Fabrication and characterization of magnetite/reduced graphene oxide composite incurred from iron ore tailings for high performance application

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HIGHLIGHTS

- A new composite was designed from IOTs with graphene support and PVP as surfactant.
- The formation of microspherical Fe_3O_4/rGO composite was confirmed by TEM analysis.
- The composite exhibits a promising performance as an electrode material.
- Preliminary cost analysis is performed for its use in energy storage applications.

GRAPHICAL ABSTRACT
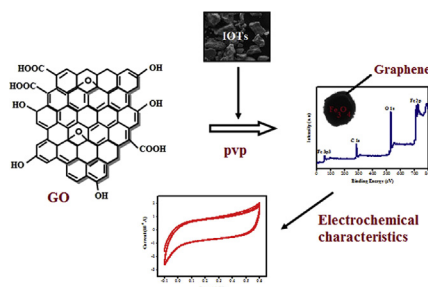
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ABSTRACT

A feasible approach to synthesis iron oxide (Fe_3O_4) from waste iron ore tailings (IOTs) to synthesis magnetic graphene (Fe_3O_4/rGO) is demonstrated in the present study. Plain Fe_3O_4 was prepared by acid leaching of IOTs with hydrochloric acid followed by co precipitation. The anchoring of Fe_3O_4 onto the graphene template was done by hydrothermal method involving polyvinylpyrollidone (PVP) as a surface directing agent. The samples were characterized by FTIR, XRD, SEM, TEM, Nitrogen adsorption—desorption studies, XPS and Raman spectroscopic analysis. The electrochemical performances of the material were evaluated by cyclic voltammetry, electrochemical impedance spectroscopy and galvano-static charge—discharge techniques. The synergistic effect between the rGO matrix and Fe_3O_4 directs to increased conductivity and ionic diffusion, leading to a material with superior electrochemical performance. Thus the synthesis of magnetic graphene composite from IOTs was technically feasible, providing additional opportunities for future application of these composites in environmental management.

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1. Introduction

There has been a growing concern about the energy and the environmental problems over the past decades and many researchers are dynamically concentrating on the water treatment by various techniques to make the treated water suitable for reusable purpose. Apart from water contamination and energy crisis, accumulation of solid wastes generated from various mining and industrial activities also has a significant role in environmental issues. Rapid industrialization is causing major damage to the environment which compels environmentalists to invent several methods in respect of generation, treatment, transport, handling, disposal and recycling of solid/liquid wastes [1—4]. Among the various solid

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wastes, (IOTs) contribute a major part of the accumulating waste over the world with serious environmental issues. As per the statistical survey, the accumulation of iron ore tailings is 130 million tons annually and every 1 ton of the concentrate discharge 3 tons of iron ore tailings, with the assumption that the tailings constitute 11% of iron [5] and is one of the fast accrued wastes and poses serious environmental threats. In India, the generation of all non-hazardous inorganic industrial wastes is estimated to be 200 million tonnes, out of which approximately 80 million tonnes are due to mine tailings mainly from iron, copper and zinc ores processing. As per record, India represents the fifth position in iron ore deposits in the world and the seventh position in production of iron ore concentrate [2].

Immediate awareness is required to find some alternative uses of iron ore tailings in order to alleviate environmental issues and attain sustainability. Several efforts have been made during the last decades for possible alternative utilization of iron ore tailings in different domains like adsorption [6], production of cementitious composites [7], clinker, forsterite refractory etc. [8–10], or as a secondary source of iron and silica for synthesis of magnetite [11] and other value added products [12,13], respectively. The traditional magnetic material Fe_3O_4 is progressing to be the thrust area of research and of immense technological interest, due to its applications in the field of magnetic data storage [14], catalysis [15], solar energy transformation, electronics [16], biomedicine, bio sensors [17,18], wastewater treatment [19] and many. Different synthesis strategies have been adopted to obtain diverse morphological size and shaped magnetic nanoparticles for specific applications. In this aspect Giri et al., 2011 [20] have synthesized magnetic nanoparticles from waste iron ore tailings and used it for the removal of congo red and methylene blue from aqueous solution and the adsorption capacity was in par with the reported values of the materials obtained from reagent grade chemicals. This study brings about the possible use of IOTs and its application in wastewater remediation process.

To elevate the advantages mentioned above, to enhance the chemical activity of the plain Fe_3O_4, to ease the ineludible difficulty in stability due to easy oxidation in atmospheric conditions and to overcome the aggregation of these fine particles [21], magnetite should be stabilized by coating it with a surfactant or with an inorganic material such as carbon or silica [22,23].

In this present study, magnetic Fe_3O_4 nanoparticles were prepared from iron ore tailings and was incorporated with graphene oxide (GO) to assess its potential as an electrode material for electrochemical capacitors. Owing to the excellent and unique properties of graphene such as large surface area, high electron mobility and electrical conductivity, higher thermal stability and mechanical properties [24,25], the material has a vast potentiality as an electrocatalyst and also provides progress in the field of electrochemistry. Typically, graphene is not mostly used in the composite preparation owing to its poor dispersion in various solvents. On the other hand GO with various oxygen containing functional groups can be obtained in large quantities with good dispersibility and hence it is favoured in the present synthesis route. The obtained GO can be reduced chemically which virtually resembles graphene and the desired electrical, thermal and electrochemical properties can be accomplished. It is well reported that metal based nanoparticles enveloped with graphene can elevate electrochemical performance.

This study paves way to a novel approach to explore an economically viable method of recycling IOTs into potentially useful material and in the present work the composite derived from IOTs have been used as an electrode material for electrochemical applications and a brief economic analysis has also been attempted. The experimental results provide another possible route for the alternative utilization of waste IOTs as an electrode material for electrochemical capacitors.

2. Materials and methods

2.1. Materials

Graphite powder was obtained from Loba Chemicals, Potassium permanganate ($KMnO_4$), sodium nitrate ($NaNO_3$), aqueous ammonia solution, hydrogen peroxide (H_2O_2), sulphuric acid (H_2SO_4), Ferrous sulphate ($FeSO_4·7H_2O$), poly-vinylpyrrolidone(PVP), double distilled water (DD water) were purchased from SRL chemicals. Iron ore tailings, collected from local iron ore industries and the samples were analysed for higher content of iron by ICP-OES analysis and the sample with high iron content of 45.2% was used in the present study. All other chemicals were of analytical reagent grade.

2.2. Preparation of iron oxide/reduced graphene oxide composite

A weighed amount of IOTs was acid leached with HCl (1:1) at 90 °C in order to leach out the iron content. The acid insoluble portion was separated by filtration and the filtrate containing $FeCl_3$ was treated with calculated amount of hydrogen peroxide (H_2O_2). Filtrate was heated to 60 °C, and its pH was maintained below 4 by adding an appropriate amount of concentrated ammonia. As a result, Fe was separated from tailings and precipitated into $Fe(OH)_3$. Finally, $Fe(OH)_3$ was washed repeatedly with de-ionized water, Then $FeCl_3$ solution was obtained by $Fe(OH)_3$ precipitate dissolution with hydrochloric acid (1:1) [25]. GO was synthesized by the previously reported procedure [26]. To the ferric chloride solution obtained from IOTs where the % weight of Fe found to be (36.45%), calculated amount of $FeSO_4.7H_2O$ (2:1), 0.60 g PVP and 30 mL as-prepared GO solution (3 mg mL^{-1}) were added and the solution was mixed with 30 mL deionized water and magnetically stirred for 30 min. Aqueous ammonia solution (5 mL) was added dropwise to the above solution and again stirred for 30 min to ensure complete ion exchange. The solution was transferred to 90 mL Teflon-lined stainless steel autoclave and maintained at 160 °C for 12 h. The resulting solution is cooled at room temperature and the black solid mass was collected by filtration, washed with ethanol and double distilled water each for several times and dried at 80 °C in a vacuum oven. A preliminary cost analysis for the synthesis of GO and the composite using IOTs as source was also attempted where the fixed capital cost for the purchase of equipments and glassware's were not considered.

2.3. Characterization

Inductively coupled plasma-optical emission spectroscopy (ICP-OES) was performed to analyse the (metal) constituent's present using Perkin Elmer Optima 5300 DV model. The Fourier transform infrared (FTIR) spectrum was analysed using FT-IR spectrometer PERKIN ELMER RX-1 FI-IR SYSTEM. X-ray Diffraction (XRD) measurement was carried out with Xpert-Pro-PAN analytical instrument using CuKα radiation (λ = 1.5406 Å) over the range of 2θ = 10–90° at room temperature with 45 (kV). Nitrogen adsorption–desorption isotherms were measured on a Micromeritics ASAP 2020. The samples were out-gassed at 250 °C for 3 h prior to the nitrogen adsorption measurements. The surface area of the particle was measured using the Brauner–Emmet–Teller (BET) equation and is expressed in m^2 g^{-1}. The pore volume and the pore diameter were measured for the adsorption and desorption separately. Scanning electron microscope (SEM) was accomplished with Carl Zeiss MA15/EVO18 Scanning Electron Microscope operating at