is attributed to the interference of nonocomposites [18] i.e., at low concentration, ZnO nanoparticles can disperse uniformly in the PA 12 matrix forming an almost homogeneous structure, while the increase in roughness at 20% ZnO may be due to nanocomposite aggregation and excess nanoparticles (ZnO), which can create areas of high concentrations and irregularities (the values of the RMS surface roughness is given in Table 1).

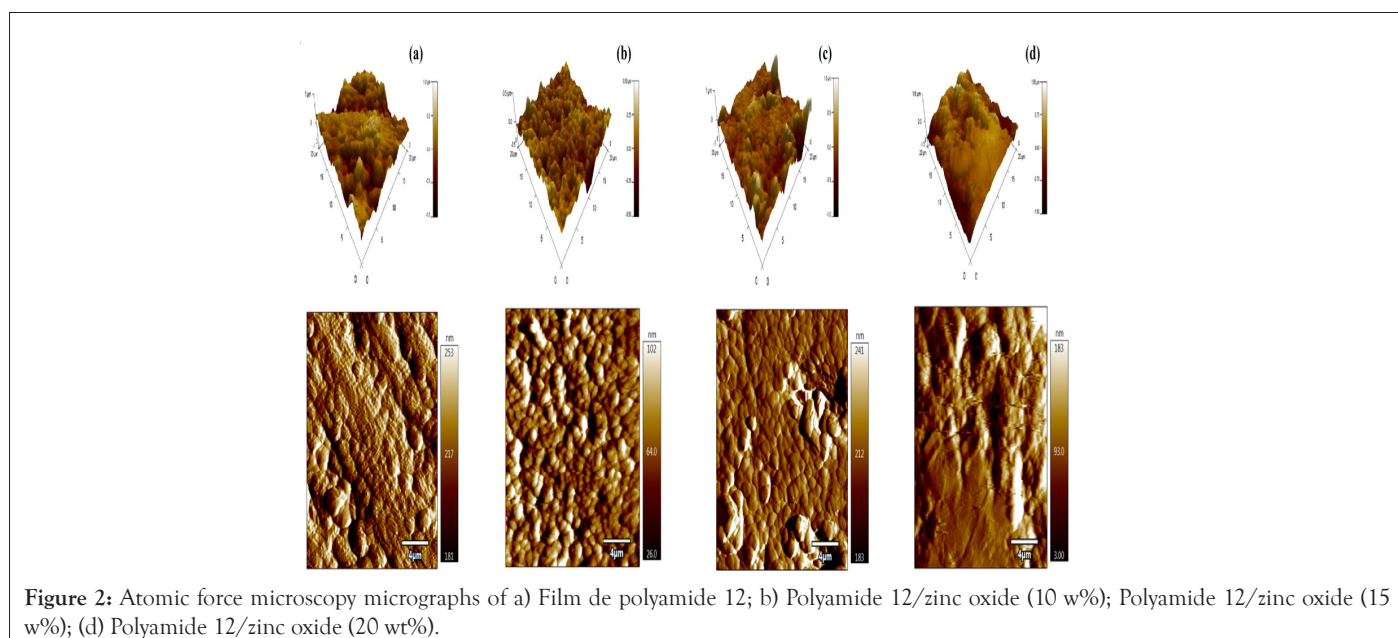


Figure 2: Atomic force microscopy micrographs of a) Film de polyamide 12; b) Polyamide 12/zinc oxide (10 w%); Polyamide 12/zinc oxide (15 w%); (d) Polyamide 12/zinc oxide (20 wt%).

Table 1: Surface roughness (RMS) values of PA12 and different nanocomposites (PA12/ZnO).

Sample (wt%)	RMS (nm)
PA12	191.458
PA12/ZnO (10%)	77.252
PA12/ZnO (15%)	188.928
PA12/ZnO (20%)	315.124

Note: PA12: Polyamide 12; ZnO: Zinc Oxide.

Ultraviolet-visible spectroscopy

Figure 3 represents the UV-visible spectra of different samples from 210 to 800 nm and the influence of the addition of ZnO on polyamide 12.

The polyamide 12 solution at a concentration of 10^{-5} M gave an intensive visible UV absorption band at 266 nm. This figure indicates that the shape of the spectra of the nanocomposites (PA 12/ZnO) at different concentrations is different from that of the spectrum of polyamide 12 (PA 12), the maxima are at 265 nm, 715 nm.

The presence of absorbance's above 300 nm indicates the presence of polyenes, the latter containing a number of conjugated double bonds greater than 11 (long sequences) (Table 2).

The UV-visible spectra of the PA 12/ZnO samples are shown in Figure 4 at various concentrations (1.5, 3, 5, 10, 15, 20) wt%, respectively and at various pH values (ranging from 2 to 13) for a period of 2 h.

In Figure 4, oxidized MB shows a UV-visible absorption peak between 500 and 800 nm and usually exhibits 665 nm λ_{\max} representing $n-\pi^*$ transitions of MB molecule [19]. This indicates that the intensity of the absorption peaks of the dye (methylene blue) was reduced much more in the PA 12 sample at pH=10, which confirms the fixation of the dye on the surface of PA 12. This is under the effect of interaction forces between the adsorbate (methylene blue) and adsorbent (PA 12) molecules.

The Figures 4 indicate that the adsorption of the dye (methylene blue) was observed at pH=12 in all the PA 12/ZnO samples at different concentrations (1.5, 3, 5, 10, 15, 20) wt%.

Figure 4, shows how the nanocomposite composed of PA 12 and nanocomposites (PA 12/ZnO) performs in terms of MB adsorption at various initial solution pH ranges (ranging from 2 to 13). With acidic conditions, the MB absorption by nanocomposite (PA 12/ZnO) is comparatively low, whereas the high adsorption property is realized under basic concentration. The cationic MB dye molecules experienced electrostatic mutual repulsion with greater H^+ ions on the nanocomposite (PA 12/ZnO) surface at lower pH levels. As we know, the OH group's active site was beneficial for the adsorption of adsorbate on activated polyamide 12 surface. Therefore, at pH=2, the elimination effectiveness. When, the pH is increased from 2 to 12, the adsorption removal the elimination effectiveness of nanocomposite (PA 12/ZnO), when pH reaches 8 and 12.

This result is in agreement with the results of Islam et al., [20]. Decreased MB adsorption at pH may be caused by the adsorbent's predominantly protonated amino and carboxylic acid functional groups, which increase the cationic MB dye's electrostatic repulsion. When the initial pH rises till an alkaline medium, the high MB adsorption onto the adsorbents was observed. Additionally, it was found that the proton generation competes with the MB cation [21].

The best adsorption was confirmed in the PA 12/ZnO sample (15 wt%), as shown by the UV-visible spectra of the various samples (PA 12/ZnO) for one hour, as shown in Figure 5.

Figure 6, show the UV-visible spectra of PA 12 at pH=10 the adsorption was completed at t=20 min and the adsorption the adsorption was noticed at 5 min for the PA 12/ZnO.

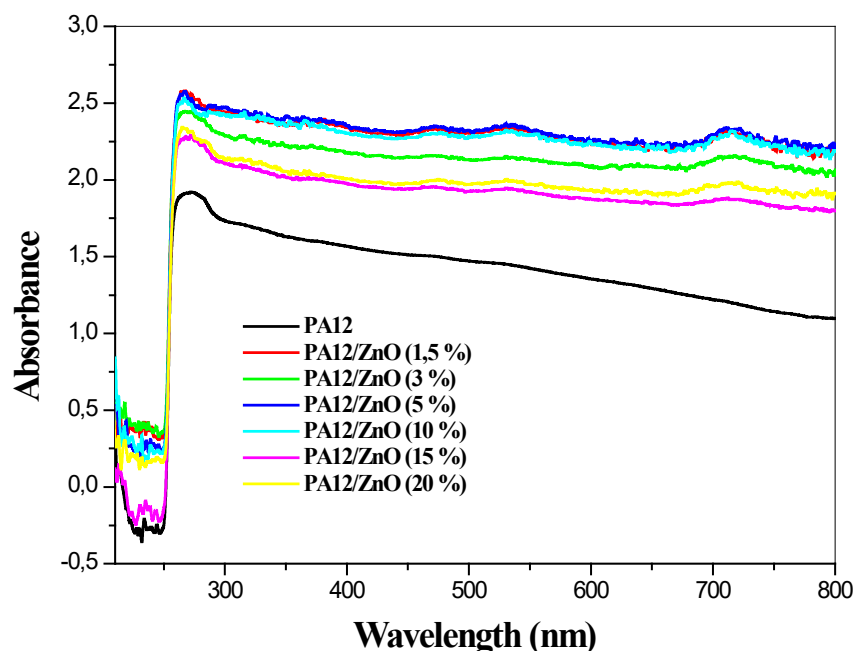


Figure 3: Ultraviolet-visible spectra of polyamide 12 and zinc oxide reinforced polyamide 12 samples at different concentrations.

Table 2: Absorption wavelengths of the maxima λ for polyenes of the type $-(CH=CH)-$.

N	3	4	5	6	7	8	9	10	11
λ (nm)	275	310	336	364	386	410	430	450	471

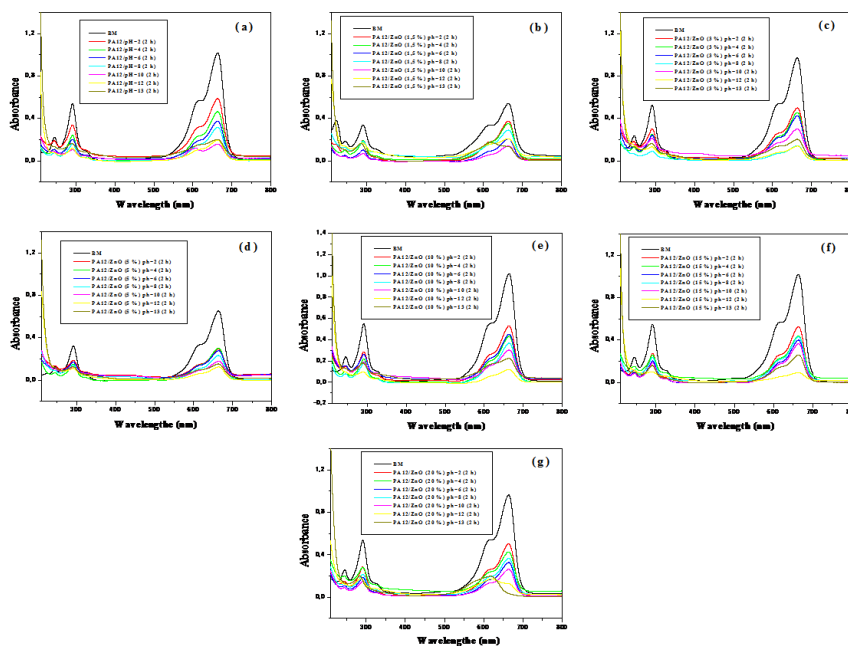


Figure 4: Ultraviolet-visible spectrum of polyamide 12 and zinc oxide reinforced polyamide 12 samples at different concentrations and pH values from 2 to 13, for 2 h.

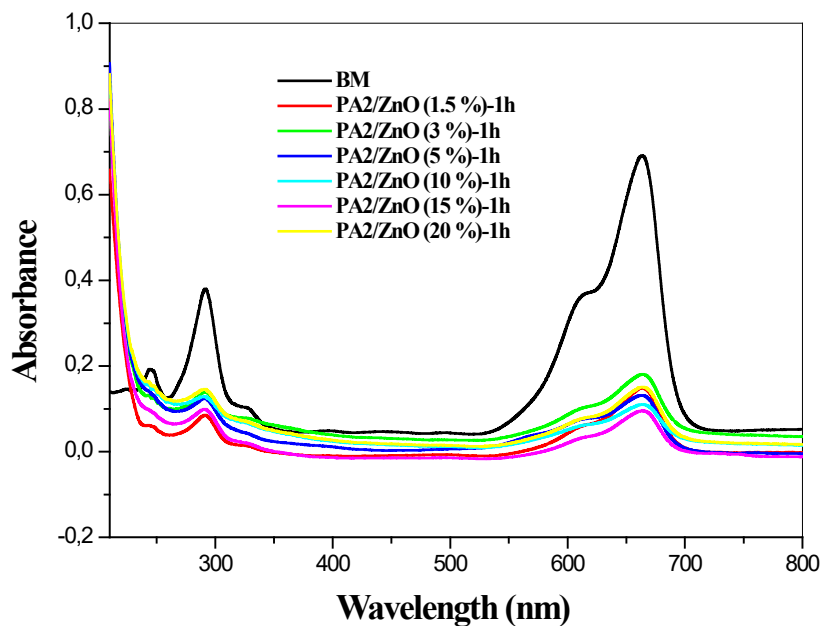


Figure 5: Ultraviolet-visible spectrum of the different samples (Polyamide 12/zinc oxide), for 1 h, pH=12.

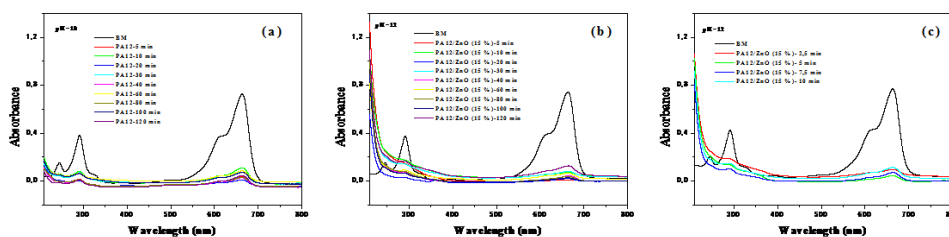


Figure 6: Ultraviolet-visible spectrum of a) Polyamide 12 (at 120 min); b) Polyamide 12/zinc oxide (15%) (at 120 min); c) Polyamide 12/zinc oxide (15%) (at 10 min).

Removal and adsorption capacity of methylene blue dye

Adsorption is dependent on the fixation of the dye grains on the adsorbent surface. The following equations were used to calculate removal and adsorption capacity of MB dye [21].

$$R\% = \frac{C_0 - C_t}{C_0} \times 100$$

$$Q = (C_0 - C_t) \times \frac{v}{m}$$

where the starting dye concentration (C_0) (measured in mg/L for MB), the residual concentration (C_t) was measured for the MB dye in mg/L and the final dye concentration (C_f) (measured in mg/L for MB) are given. R% is the of MB dye solution removed after adsorption; Q is the adsorption capacity (mg/g) at various times; v is the volume of solution (mL) and m is the amount of sample (g) (PA112 and PA 12/ZnO (15 wt%)).

It was observed that the removal and adsorption capacity of MB dye by PA 12 increased with time (Figure 7). At time interval of 10 min, the removal was 84.78% and the adsorbed quantity was 1.034 mg/g, however, at a time interval of 20 min, the rates and quantities were 98.61% and 1.27 mg/g, respectively.

Figure 7, depict the removal and quantity adsorbed of BM by the nanocomposite PA 12/ZnO (15 wt%). It was observed that the highest removal occurred at t=5 min (98.96%), with an adsorbed quantity of 1.3 mg/g, at a time interval of 120 min, the rate decreased by 82.79%, resulting in an adsorbed quantity

of 1.17 mg/g. The increased removal and adsorption capacity of BM is due to the strong affinity between the adsorbate and the adsorbent (nanocomposite) and the availability of free adsorption sites on the surface of the nanocomposite (PA 12/ZnO) 15 wt% from the first contact. La fixation of the adsorbate on the surface of the solid is essentially done by electrostatic forces such as dipoles, hydrogen bonds or van der Waals.

Better MB adsorption yields were recorded with the nanocomposite PA 12/ZnO (15 wt%). This could be explained by the presence of ZnO in PA 12 which also gives it a much larger pore volume than PA 12 alone. The adsorption of dyes can be divided into at least four major stages. The first stage involves the mass transfer of dye molecules towards the adsorbents (bulk movement). Unless stirring is set at particularly low speeds, this stage is a fast process which takes place right after the addition of the adsorbents into the aqueous solution. When the dye molecules are about the adsorbents, the second stage is initiated, which involves a slow diffusion of these molecules towards the surface of the adsorbents (film diffusion). It is followed by the third stage, which is a slow diffusion of the dye molecules into the pores of the adsorbents (intra-particle diffusion). During the final stage, the dye molecules are rapidly anchored to the active sites of the adsorbents. Generally, the film and the intra-particle diffusions qualitatively determine the rate of the adsorption of the dyes onto the adsorbents. Among them, one factor might be more predominating than the other in certain cases [22].

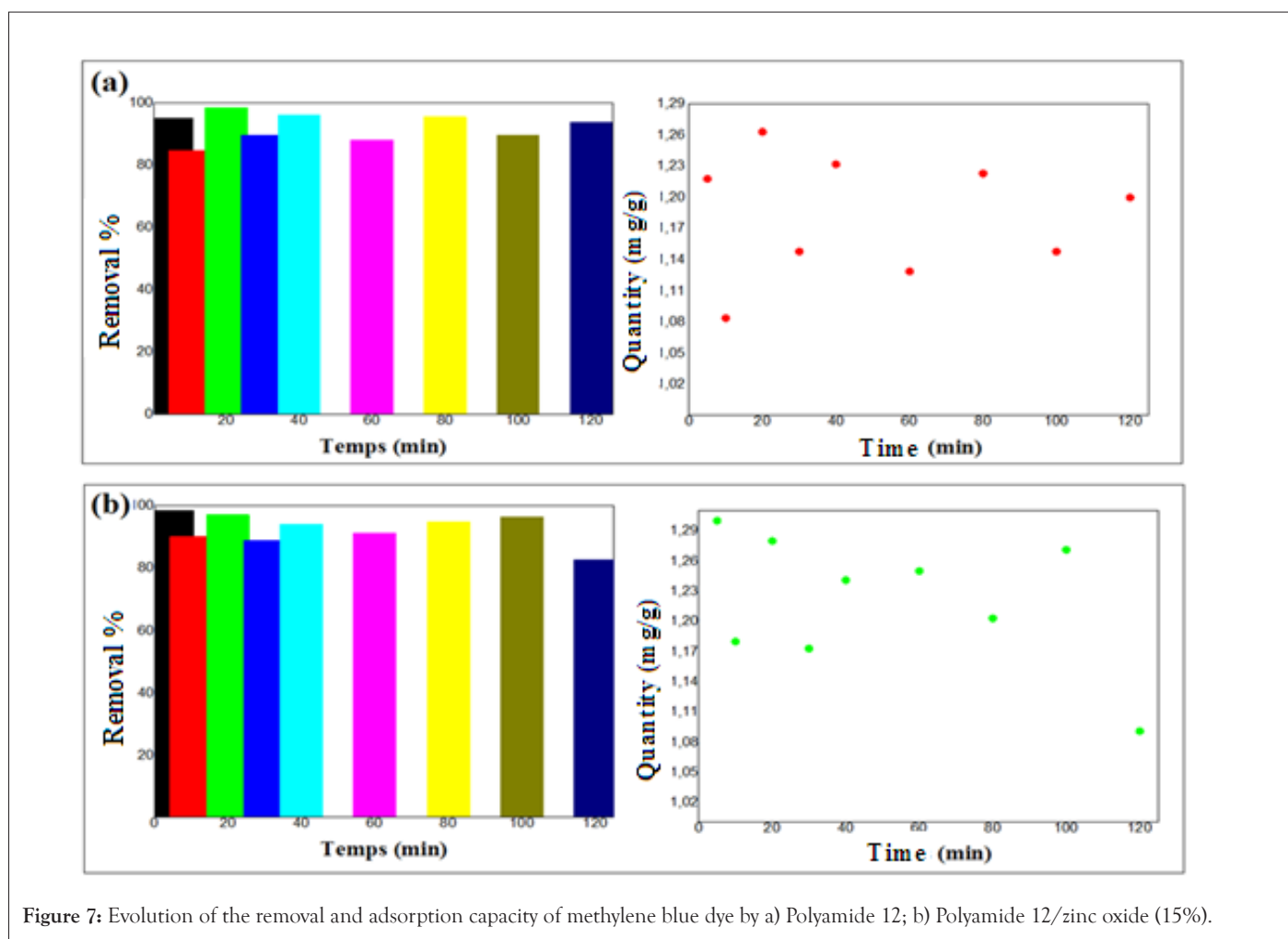


Figure 7: Evolution of the removal and adsorption capacity of methylene blue dye by a) Polyamide 12; b) Polyamide 12/zinc oxide (15%).

Fourier transform infrared spectroscopy

Fourier Transform Infrared Spectroscopy (FTIR) is an analysis method for characterizing chemical bonds or the composition of the material. This technique is based on the principle that when a polymer is illuminated by an infrared beam, the different bonds and chemical functions present in its structure vibrate, absorbing energy at a particular frequency. Thus, by identifying the location and intensity of the absorption bands of the spectra obtained during the analysis, we can know the nature and concentration of the different groups that make up the polymer chains. The samples were measured in the region of 500 cm^{-1} to 4000 cm^{-1} .

Figure 8, shows the FTIR spectrum of polyamide 12. The characteristic bands at a wavelength of 3298 cm^{-1} and 1643 cm^{-1} are attributed to the bending and stretching of the $-\text{NH}_2$ bond. Furthermore, this region ($1643\text{-}1650\text{ cm}^{-1}$) corresponds to $-\text{CO}$ and the band at 1553 cm^{-1} is due to the $-\text{NH}$ and $-\text{CN}$ deformation of the secondary amides. The peaks between 2800 and 2900 cm^{-1} due to the presence of $-\text{CH}_2$ and $-\text{CH}_3$ and $-\text{NH}$, the bands in the region ($720\text{-}1643\text{ cm}^{-1}$) are attributed to the N-H, C-CO-NH₂ and C=O of the primary amide.

NH, the bands in the region ($720\text{-}1643\text{ cm}^{-1}$) are attributed to the N-H, C-CO-NH₂ and C=O of the primary amide.

Figure 8, indicate the presence of typical ZnO peaks, stretching vibration bands of metal oxides of Zn-O bonds in the region ($500\text{-}1050\text{ cm}^{-1}$). The peaks at 1380 and 1740 cm^{-1} represent the stretching vibrations of C=O bonds and a broad band in the region ($3400\text{-}3500\text{ cm}^{-1}$) represents the stretching vibrations of O-H bonds, which can respectively indicate d impurities and humidity [23]. The peak at 1740 cm^{-1} may also be related to an additional common band attributed to the absorbed water bending mode. Furthermore, in their study, Pholnak et al., used the same precursor and reported its spectrum with prominent peaks obtained at 840 and 1380 cm^{-1} attributed to various vibrational modes of its nitrate groups [24,25].

Figure 9, illustrate the superposition of FTIR spectra of nanocomposite (PA 12/ZnO) at different concentrations in comparison with PA 12 alone. These spectra are similar, because the same materials were used and show differences in the shift and intensity of the peaks.

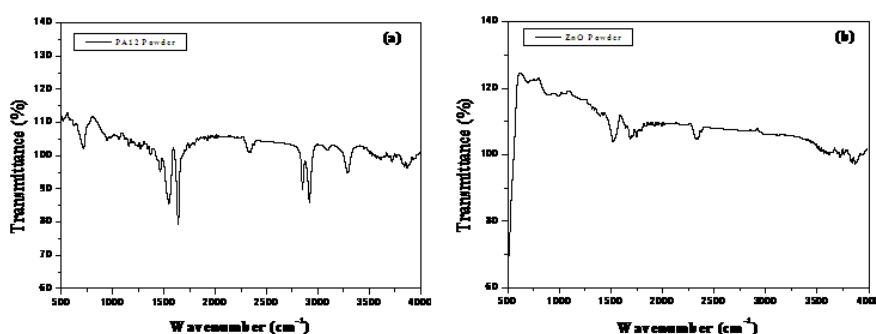


Figure 8: Fourier transform infrared spectra of a) Polyamide 12 powder; b) Zinc oxide powder.

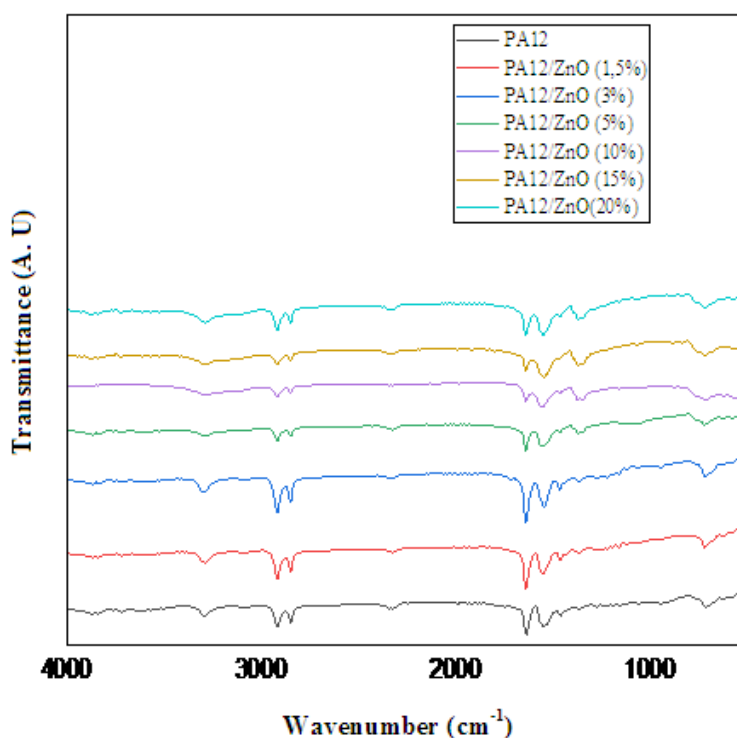


Figure 9: Fourier transform infrared spectra of polyamide 12 and PA12/zinc oxide at different concentrations.

CONCLUSION

In conclusion, the study successfully developed Polyamide 12 (PA 12) nanocomposites reinforced with Zinc Oxide (ZnO) nanoparticles at varying concentrations, evaluating their potential for adsorbing Methylene Blue (MB) dye. The results revealed that the PA 12/ZnO nanocomposites exhibited improved adsorption capacity, with the highest performance observed in the PA 12/ZnO (15%) sample, particularly under basic conditions (pH=12). The adsorption rate and capacity were influenced by factors such as nanoparticle concentration, pH and contact time. The nanocomposite showed a significant reduction in MB concentration, demonstrating its potential as an effective and economical material for wastewater treatment applications. The incorporation of ZnO nanoparticles enhanced the surface roughness and adsorption efficiency of PA 12, making it a potential candidate for environmental remediation.

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