IJCRT.ORG ISSN : 2320-2882

INTERNATIONAL JOURNAL OF CREATIVE RESEARCH THOUGHTS (IJCRT)

An International Open Access, Peer-reviewed, Refereed Journal

One Pot Synthesis And Characterization Of Iron-Graphite Oxide Nanocomposites For The Electrochemical Decoloration Of Textile Dye; Deep Green 474

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Abstract

This work explores the green, convenient and one-pot preparation of Iron- graphite oxide nanocomposite. A series of measurements like X-ray powder diffraction analysis (XRD) was carried out to identity the crystalline structure and phase of the synthesized sample. The surface morphological features, crystal structure and basic chemical elements of synthesized nanocomposite were analysed using SEM and EDAX analysis. A study is carried out for the application of synthesized nanocomposites for the electrochemical degradation of a carcinogenic textile dye, Deep Green 474, in an electrochemical cell having carbon electrodes. The dye decoloration of 99.8% takes place in the presence of 0.003g/L of GO, at a current density of 0.04A/cm^2. The results indicated that the synthesized nanocomposite has high dye removal capacity with good reusability. Therefore, the obtained nanocomposite from this facile one-pot synthesis method exhibit great potential in biological and environmental remediation.

Key words: carcinogenic, dye degradation, electrochemical, graphene oxide, nano composite

I. INTRODUCTION

In the Current era of research, graphite oxide (GO) is an emerging innovative material in the world of science and technology because of their unique and outstanding properties [1, 2]. There are lots of research is going on graphene with good mechanical and electrical properties are devoted to prepare nanostructures which offer the desired properties [3-5]. Because of its unique structure, excellent performance, and low cost, graphene can be applied in various fields like electrical, medical fields etc. Many functional groups, for instance, carboxyl and hydroxyl groups, are present on the surface of hydrophilic GO, which can combine with other substances [6–8]. Recently, many researchers are fabricating and utilizing novel graphene oxide–metal oxide nanocomposites for environmental remediation by the degradation and elimination of toxic organic contaminants and heavy metals, and for antibacterial applications.

Due to the unique properties and simplicity in the method of synthesis in laboratory, iron oxide nanostructures (IONs) have achieved a special position among other nanosized metal oxides [9, 10]. Electrical, optical, magnetic and catalytic properties of iron based materials have been exploited for realizing many different purposes in a vast variety of research items. They have been extensively used in supercapacitors, data storage, lithium ion batteries, catalysis, drug delivery, therapeutic agents as well as water treatment [11, 12].

Graphene-based iron oxide (Fe_3O_4) nanocomposites can be synthesized by various methods such as hydrothermal synthesis, thermal decomposition [13, 14], co-precipitation [15,16], sol-gel method [17], and colloidal chemistry method. Among these preparation techniques, chemical co-precipitation technique has proven to be the most promising technique for the production of nanomaterials. Chemical co-precipitation technique is quite simple, cheap, the most environmentally friendly and the particles can be obtained with controlled particle size.

Dyes have been extensively used in textile, leather tanning, cosmetics, pigment and many other industries [18, 19]. The presence of the toxic chemical levels of aquatic sources, and pose a threat to the human health. [20]. Therefore, it is necessary to eliminate dyes from wastewater effectively prior to their final discharge to the environment. Advanced oxidation processes (AOPs) have been considered as a robust and efficient alternative for treating the dye contaminated wastewater when the common treatment processes, such as sedimentation, flocculation, adsorption and membrane filtration are insufficiently effective.

In the present work, our motivation is to synthesize and characterize the iron based GO nanocomposite to show its enhanced properties for its application in decolouration of a toxic textile dye.

II. MATERIALS AND METHODS

Chemicals and Reagents:

Natural graphite flakes, Mohr's salt, NaCl, NH_4OH, $NaNO_3$, $KMnO_4$, H_2SO_4, HCl, H_2O_2 (30%), $KMnO_4$, are obtained for SD Fine chemicals, India and the toxic textile dye Deep Green 474 was obtained from Molaklmuru textile dying industry. All the chemicals were of analytical reagent grades and used as received, without further purifications. The aqueous solutions were prepared in double distilled water. The carbon electrodes of > 90% purity were obtained from commercial dry cell , tested for purity and proper surface treatment were given before electrochemical experiments.

Preparation of graphite oxide:

The graphite oxide was prepared by Hummer's method [21]**.** The prepared graphite oxide (GO) was characterized by UV-Visible and FT-IR spectroscopy.

Synthesis of Iron - graphite oxide nano composite:

The prepared 10 mg of GO was dispersed in 50 mL deionized water and ultrasonicated for 20 minutes. About 2-3 cm^3 of con. HNO_3 is added to the 25mL of 3mM Mohr salt solution taken in a beaker. The solution was boiled for about five minutes in order to convert Fe^{2+} to Fe^{3+} (The solution turns from green to yellow). This reduced iron solution was added to the above ultrasonicated GO suspension and heated slowly to 80^oC. Then 40% ammonium hydroxide solution added with a burette for about thirty minutes with continuous stirring. After the addition, the solutions turns to black colour and finally pH was reached to 9 to 10. The obtained black compound was washed several times with water, filtered and dried in the vacuum to get Fe-GO composite [22].

Instrumentation:

Scanning Electron Microscopic studies:

The surface morphologies of the composite samples were examined by scanning electron microscopy, using a ZEISS Supra 40 scanning electron microscope (SEM).

EDAX analysis:

The weight percentage of elements in the metal nano-composite coatings were verified by using energy dispersive X-ray analysis using FEI ESEM Quanta (EDAX) machine.

UV-Visible Spectroscopic studies:

Ultraviolet-Visible (UV-Vis) spectra of synthesized graphene oxide samples were collected on a UV-Vis spectrophotometer (Systronics 119).

FTIR Spectroscopic studies:

Characterization techniques Fourier transform infrared (FTIR) spectra of the synthesized graphene oxide samples were recorded on a Shimadzu spectrophotometer using KBr as the mulling agent.

XRD studies:

XRD analyses of the powdered samples were performed using an X-ray power diffractometer with Cu anode (PAN Analytical Co., X'pert PRO, Almelo, The Netherlands), running at 40 kV and 30 mA, scanning from 4 to 80^o at 3/min, for data including particle size or crystallinity measurement.

Electrochemical degradation of textile dyes:

Graphite carbon electrodes of 4.5 cm length and 0.8 cm diameter were used as anode and cathode for electrochemical degradation studies [23]. The supporting electrolytes such as NaCl were added to the electrolytic solution, which increases the conductivity of the solution and reduces the electrolysis time. The solution was kept under agitation using magnetic stirrer. The experimental set up is as shown in the Figure 1.

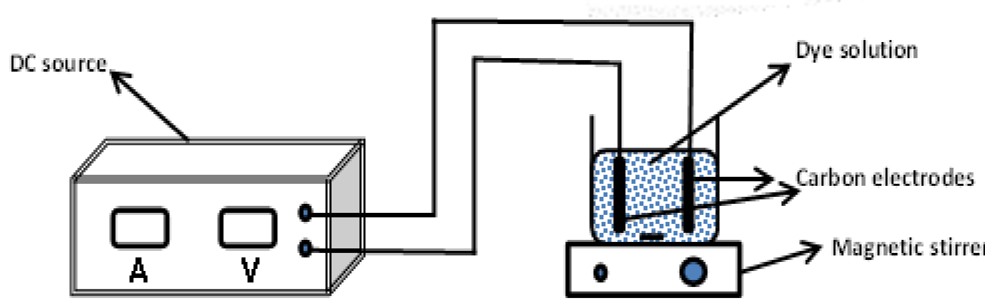

Figure 1. Experimental setup for the electrochemical dye drgradation

Batch Studies for the electrochemical degradation of dye Deep Green 474:-

Few batch studies were carried out in 250-mL of dye solution. A weighed amount (0 to 0.003g) of nanocomposites was added to the dye solution in flasks. The flasks were agitated at a speed of 140 rpm in an incubator shaker at 308 K. The influence of pH (2.0-14.0), initial dye concentration (0.01 – 0.04 mg L^{-1}), nanocomposite dosage (0-0.012 g L^{-1}), current density (0-0.06 Amps) and temperatures (298, 303, 310, 313, 318 K) were evaluated. At regular time intervals samples were collected for measuring the residual dye concentration in the solutions.

Now at a time interval of 2 minutes, 5 minutes, 8 minutes, 12 minutes and 15 minutes samples were taken out, centrifuged at 10000 rpm for 15 minutes and the amount of dye removed from the solution and the residual amount of dye in each flask was explored was measured using a spectrophotometer. The same process was carried out for nanocomposites.

UV-visible studies: A UV-Vis Spectrophotometer (ELICO, SL-159) was employed to measure the optical density of (at λ_{max}) dye effluent before and after electrolysis. The decolourisation efficiency was calculated using the relation:

$$\%E = \left\{\frac{(A_i - A_e)}{A_i}\right\} \times 100$$

where, A_i and A_f are absorbance values of dyes solutions before and after treatment with respect to their λ_{max}, respectively.

III. RESULTS AND DISCUSSIONS

Characterization of Fe-GO composite:

Figure 2 shows the XRD patterns of GO / Fe composite. The diffraction pattern of it is shows a weak peak at around $2\Theta = 12^o$ and 45^o, originated from their respective (001) and (100) reflections. Another wide peak around $2\Theta = 28^o$ can also be observed, which is the characteristic (002) peak of residual unoxidized graphite. The diffraction peaks correspond to the (37) and (64) crystal planes characteristics of Fe-GO bondings [24]. A diffraction peak appears at $2\theta \approx 22\,^o$ due to the short range order of stacked graphene sheets [25].

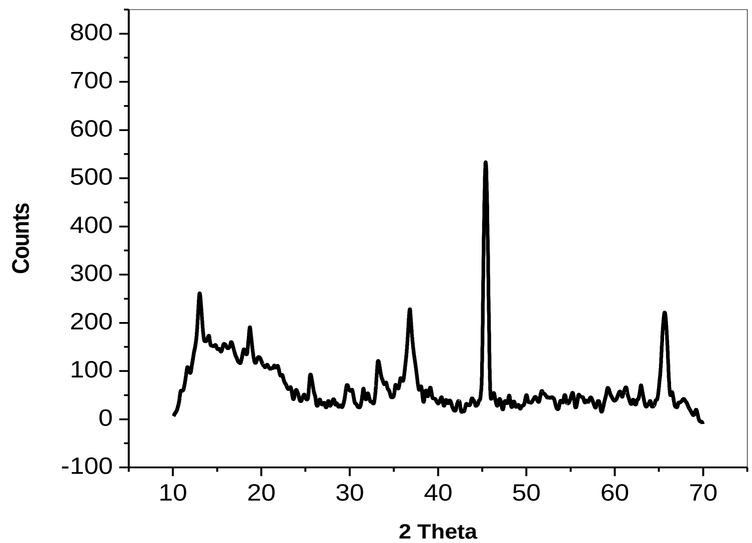

Figure 2. XRD patterns of Fe/GO composites

The SEM image of Fe/GO (shown in Figure 3) indicates that the GO sheets are tightly bound onto the Fe microspheres. Fe spheres greatly help in preventing the restacking of the GO sheets, avoiding the loss of a highly active surface area. Furthermore, due to the good exfoliation of graphite, the obtained GO layers are apparently transparent even under SEM observation [26]. The dispersion of Fe particles is well, and there is little observable aggregation of those nanospheres, which is attributed to the in-situ growth of may be nanosized Fe particles followed with the chemical interaction between ferric or ferrous ions and the carboxylate or hydroxyl groups [27].

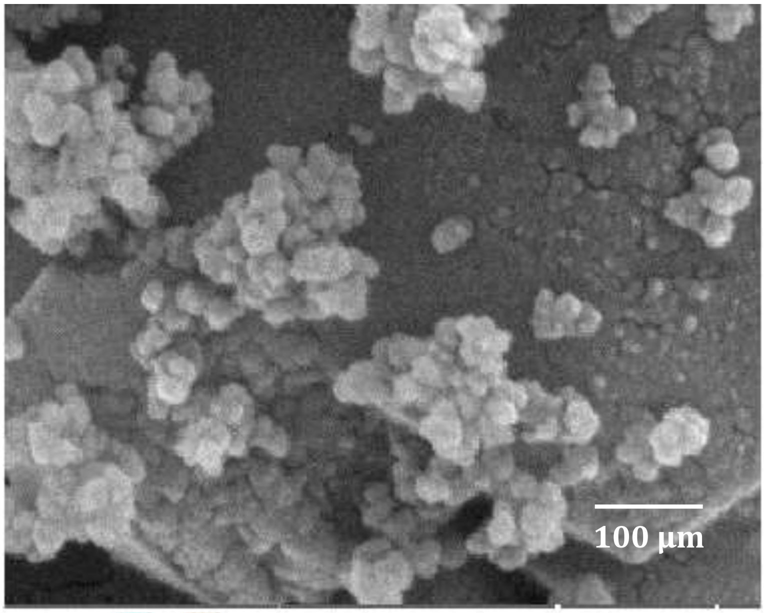

Figure 3. Scanning electron microscopy (SEM) image Fe– GO composite structures.

Figure. 4 shows EDX spectrum of the GO/Fe nanocomposite. The analysis shows that the prepared composite includes only iron, carbon, and oxygen in similar with the chemical composition of the composite as shown in the inset.

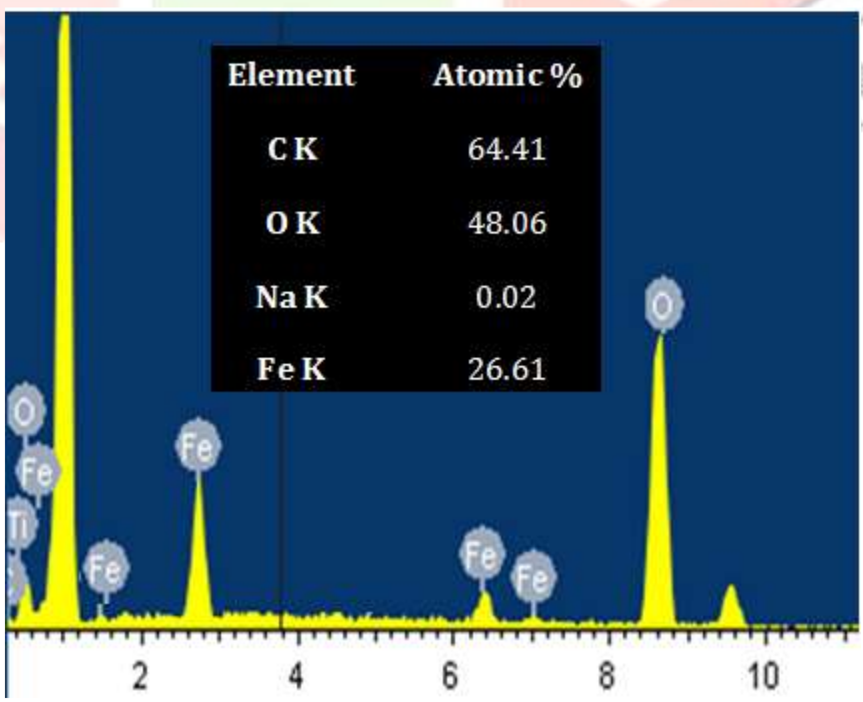

Figure 4. Energy dispersive X-ray spectroscopy of Fe –GO composite.

Degradation of Textile Wastewater by Electrochemical Method using synthesized nano composites; Application of Fe-GO nano composite for the electrochemical degradation of textile dye Deep Green 474:

Influence of electrolytic conditions on dyes degradation

Effect of initial pH: Solution *p*H is one of the important factors that affect the performance of electrochemical process. Hence experiments were conducted to study the effect of *pH* on the degradation efficiency of textile effluent. A significant difference in the extent of decolourisation was noted when concentration of NaCl was at 0.75 g /250mL. The initial *p*H of the solution (3-11) was adjusted using 1N H_2SO_4 or NaOH [28]. The electrolysis was carried out at the current density of 0.02 Acm^{-2} for 10 mins with a textile effluent and at room temperature (308K). After electrolysis the results indicate that final *pH* was slight varied from acidic condition and decreased from basic conditions. The decolouration efficiency of dye effluent was found percentage of 99.5 % in acidic *pH*-8 It indicated that the degradation of dye effluent in acidic solution is higher than that of in the basic media. Therefore the optimum *pH* 8 was maintained in subsequent experiments.

Effect of current density: Current density is a very important variable in electrochemical engineering. As shown in the Figure 5, the colour and removal efficiency was increased by increasing the applied current density (0.01to 0.06 A/cm^{-2}) the results may attributed to the increased oxidant such as: chlorine/hypochlorite, hydroxyl radicals at higher current densities. This is because of the increased rate of generation of oxidants, such as chlorine/hypochlorite and hydroxyl radicals at higher current densities. Up to a current density of 0.03 A cm^{-2}, the degradation efficiency of the dye was increased almost linearly [29]. At the same time, more energy will be consumed at higher current density applied. Therefore, the optimal current density for the successive electrochemical degradation of dye effluent was $0.04 A/cm^2$.

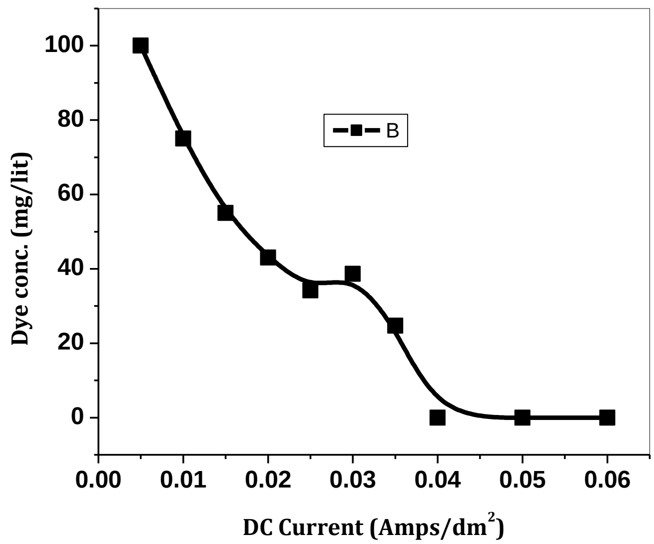

Figure 5. Effect of current density

Effect of supporting electrolytes

When NaCl is added, the decolourisation efficiency increased with a subsequent decrease in the applied voltage. From this observation it concluded that the introduction of NaCl increases efficiency of decoloration and obtained maximum efficiency at 0.75g/250mL [30].

Effect of Fe-GO nanaocomposite:

Figure 6. shows the effect of Fe-GO nano particle concentration on the decoloration of Deep Green 474. In these conditions, the removal of ions in dye from wastewater is mainly due to the combination of the electro-adsorption of particle electrodes and anodes and the enrichment of ions in the solution [31]. The concentration of Fe-GO nanoparticle is increased from 0 to 0.003g/250mL.

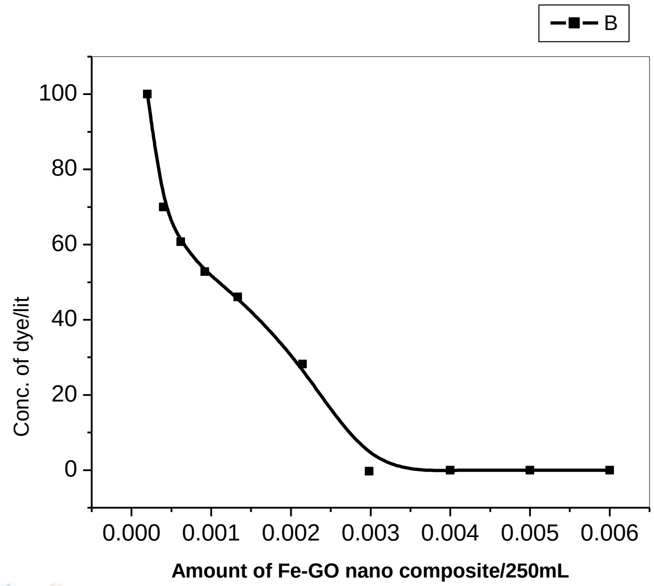

Figure 6. Effect of Fe-GO nano composite

IV. CONCLUSIONS

In the present work, Iron- graphite oxide nanocomposite was prepared by a green, convenient and one-pot preparation method. The surface morphological features, crystal structure and basic chemical elements of the prepared Fe-GO composite, were confirmed by using XRD, SEM and EDAX analysis. The electrochemical degradation of Deep Green 474 was carried out using carbon as anode and cathode, in the optimal operating conditions (current density 0.04 A cm^{-2} , NaCl concentration 0.75g/250mL and at room temperature). The effect of conducting salt clearly showed that the introduction of Cl^{-} containing electrolytes enhance the degradation efficiency of the dye. The degradation of dye effluent in acidic solution is higher than that of in the basic medium. The dye decoloration of 99.8% takes place in the presence of 0.003g/L of GO, at a current density of $0.04A/cm^2$. The results indicated that the synthesized nanocomposite has high dye removal capacity with good reusability. Therefore, the obtained nanocomposite from this facile one-pot synthesis method exhibit great potential in biological and environmental remediation.

Acknowledgements

The authors would like to thank all the administrative authority of Sir M. V. Government Science College, Bommanakatte, Bhadravathi who helped to carry out this work.

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