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Recovery of ZnO nanoparticles from spent Zn-C batteries and their application in the degradation of methyl orange dye

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Abstract
Zinc Oxide nanoparticles are recovered from spent Zn-C batteries using Cyphos IL 102 by liquid-liquid extraction technique. The synthesized nanomaterials were characterized in terms of their morphological, compositional, optical and photocatalytic properties. Synthesized ZnO nanoparticles have been used for the photocatalytic degradation of methyl orange dye under UV irradiation. Various parameters have been studied such as effect of irradiation time, dye concentration, catalyst dose, and effect of pH on the percentage degradation of methyl orange. The degradation studies exhibited 82.2% degradation of methyl orange within 180 min under UV irradiation.

Keywords: nanoparticles, batteries, degradation, methyl orange dye

Introduction
World is passing through a phase where new technologies are emerging at fast rate. At the same time new chemicals and materials are being designed and investigated. These advancements in science and technologies on one hand are making the life of human beings easy and comfortable and on the other hand new environmental hazards are posing threat to their life. Two major problems of today's world are ever increasing e-waste and contamination of water and land by industrial waste.

Batteries in the world of science work as a store of energy for consistent power supply at dynamic and static needs and their demand is rapidly increasing around the world. In USA, nearly 3 billion household batteries also called dry cells are sold annually and are used in around 900 million battery-operated devices. In Europe 5 billion units of batteries were produced in year 2000 [1]. Primary (non-rechargeable) and secondary (rechargeable) cells are used in household devices [22]. Among primary cells, alkaline-manganese and zinc-carbon batteries are the ones which are used most.

Zinc-carbon (Zn-C) batteries are primary disposable batteries which are utilized in diverse digital portable devices such as cell phones, alarm clocks, cameras, electric shavers, laptops and recorders, due to their versatility, low maintenance, long life and low cost [3]. In view of their wide spread and varied uses a substantial amount of e-waste is generated every year. To date, management of e-waste is very critical and cannot be overlooked. As a result of the low paybacks recycling industry in e-waste management area has not been fruitful enough to get a favor from business visionaries. In developing countries, the issue of e-waste production has turned out to be phenomenally critical [4]. Mumbai, Delhi, Chennai, Bangalore, Kolkata, Ahmadabad, Hyderabad, Pune, Surat and Nagpur are the top 10 cities producing a major fraction of e-waste in India.

Recycling and further reuse of spent alkaline battery materials leads to provide satisfactory choice to solve the ecological problems rising from this popular electrochemical energy source and is more adapted to sustainability models. According to a report of European Portable Battery Association (EPBA 2011), 79% of the primary batteries that were sold in Europe in 2009 were incinerated or landfilled and only 21% of the overall were recycled [5]. Improper disposal either through incineration or land-filling can raise serious environmental and health concerns. In case of landfilling, toxic metal constituents of batteries are leached by rain water resulting in infiltration. This increases metal toxicity in surface and groundwater streams which cause a serious threat to aquatic life and humans [6]. On incineration of spent batteries, toxic metals such as Cd, Hg and dioxins are released into the atmosphere.

Zn-C and alkaline batteries mainly contain Zn and Mn. Though zinc is not considered a hazardous waste, a serious hassle is ought to pose on its consumption in high concentration by living beings. For instance, excessive Zn uptake in fishes disrupts calcium absorption ensuing in hypocalcaemia and leading to fish death. Zinc toxicity for humans are also reported. ZnO exposure from inhalation causes acute manifestations like fever, respiratory effects, muscle soreness, fatigue and nausea [7]. Zn exposure for a long time might result in bronchiolar leukocytes.

Zinc metal from spent alkaline or Zn-C batteries can be extracted to be used again for making new batteries as raw materials or can be utilized for other functions. In this situation, recycling of spent batteries for metal will be beneficial from both financial and ecological perspective. Distinctive recycling approaches have been proposed for the waste batteries based on hydrometallurgical and pyro-metallurgical routes [8]. High energy consumption, evolution of harmful gases and dust emission into the environment are major limitations of the pyro-metallurgical route [9]. In this case, some undesirable heavy metal impurities may also come along with recovered Zn [2]. Hydrometallurgical processes are usually more economical and efficient. Other advantages are less air pollution, less energy consumption, easy scale up and high selectivity [10]. A number of hydrometallurgical processes such as coagulation, precipitation, adsorption, membrane separation, ion exchange and liquid-liquid extraction have been utilized for the recovery of different metal ions. The majority of these methods is long or time consuming, require high cost and are complex. Whereas, liquid-liquid extraction is a convenient, less time consuming method with less operational cost [11].

A variety of extractants such as Tri-n-butylphosphate (TBP), [12] Cyanex 301 [13] and Cyanex 272 [13] have been investigated either singly or as a mixture for the removal and separation of Zn(II) from spent batteries.

Recently ionic liquids (ILs) have come up as a new generation of solvents due to some categorical features such as low vapour pressure, nonflammables, high thermal stability, low melting point, good recycling capacity and good extraction power of metal ions [14, 15]. Ionic liquids (ILs) have some unique properties which can be altered by changing the substituent group on the combined anion or the cation, making them more fascinating as “green designer” solvents. Lately use of ionic liquids uses for the extraction of metals and organic compounds, biodiesel recovery processes [16] and spent nuclear fuel purification [17] has been reported. A series of phosphonium ionic liquids popularly known as Cyphos ionic liquids is being marketed by Cytec industry. Cyphos IL 102, one of the Cyphos ionic liquid is reported for the recovery of zinc from spent Zn-C batteries [17] The zinc has been recovered as pure ZnO.

Now a days, synthetic organic dyes and pigments are extensively used in different consumer industries such as textile, leather, plastic, paper and cosmetic industry due to their stability and special color characteristics. Among various classes of dyes, the azo dyes represent a major group of dyes and widely used in textile industries due to their easy synthesis, cost-effectiveness and versatility. Non-biodegradability of the synthetic organic dyes causes a severe problem to the aquatic life [18]. The traditional biological treatment methods are not much effective for complete degradation and removal of organic dyes because of their higher stability of dyes [19]. Hence, the removal of dyes from industrial wastewater below environmentally accepted levels before safe disposal is highly desirable.

Methyl orange is one of the azo dye widely used in textile and other industries. It can also be used as coloring agent for the detection of hydrogen gas. Discharge of methyl orange into water bodies is causing many health hazards due to its toxic and carcinogenic (can induce mutations) behaviour [20]. A number of studies are being focussed for the removal or degradation of these dyes such as adsorption [21, 22], filtration [23] and photocatalytic reduction [18].

Use of metal oxide semiconductors is a promising method for photocatalytic purification of wastewater. The photodegradation of organic dyes such as methyl orange (MO) in water is of great importance due to its economic and severe ecological effect on different industrial pollutants. Different semiconductor nanomaterials such as ZnO, Fe2O3, SiO2, TiO2, ZnS and CdS have been widely used as photocatalyst for photocatalytic degradation of dyes [24-27].

As previously mentioned, the reusing of metals from spent batteries should be made more beneficial from an economic point of view. The recovery of largely marketable nanomaterials (especially ZnO) is a suitable option in this regard. ZnO nanoparticles have a broad commercial potential owing to broad applicability as it finds numerous promising applications in optical waveguides, varistors, piezoelectric transducers, photonic crystals, bio-labeling, light-emitting devices, phototransistors, gas sensors, transparent conductive films, photodiodes and solar cell [28-30]. ZnO nanoparticles is a fascinating semiconductor (n-type) possessing a large exciton binding energy of 60 meV and a band gap of 3.37 eV and thus has gained attention in the decomposition of organic dye pollutants with having additional advantages of chemical stability and nontoxicity [31].

In the present study, the conditions optimized by Singh *et al*. [32] have been used to recover zinc as ZnO from spent batteries by using Cyphos IL 102 ionic liquid. Characterization of synthesized nanoparticles has been ascertained by energy dispersive X-ray spectroscopy (EDX), field emission scanning electron microscopy (FESEM), diffuse reflectance spectroscopy (DRS) and X-ray diffraction spectroscopy (XRD). We planned to use these ZnO nanoparticles as photocatalyst to degrade methyl orange. The photocatalytic activity of ZnO nanoparticles was then evaluated by studying the degradation of methyl orange dye under UV irradiation with freshly synthesized ZnO nanoparticles. The effect of various experimental parameters such as dye concentration, irradiation time, catalyst loading and solution pH was examined. The ZnO nanoparticles exhibited ~81% MO decomposition within 180 min which showed comparable results with ZnO synthesized from spent batteries.

2. Experimental Section

2.1 Extraction of zinc

Spent Zn-C batteries were dismantled and the black powder was separated and dried in an oven at 80 ^{0}C for 24 hours. Dried powder was then sieved through 75 µm sieve to obtain a fine black powder. For digestion, 1.0 g black powder was heated with 20 mL aqua-regia up to boiling for 30 minutes, cooled and filtered [33]. Filtrate and washings were collected and then appropriately diluted with ultrapure

water. Metal contents of digested sample were analyzed using ICP-MS (Table 1).

Leaching was performed by heating 10 g of the black powder with 100 mL of 5.0 mol/L HCl for 2 hours at 70 ^{0}C [34]. The contents were cooled, filtered and diluted to 400 mL maintaining the acidity at 0.8 mol/L HCl. Concentrations of different metal ions in leach liquor were checked by ICP-MS (Table 1).

Table 1: Concentrations of metals in digest and leach liquor of spent Zn-C batteries.

Metals analyzed	Concentration in digested liquor (mg/ L)	Concentration in leached liquor (mg/ L)	Leaching efficiency (%)
Zinc	3840	3805	99.09
Manganese	5090	5020	98.62

2.2 Synthesis of zinc oxide (ZnO)

For the synthesis of ZnO from Zn-C battery leach liquor, the reported method was used [32]. 50 mL of 0.2 mol/L Cyphos IL 102 was shaken repeatedly with equal volume of leach liquor (5 times) of Zn-C battery for 5 minutes to get Zn enriched loaded organic phase. The loaded organic phase was scrubbed with 1.0 mol/L HCl to remove minute amounts of other co-extracted metal ion if any. 50 mL of 0.2 mol/L oxalic acid was added drop wise into the loaded organic phase with continuous stirring and the resulting mixture was stirred for two hours at room temperature. The resulting solution was centrifuged at 2500 rpm for 10 minute. White precipitates thus obtained were washed with methanol, filtered and dried in an oven at 60 °C. The obtained white product was grinded in pestle mortar for 30 min at room temperature and ZnO nanoparticles were obtained by thermal decomposition of the grinded material at 400 °C for 3 hour [35]. Synthesized ZnO nanoparticles were characterized using XRD, FE-SEM, EDX and UV-DRS techniques.

From ten spent Zn-C batteries around 1.5 g ZnO was obtained which was not sufficient for the entire study. So, it was planned to synthesize ZnO from zinc acetate using the same procedure and to study the effect of various parameters on the degradation of methyl orange dye with this ZnO. The ZnO obtained from zinc acetate was designated as ZnO-synthetic and the one obtained from battery leach liquor was named as ZnO- battery. Finally, the degradation of methyl orange in presence of ZnO-battery was carried out under the conditions optimized with ZnO-synthetic and the results were compared.

2.3 Photocatalytic degradation of methyl orange

For the photocatalytic degradation study,10 mL of 20 ppm methyl orange solution was irradiated with UV radiation at 365 nm in presence of 80 mg of synthesized ZnO as photocatalyst at neutral pH (unless mentioned otherwise). Before UV irradiation, the mixture of ZnO and dye was shaken for 30 min to stabilize the absorption of methyl orange over the photocatalyst surface. After that, the photoreaction vessel was exposed to UV light under ambient conditions. After irradiation, the photo reacted mixture was taken out and centrifuged at 2500 rpm to separate the ZnO catalyst. The change in the absorbance of methyl orange peak was monitored using UV–Visible spectrophotometer.

3 Results and Discussion

3.1 Characterization of ZnO nanoparticles

3.1.1 P-XRD

Powder XRD of zinc oxide (ZnO-synthetic and ZnO-spent batteries) is illustrated in Figure 1. All the diffraction peaks of ZnO are well indexed. Both the ZnO nanoparticles revealed nine characteristics peaks at (100), (002), (101), (102), (110), (103), (200), (112) and (201) planes at 2θ values; 31.52, 34.12, 36.08, 47.3, 56.43, 62.61, 66.19, 67.66 and 68.8 and at 31.52, 34.28, 36.08, 47.3, 56.43, 62.77, 66.19, 67.82 and 68.97 for ZnO-synthetic and ZnO-battery, respectively. These peaks correspond to the hexagonal ZnO zincite structure (JCPDS no. 36-1451).Crystallite size of zinc oxide was calculated using Debye-Scherrer equation:

$$D=0.9\boldsymbol{\lambda}/\beta Cos\theta$$

Where, $\boldsymbol{\lambda}$ is wavelength of X-ray beam, β is line broadening measured at half-height of the most intense peaks and is the Bragg angle. The crystallite size was 18.9 nm and 14.7 nm for ZnO-synthetic and spent batteries respectively.

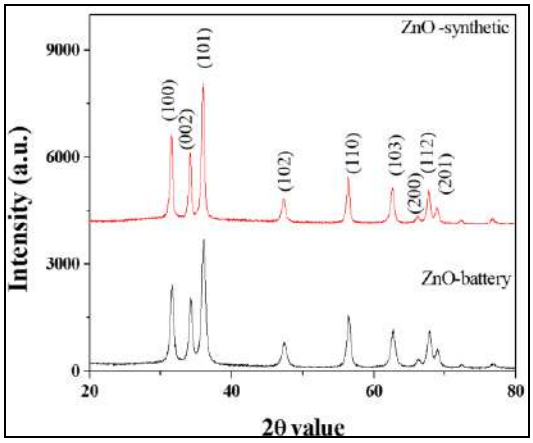

Fig 1: P-XRD pattern of ZnO-synthetic and ZnO-battery nanoparticles.

3.1.2 FE-SEM and EDX

FE-SEM images [Figure 2(a) and 2(b)] depict the morphology of the synthesized nanoparticles. FE-SEM exhibits spherical morphology and agglomeration. Particles are uniform in size and shape with an average particle size of 26 nm and 39 nm for ZnO synthetic and spent batteries, respectively. The elemental composition of ZnO nanoparticles (synthetic and spent batteries) was analyzed by energy dispersive X-ray (EDX). EDX spectra as shown in Figure. 3 (a) and (b) indicate that ZnO nanoparticles contain Zn and O only, with nearly 1:1 atomic percentage. Elemental analysis obtained by EDX is given in Table 2. No other characteristic peaks of impurities have been detected in EDX spectra indicating the purity of synthesized product.

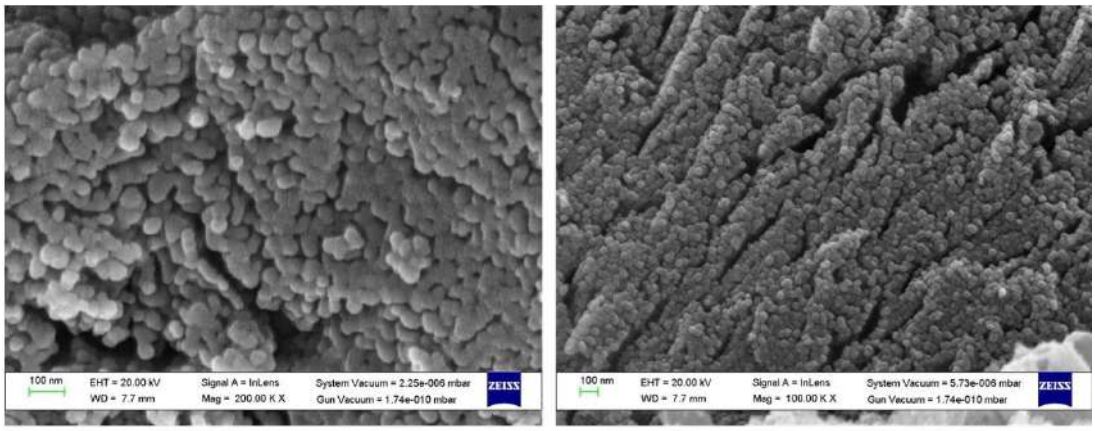

Fig 2: FE-SEM images of (a) ZnO-synthetic and (b) ZnO-battery nanoparticles

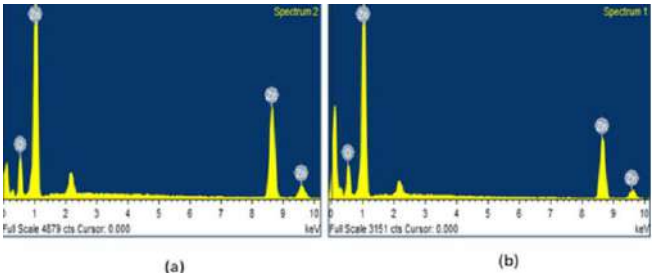

Fig 3: EDX spectra of
(a) ZnO synthetic and (b) ZnO- battery

Table 2: Elemental analysis of (a) ZnO-synthetic and (b) ZnO-battery

Element	Weight%	Atomic%
O K	20.27	50.95
Zn K	79.73	49.05
Totals	100.00	

(a)

Element	Weight%	Atomic%
O K	20.02	50.56
Zn K	79.98	49.44
Total	100.00	

(b)

3.1.3 UV-DRS

The UV-DRS spectra (Figure 4) of ZnO nanoparticle (both ZnO- battery and ZnO- synthetic) were recorded by using SHIMADZU UV-2450 spectrophotometer that shows a clear flat band structure. The band gap of the ZnO nanoparticles was calculated using the data of UV-DRS spectra, which comes out to be ~ 3.21 eV for ZnO synthetic and ~3.19 eV for ZnO battery.

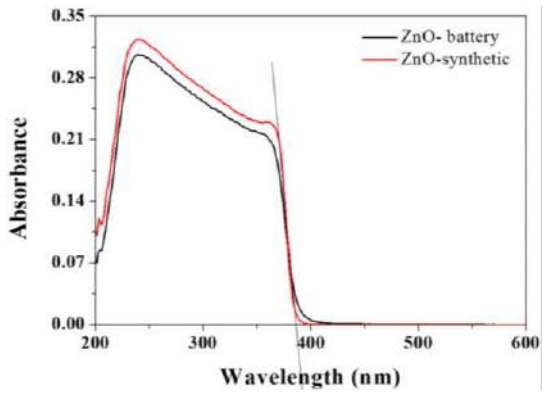

Fig 4: UV-DRS spectra of ZnO nanoparticles

Results of characterization studies indicate that ZnO-synthetic and ZnO-battery both have similar characteristics such as structure, morphology, atomic percentage and band gap.

3.2 Photodegradation of methyl orange

A 20 ppm solution of methyl orange (10 mL) was taken and irradiated in UV light. The λmax of methyl orange comes at 461 nm.

3.2.1 Effect of irradiation time

The percentage degradation of methyl orange (20 ppm, 10 mL) was assessed at different irradiation time intervals. Figure 5(a) represents the UV–visible spectra of the decomposed methyl orange over the surface of ZnO (80 mg) serving as a photocatalyst. With the increasing irradiation time the absorbance intensity of methyl orange decreased continuously resulting in degradation of MO up to 81% after 180 min UV- irradiation Figure 5(b).

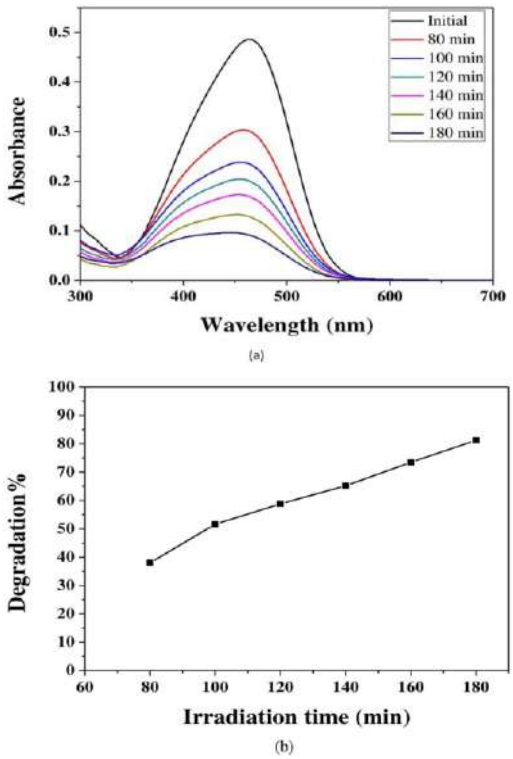

Fig 5: (a) UV–visible absorbance spectra of methyl orange (20 ppm) and (b) degradation % at different irradiation time intervals in the presence of ZnO-synthetic nanoparticles (80 mg), pH=7.4.

3.2.2 Effect of methyl orange concentration

Figure 6 represents the photocatalytic activity of ZnO at various methyl orange concentrations at optimized irradiation time 180 min and 80 mg ZnO. Maximum degradation of ~ 94.0% at 5 ppm methyl orange concentration was observed which suggests that as the concentration of methyl orange in solution decreases, photocatalytic efficiency of ZnO increases. From the results, 20 ppm dye concentration was selected for further studies.

3.2.3 Effect of photocatalyst dose

Photodegradation of methyl orange (20 ppm) at different catalyst dose was examined for an irradiating time of 180 min shown in Figure 7. The % degradation increases on increasing the amount of ZnO up to 80 mg of ZnO and then remains constant. It is found on increasing the amount of photocatalyst, the degradation of methyl orange increases which is attributed to the increased number of active sites and available adsorption sites. Almost constant degradation with further increase in the amount of photocatalyst could be attributed to the particle interaction, such as aggregation, which would lead to decrease in total surface area.

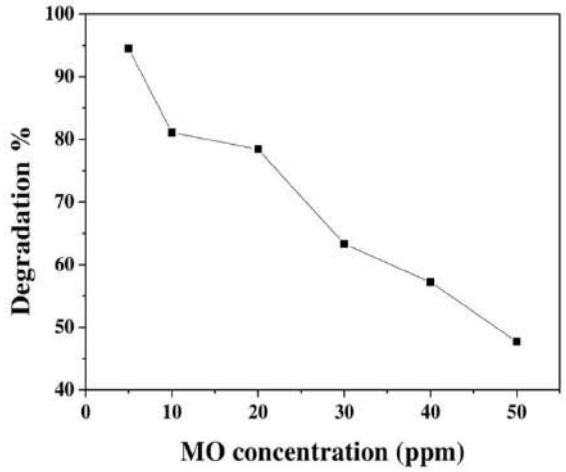

Fig 6: Degradation of methyl orange at different concentration, 180 min UV- irradiation and ZnO (80 mg), pH=7.4.

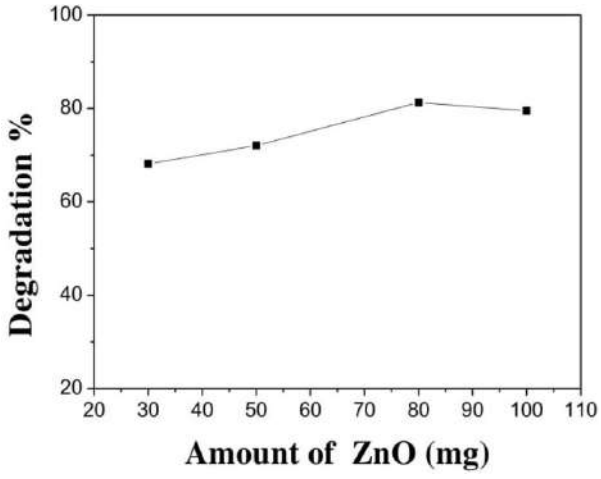

Fig 7: Effect of catalyst dose on percentage degradation of methyl orange (20 ppm), irradiation time (180 min), pH=7.4.

3.3 Methyl orange degradation using ZnO-battery

Zinc oxide which was synthesized from spent batteries was used for the degradation studies of methyl orange at optimum conditions. The Figure 8 shows the absorption spectra of the methyl orange before and after UV-irradiation for both ZnO-synthetic and ZnO-battery. Methyl orange degraded ~82.2% after 180 min of irradiation which is almost equal/ comparable to degradation by synthetic zinc oxide.

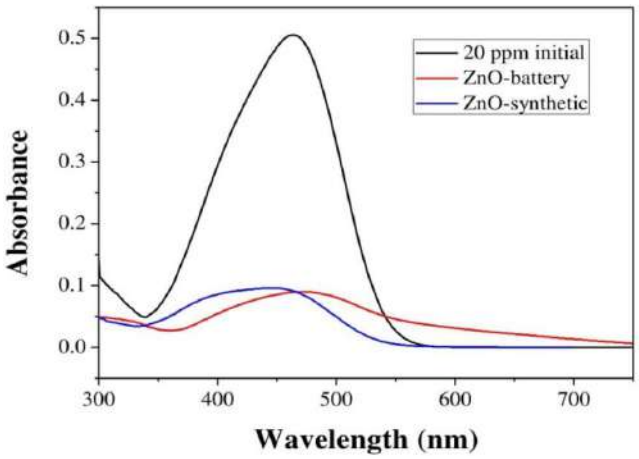

Fig 8: Absorption spectra of methyl orange before and after 180 min UV irradiation using ZnO-battery and ZnO-synthetic, pH=7.4.

4. Conclusion

Present studies reveal that spent Zn-C batteries can be recycled by liquid-liquid extraction route to recover zinc as zinc oxide nanoparticles using a phosphonium ionic liquid. The synthesized ZnO nanoparticles are spherical in shape with a size of 39 nm. Calculated band gap for ZnO particles is ~3.19. Recovered ZnO was found to be efficient catalyst for the photodegradation of methyl orange dye under UV irradiation. Experimental results revealed that presence of ZnO and UV light is necessary for degradation of dye. It was observed that degradation of methyl orange is dependent upon parameters such as irradiation time, finally, the study demonstrates recycling of waste spent batteries and use of recovered product to minimize another waste, methyl orange, by photocatalytic degradation.

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