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SYNTHESIS AND APPLICATION OF RAYON ZINC OXIDE NANOCOMPOSITIE

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Abstract

The mean of composite are combination of two or more materials present as separate phases and combined to from desired structures so as to take advantage of certain desirable properties of each component. The constituents can be organic, inorganic or metallic in the form of particles, rods, fibers and plates. In this research work, the matrix material (rayon) was prepared from waste paper (A4 printed paper) by using viscose method. The rayon-ZnO nanocomposite fiber was synthesized from zinc chloride and rayon by using melt compounding technique. The synthesized rayon-ZnO nanocomposite was characterized by using EDXRF, FT-IR, SEM and TG-DTA analysis. Synthesized rayon-ZnO nanocomposite was applied in wastewater treatment process. Coagulation and filtration methods were also used to treat the textile wastewater sample. According to the results, rayon-ZnO nanocomposite has good removal efficiency of organic and inorganic pollutant from wastewater. Furthermore, the efficiency of rayon-ZnO nanocomposite was examined by calculation of percent removal efficiency and water quality index (WQI).

Keywords: Viscose, Rayon, Nanocomposite, Textile Wastewater, Water Quality Index

Introduction

Metal oxide nanoparticles and composite materials are widely applied in the field of research development and diverse applications in industries including surface coatings optoelectronic, bioengineering, biodignostics and agriculture. Their intrinsic properties are mainly determined by size, shape, composition, crystallinity and morphology (Soosen, *et al*. 2009). The mean of “composite” is when two or more different materials are combined together to create a superior and unique material. This is an extremely broad definition that holds true for all composites however, more recently the term “composite” describes reinforced plastics. Composites materials can be made organic and inorganic substances by using different methods. The main types of composite are polymer matrix composite, metal matrix composite and ceramic matrix composite (Soosen, and *et al*. 2009). Polymer matrix composite with discontinuous fillers are widely used for the application like die attachment, electrically and thermally conductive, adhesives encapsulations and thermal interface materials. It is well known that polymers are easily process able and need low processing temperatures. However, compared to ceramics they have lower electrical and thermal of the most popular areas for current research and development. At present, easily availability of nanomaterials offers the promise of developing polymer matrix nanocomposites with tailored thermal mechanical and electric properties for a particular application. Polymer matrix nanocomposites are polymer matrix containing fillers with at least one dimension in the range of 1 nm to 100 nm (Divij and Goyal, 2014). Nanocomposite fibers have attracted attention in recent years because improved mechanical, thermal, solvent resistance and fire retardant properties compare to the pure or conventional composite fibers. Therefore, much work has focused on developing nanocomposite fibers using various polymers (Kato, Usuki, and Okada, 1997). In this research, rayon-ZnO nanocomposite was synthesized from zinc chloride and rayon by using melt compounding process. The synthesized rayon-ZnO nanocomposite was applied as superior adsorbent material in wastewater treatment process. Moreover, the efficiency of synthesized rayon-ZnO nanocomposite has been studied.

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Materials and Methods

Elimination of ink from the waste paper

In this research, waste papers (A4 printed papers) were collected**.**

Aging: For aging step, the collected samples were placed in an oven for accelerated aging at 60º C for 24 hours. Accelerated ageing of the samples is necessary because the storage of the recovered papers can influence their deinkability.

Defibration: Second step is defibration step. The pieces of sample 50 g were placed in a 1 liter glass vessel 150 mL of sodium complex solution was added into it and the heated dilution water was filled up to a total volume of 500 mL. Then, it was stirred, 38 mL of solution and 10 mL of EDTA solution was added and it was stirred again to obtain the disintegrated sample pulp. At the end of pulping the pH of pulp was measured by pH meter.

Storage: The disintegrated sample for subsequent treatment was stored for 60 minutes in a water bath at 45ºC.

Homogenization: After storage, the stock pulp was stirred for homogenization. Then, it was diluted with the warm water to terminate any chemical reaction**.**

Floatation: The glass bottle (1 L) containing some hot dilution water was heated for some minutes. Disintegrated samples were added into the bottle and it was filled up with dilution water. Then, the floatation process was done by stirring with stirrer and giving air supply with air- pumper. The starting point is for the floating time, when the air supply is started. During the entire floating process, the froth was removed by using scraper as possible. The skimmed-off floatation rejects was collected in a tank. The dilution water was continually added to maintain for the drainage during the floatation. This process was run for 15 minutes. Finally, the solution containing the pulp in a bottle was filtered and the deinked pulp was collected. The resulting deinked pulp was dried in oven at 30ºC until it was dried moderately. Then, the recycle pulp was obtained.

Preparation of Viscose Rayon from Recycle pulp

Cellulose (recycle pulp from waste paper) was immersed in 20% aqueous sodium hydroxide (NaOH) at a temperature in the range of 18 to 25℃ in order to swell the cellulose fiber and to convert cellulose to alkali cellulose. The swollen alkali cellulose mass is pressed to a wet weight equivalent of 2.5 to 3.0 times the original pulp weight to obtain an accurate ratio of alkali to cellulose. These alkali cellulose placed in beaker are allowed to react with 25 mL of (100 %) carbondisulphide, CS_2 at room temperature to form cellulosexanthate. The orange cellulosexanthate is dissolved in 5% sodium hydroxide to obtain a viscous orange coloured solution called viscose. The viscose solution was passed at 40% sulphuric acid solution. The fibers were getting formed in the acid bath. The freshly regenerated rayon contains many salts and other water soluble impurities which need to be removed. Therefore the prepared rayon washed with distilled water, until the neutralization occurs. Finally, the rayon product was obtained.

Preparation of Rayon-ZnO Nanocomposite

Rayon (15) g was completely dissolved in 100 mL of 65% $ZnCl_2$ aqueous solution at 80ºC with 500 r/min constant stirring. Then, 15% NaOH aqueous solution was added drop-wise to the rayon-zinc chloride aqueous solution and heated with 500 r/min constant stirring to achieve a final pH value of 8.4. After the composite was aged for 30 min with constant stirring at 80ºC, the rayon-ZnO nanocomposite was obtained (Jinxia, Wenhua, Yajun, and Zhiguo, 2016).

Characterization of Synthesized Rayon and Rayon-ZnO Nanocomposite

Energy Dispersive X-ray Fluorescence Analysis

The relative abundances of the prepared samples were determined by EDXRF (EDX-700 Spectrometer) at the Universities' Research Center, Yangon University.

FT-IR Analysis

The functional groups present in prepared samples were investigated by FT-IR (SHIMADZU-8400, Spectrometer) at the Universities' Research Center, Yangon University.

Scanning Electron Microscopy Analysis

The surface morphology of prepared samples were examined by SEM (JSM 5610 LV, JEOL, Ltd) at the West Universities' Research Center, Yangon.

Thermal Stability (TG-DTA) Analysis

Thermal stability of rayon-ZnO nanocomposite was investigated by thermogravimetric differential analysis (TG-DTA) employing Shimadzu DTG 60H differential thermal analyzer at Universities' Research Center, Yangon University.

Wastewater Treatment Process

Sample collection

In this research, the wastewater sample was collected from Textile Dyeing Area (weaving zone) of Inn Baw Khone Village, Inlay Lake, Nyaung Shwe Township, Taunggyi District, Southern Shan State.

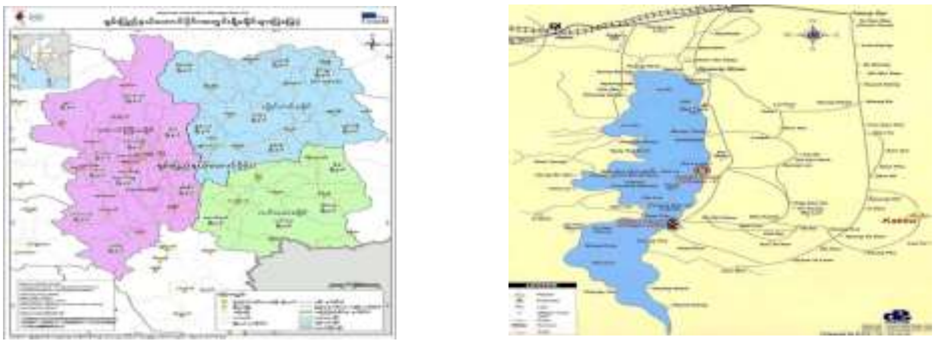

Figure 1 Location map of the wastewater sampling area (Khurtsia, 2015)

Wastewater Characteristics

Physical Characteristics

The important physical characteristics of wastewater such as total solids content, suspended solids, colour, odour, dissolved oxygen (DO), temperature and turbidity were determined (Korey, C. PASCO Scientific, 2010).

Chemical Characteristics

The chemical characteristics of wastewater sample such as chemical oxygen demand (COD), pH, alkalinity, total dissolved solids (TDS) and total hardness were determined (Korey, C. PASCO Scientific, 2010).

Determination of Elemental Contents in Water Samples

The contents of some element and trace heavy metals were determined by using EDXRF analysis.

Bacteriological Examination of Water Samples

E. Coli was determined at water and soil examination laboratory, Yangon.

Examination the Efficiency of Synthesized Rayon-ZnO Nanocomposite

Wastewater sample was treated with rayon-ZnO nanocomposite by using coagulation and filtration methods. The experimental conditions, different contact times (5, 10, 15, 60 min and overnight) and different coagulant weight (0.1, 0.2, 0.5, 1 and 2 g) were used for the process of removal impurities from wastewater sample. According to results, the optimum conditions were selected. Therefore, coagulant weight (0.1 g), contact time (15 min) adsorbent dosage (0.1 g) and volume of wastewater (100 mL) were used for three times in this treatment process. Moreover, the efficiency of rayon-ZnO nanocomposite was examined by Percent Removal Efficiency and Water Quality Index (Korey, C. PASCO Scientific, 2010).

Results and Discussion

Characterization of Rayon-ZnO Nanocomposite

EDXRF Analysis

The characteristic peaks for different element in the functional layer are presented in EDXRF spectra, which were obtained for the surface of sample shown in Figure (2). It can be seen that the ZnO was found to be present on the surface of rayon samples as 46%.

Figure 2 EDXRF spectrum of synthesized rayon- ZnO nanocomposite

FT-IR Analysis

FT-IR studies were carried out to confirm the identification and bond structure of associated functional groups of synthesized rayon-ZnO nanocomposite using optimized parameters. The FT-IR spectra of synthesized rayon, nano ZnO and rayon-ZnO nanocomposite were shown in Figure (3). In comparison of rayon, nano ZnO and rayon-ZnO nanocomposite of spectra resulted data are found to the intermolecular hydrogen bonds in rayon may be weaker than those in the rayon-ZnO and the low crystallinity and intermolecular hydrogen bonds in rayon make it more reactive component when participating in chemical reaction (Moosavi-Nasab, and Yousefi, 2011). Rayon has the characteristic peak at 893 and 1012 cm^{-1} while the correlated bands of rayon-ZnO centered at around 904 and 1047 cm^{-1}, respectively. In the FT-IR spectrum of rayon, the broad band appears at 3541 cm^{-1} (OH group of rayon) and this value was found to be 3452 cm^{-1} for rayon-ZnO. This broadening might be due to intermolecular hydrogen bonding between ZnO nanoparticles and cellulose rayon fabric.

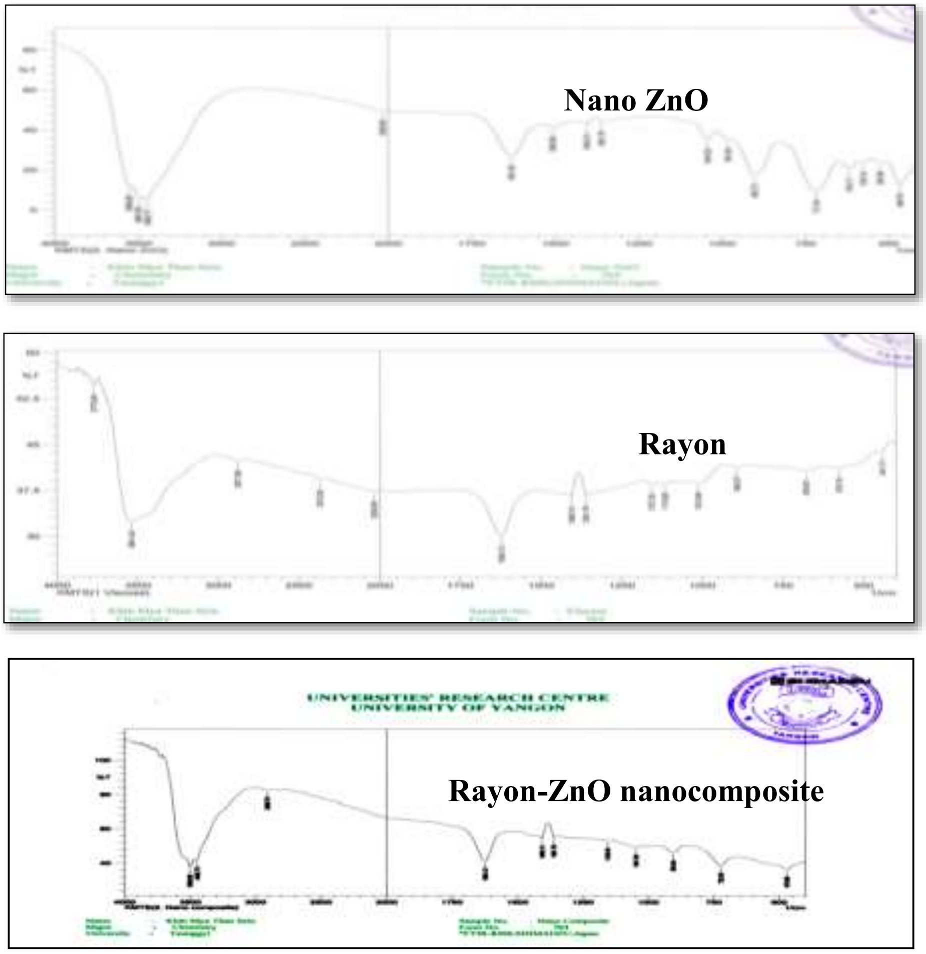

Figure 3 FT-IR spectrum of synthesized rayon, nano ZnO and rayon-ZnO nanocomposite

FT-IR spectrum shows the presence of ZnO stretching vibration at 3452 and 470 cm^{-1}. In the initial nucleation state the O-H functional groups on the rayon could bind to the surface of the ZnO particles. This clearly indicates the FT-IR spectrum of rayon-ZnO nanocomposite as compared to that the FT-IR spectrum of prepared rayon and ZnO nanoparticles. The proposed structure of rayon-ZnO nanocomposite might be as follows.

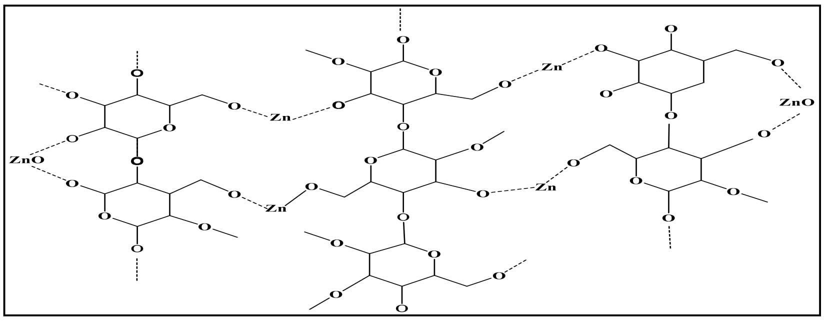

Figure 4 Proposed structure of synthesized rayon-ZnO nanocomposite

SEM Analysis

Figure (5) shows the SEM micrographs of synthesized rayon-ZnO nanocomposite. It can be seen, the SEM photograph of rayon-ZnO nanocomposite as compared to that SEM image of prepared rayon.

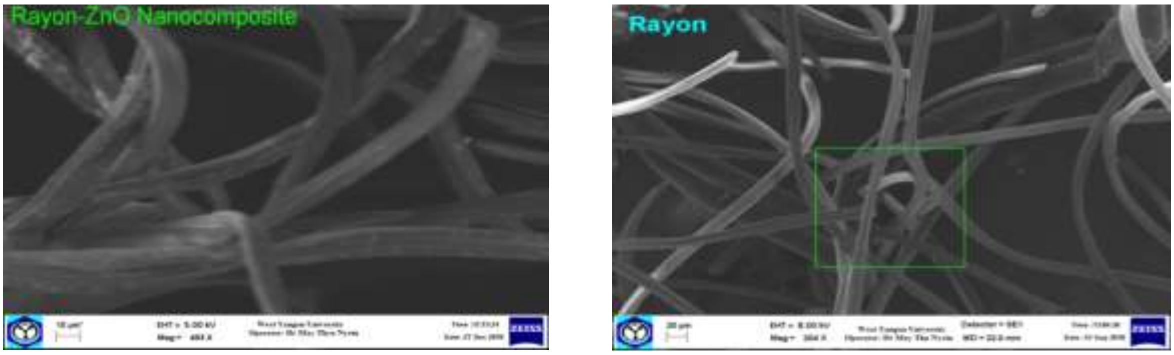

Figure 5 SEM micrographs of synthesized rayon and rayon-ZnO nanocomposite

This figures can be seen that good dispersion of ZnO nanoparticles into the rayon matrix. It is clear from many references that the ZnO nanoparticles show spherical morphology. Due to the large specific surface area and high surface energy, some nanoparticles are aggregated. The aggregation occurred probably during the process of drying (Attarad, *et al* 2016). The particle size distribution of the zinc oxide is uniform with diameters of approximately 60- 90 nm in nanocomposite.

Thermal Analysis

The TG-DTA thermogram of synthesized rayon-ZnO nanocomposite was showed in Figure (6). TG-DTA curve showed the nature of decomposition such as the release of free water as well as the liberation of volatile materials and combustion between 38°C and 600°C was presented. Thermal analysis data of synthesized rayon-ZnO nanocomposite were listed in Table (1).

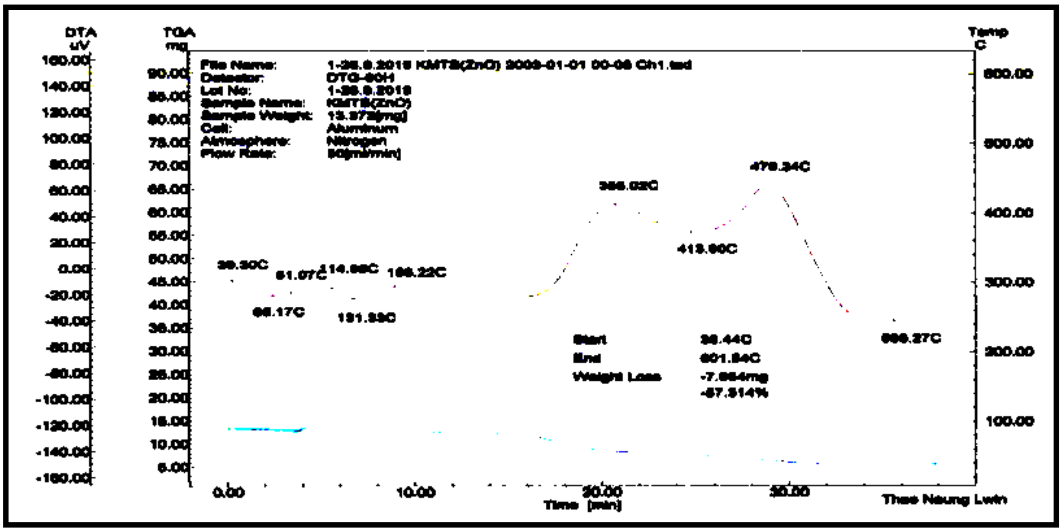

Figure 6 TG-DTA thermogram of synthesized rayon-ZnO nanocomposite

Table 1 Thermal Analysis Data of Synthesized Rayon-ZnO Nanocomposite

No.	TG		DTA		
	Beak in Temp (℃)	**Weight loss (%)**	**Peak Temp (℃)**	**Nature of reaction**	**Remark**
1	39-131	17	81	Endo	Dehydration
2	168-356	57	356	Exo	Cleavage of the glycossidic linkages
3	413-479	20	413	Exo	Degradation of composite
4	-	-	479	Exo	Decomposition of polymer fiber matrix

Wastewater Treatment Process

Examination the Efficiency of Synthesized Rayon-ZnO Nanocomposite

The observed data for some physicochemical parameters of samples (wastewater, treated water and removal efficiency of rayon-ZnO nanocomposite) were shown in Table (2).

Table 2 Some Physicochemical Parameters of Water Samples

No.	Parameter	Units	Resulted Data			*Guide Line* USA (2015)	
			Waste water	**Treated water**	**Removal Efficiency (%)**	**Aquatic life**	**EPA**
1	pH	-	3.06	8.75	-	6.5-9.0	6.5-9.0
2	Colour	-	358.5	-	**99.99**	<40	5-50
3	Temperature	℃	34.8	0.62	-	0-40	-
4	Turbidity	NTU	0.42	-	**99.99**	<80	5-25
5	Conductivity	ms/cm	5160.5	-	**99.99**	100-2000	750
6	Total hardness	mg/L	202.49	71.25	64.81	50-150	9-100
7	Total alkalinity	mg/L	470.0	-	**99.99**	50-150	30.5
8	Total solid (TS)	mg/L	28950	3030	89.53	<80	600
9	Total dissolved solid (TDS)	mg/L	27030	3030	88.79	-	500
10	Total suspended solid (TSS)	mg/L	1950	-	**99.99**	-	-
11	Nitrate	mg/L	16.74	0.75	95.51	0-2	0.015
12	Sulphate	mg/L	20.74	14.23	31.38	<1000	4.8
13	Chloride	mg/L	6.73	3.77	43.98	>60	3.9
14	Phosphate	mg/L	10.52	0.41	96.10	0.02	0.012

The results of before treatment and after treatment using rayon-ZnO nanocomposite exceed the limit of public use compared with guide line (Aquatic life and EPA, USA 2015). According to the results, wastewater sample gave unsatisfactory remarks.

Some organic pollutant parameters in water samples

The observed data for some organic parameters of samples (wastewater, treated water and removal efficiency of rayon-ZnO nanocomposite) were shown in Table (3).

Table 3 Some Organic Pollutant Parameter in Water Samples

No.	Parameter	Unit	Resulted Data			*Guide Line* USA (2015)	
			Wastewater	Treated water	Removal Efficiency (%)	Aquatic life	EPA
1	COD	mg/L	47	4.78	88.82	-	<40
2	DO	mg/L	2.0	4.5	-	>6	4-6
3	BOD	mg/L	98.7	0	**99.99**	-	<15

As described above Table (3), the results of before treatment and after treatment by using rayon-ZnO nanocomposite exceed the limit of public use compared with guide line (Aquatic life and EPA, USA 2015). These results indicate that the wastewater sample is highly polluted. DO value of water sample was very low and oxygen dissolved insufficiently. So, pretreatment of dyeing wastewater is required for the control of water quality to achieve minimal impact on the receiving ecosystems.

Determination of elemental contents in water samples

Elemental contents of samples (wastewater, treated water and removal efficiency of rayon-ZnO nanocomposite) were expressed in Table (4).

Table 4 Elemental Contents in Water Samples by EDXRF

No.	Element	Unit	Resulted Data			*Guide Line* USA (2015)	
			Waste water	Treated water	Removal Efficiency (%)	Aquatic life	EPA
1	Magnesium	ppm	363	0.148	99.95	-	-
2	Aluminum	ppm	182	0.0541	99.99	-	-
3	Silicon	ppm	185	0.0141	99.23	-	-
4	Phosphorus	ppm	15.1	0.0736	99.51	-	-
5	Sulphur	ppm	1310	0.0730	99.44	30-150	30-150
6	Chlorine	ppm	274	1.51	99.44	-	-
7	Potassium	ppm	39.4	0.0052	99.99	10-12	10-12
8	Calcium	ppm	275	0.0945	99.96	75-200	75-200
9	Titanium	ppm	4.88	0.0005	99.98	-	-
10.	Chromium	ppm	1.76	**ND**	**99.99**	-	0.01- 0.1
11	Iron	ppm	6.39	**ND**	**99.99**	<10	0.05-0.5
12	Copper	ppm	2.26	**ND**	**99.99**	0.05-1.5	0.05-1.5
13	Zinc	ppm	10.2	1.31	87.15	-	-
14	Tin	ppm	12.7	0.0015	99.98	-	-

According to the results, adsorption is viewed as successful, productive and economic strategy for the removal of various contaminations from wastewater. The resulted percent yield of wastewater sample gave satisfactory remarks.

Bacteriological examination of wastewater sample

By microbial examination, E.coli was absent in wastewater. On the other hand according to the analysis results, the wastewater was found to be harmful for aquatic plants and animals on the dyeing area zone flow down into lake. Therefore, dyeing wastewater is required for the control of water quality to its suitability for a particular purpose such as drinking water source, recreation and health, aquatic lives and agricultural use etc. and to achieve minimal impact on the receiving ecosystems.

Calculation of the water quality index

In the present study, the attempt has been made to apply the WQI as useful method in assessing the suitability of water for various uses. Water Quality Index of wastewater was shown in Table (5).

Table 5 Water Quality Index of Wastewater

No.	Parameter	Results	Q-value	Weighting Factor	Parameter Index
1	BOD	98.7	2	0.11	0.22
2	Dissolved Oxygen	2.0	8	0.17	1.36
3	Fecal Coliform	ND	98	0.16	15.68
4	Nitrates	16.74	37	0.10	3.70
5	pH	3.06	4	0.11	0.44
6	Temperature	34.8	10	0.10	1.00
7	Total Dissolved Solids	27030	20	0.07	1.40
8	Total Phosphate	10.52	2	0.10	0.20
9	Turbidity	0.42	84	0.09	7.56
Water Quality Index: WQI					**31.56**
Quality Rating					**Bad**

According to W.Q.I value, water quality level of wastewater sample was found to be bad (Korey, C. PASCO Scientific, 2010). Moreover, Water Quality Index of after treatment by using rayon-ZnO nanocomposite was shown in Table (6).

Table 6 Water Quality Index of Treated Water Sample

No.	Parameter	Results	Q-value	Weighting Factor	Parameter Index
1	BOD	0	96	0.11	10.56
2	Dissolved Oxygen	4.5	8	0.17	1.36
3	Fecal Coliform	ND	98	0.16	15.68
4	Nitrates	0.75	95	0.10	9.5
5	pH	8.75	67	0.11	7.37
6	Temperature	0.62	89	0.10	8.90
7	Total Dissolved Solids	3030	20	0.07	1.40
8	Total Phosphate	0.41	78	0.10	7.8
9	Turbidity	0	97	0.09	8.73
Water Quality Index: WQI					**71.3**
Quality Rating					**Good**

W.Q.I values (quality rating) of water sample level were found to change from bad to good (Korey, C. PASCO Scientific, 2010). Therefore, synthesized Rayon-ZnO nanocomposite has strong absorption and adsorption abilities for a series of organic and inorganic contaminants.

Conclusion

In this research, the synthesis of rayon-ZnO nanocomposite was achieved from rayon and zinc chloride in alkaline condition by using melt compounding process. The synthesized rayon-ZnO nanocomposite could be applied in the wastewater treatment for removal of organic and inorganic pollutant. The removal efficiency of rayon- ZnO nanocomposite was deeply investigated for possible application of textile wastewater treatment. According to the results, rayon-ZnO nanocomposite can remove organic and inorganic pollutant from wastewater. WQI values of water samples were used to indicate the removal efficiency of synthesized rayon-ZnO nanocomposite. According to W.Q.I values (quality rating) of after treatment, treated water can be used in domestic use, specialized industrial application and agriculture. Furthermore, it is suitable for optimizing growth and survival of fish and other aquatic life. So, the composite material as commercial product could be prepared from using raw materials such as ZnO and cellulose (recycle pulp), easy preparation method with low cost and dose.

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