Preface

Nanometric magnetic materials are important in various domains of scientific research and applications. These applications range from drug delivery, magnetic resonance imaging (MRI), magnetic hyperthermia treatment (MHT), data storage, photocatalysis for H_2 production and electrochemical energy storage devices etc. Due to their submicroscopic dimension, the magnetic nanoparticles (MNPs) can differ drastically in physical characteristics in comparison to their bulk form. These MNPs have gained popularity because of their ability to get functionalized at both cellular and molecular levels. Metallic iron has much higher saturation magnetization value ($M_{S,}$ e. g. 220 Am^2/kg for bulk Fe) than its oxides such as (e. g. Fe_3O_4, γ-Fe_2O_3 etc. ~90 Am^2/kg for bulk Fe_3O_4). Nevertheless, the former is inadequate for medical applications due to its toxicity. On the other hand, iron oxides are explored extensively for various biomedical applications due to their suitable biocompatibility, size and magnetic characteristics.

In contrast, iron carbide (Fe_3C) could be an interesting material for bioapplications due to its higher M_S values (~140 Am^2/kg for bulk) and higher chemical stability than iron oxides. The bulk or nanoparticles of Fe_3C have several advantages over iron oxides. Further, there are substantial literatures on the synthesis and properties of pure and substituted magnetic iron oxides ($M_xFe_{3-x}O_4$ or γ-$M_xFe_{2-x}O_3$, M = Co, Ni, Mn, Zn, Al, Zr, Hf, Li etc. $0 \leq x \leq 1$). These studies recognize the huge potential of these MNPs for various applications. However, the tedious processes to get pure form of Fe_3C

limits its applicability. Though, there are a few reports on the synthesis techniques to get Fe_3C nanoparticles but reports on the substituted Fe_3C are limited. The extensive studies on the effect of substitutions on the structural, magnetic biocompatible behavior of Fe_3C are also lacking in the literature.

The MNP_S can also be utilized for visible-light-driven (VLD) magnetically separable photocatalysts for the waste water treatment and H_2 production. This is due to their good magnetization, electrical resistivity, optical (narrow band gap) properties and low toxicity. Nevertheless, these material also displays a high recombination rate of the photogenerated electron-hole pairs which lowers the efficiency. These shortcomings can be resolved either by forming a core-shell structure (activated carbon, carbon nanotubes and graphene) or by coating with ceramics (e.g. SiO_2 and Al_2O_3) or by doping of transition metal ions (Ni, Cu, Fe, Cr, etc.) or doping with reactive nonmetal ions (C, N, S, F, etc.). Out of various MNPs, iron carbide has lower Fermi level and higher conductivity due to its metallic nature. Further, its low cost and higher magnetization value make it a relatively suitable candidate for this application. In addition, carbon over the Fe_3C MNPs protect from chemical oxidation. The carbon also promotes the transfer of photogenic electrons which improves its photocatalytic performance.

The carbon has lower specific capacity (372 $mAhg^{-1}$) during its application as anode in Li-ion battery (LIB). In contrast, the transition metal oxides (e.g. Fe_3O_4) has displayed two and half times more theoretical specific capacity (928 $mAhg^{-1}$) as anode. But the significant volume change causes high initial capacity loss which restrict its applicability. This shortcoming can be resolved either by encapsulating oxide inside carbon or making its composite with intermetallic Fe_3C (where carbon atoms occupy the interstices of close-packed iron atoms). The presence of carbon in Fe_3C even provides better mechanical strength and chemical inertness as compared to that of oxide materials. Further, being ceramic materials, they display excellent oxidation as well as corrosion resistance. Finding better magnetic strength, photocatalytic behavior and specific charge capacity for Fe_3C, this was opted as a base material for present investigation. Subsequently, Zn, Mn or Ni was doped into it and their suitability for MHT or photocatalytic or LIB applications was evaluated.

This thesis consists of seven chapters.

Chapter-1 describes the literature on the structural and magnetic properties of Fe_3C and Fe_3O_4, synthesis protocols and brief introduction to the various applications such as MHT, photocatalysis and electrochemical energy storage devices.

Chapter- 2 gives the details of the materials used for the synthesis of pure and Zn-substituted iron carbide samples. Further, it also illustrates the preparation of nanocomposites of carbon with pure (Fe_3C/Fe_3O_4) as well as Ni or Mn substituted (Fe_3C/Fe_3O_4). This chapter also includes the characterization techniques utilized for evaluation of various properties of the samples.

Chapter- 3 focuses on the physical and *in-vitro* evaluation of Fe_3C particles for the magnetic hyperthermia application. For this, the sample was prepared by sol gel technique followed by calcination at 700 ºC for 3 h in N_2 atmosphere. The monophasic sample displayed room temperature saturation magnetization at 2 T of 78.2 Am^2/kg, and the coercivity was 2 mT approximately. Its ferrofluid was prepared using pluronic acid F-127 as a stabilizer. The ferrofluid displayed substantial temperature rise with time during the magnetic hyperthermia experiment. Consequently, the obtained specific loss power (SLP), as well as intrinsic loss power (ILP) values, were 46 W/g and 0.526 nHm^2/kg respectively, at a field of 23 mT and 261 kHz. After 48 h of treatment with A549 human lung carcinoma cells, the iron carbide nanoparticles was found to be compatible up to a concentration of 1 mg/mL.

Chapter-4 provides to the Structural and *in-vitro* assessment of $Zn_xFe_{3-x}C$ ($0 \leq x \leq 1$) nanoparticles as magnetic biomaterials. The saturation magnetization value for x = 0.1 sample was 58 Am^2/kg, which decreased minutely with increased Zn substitutions. The heating abilities of the ferrofluids, prepared using F127 polymer were measured. The optimum SLP as well as ILP values, were 85 W/g and 1.9 nHm^2/kg for the sample x = 0.7, at 25 mT external magnetic field. The cells were viable up to ~ 88% after the treatment with 2 mg/mL of each of $Zn_{0.5}F_{2.5}C$ and $ZnFe_2C$ nanoparticles after 48 h. Fluorescence microscopy further confirms that the cells remain unaffected even after treatment for 24 h with $Zn_{0.5}Fe_{2.5}C$ nanoparticles of concentration 1 mg/mL.

Chapter- 5 deals with structural and catalytic behavior for nanocomposites such as Fe_3C/C, $Fe_3C/Fe_3O_4/C$ and (Ni-substituted Fe_3C/Fe_3O_4)/C which were synthesized by similar route. The structural and coexistence of the phases present in the nanocomposite were analyzed by X-ray and electron diffractions. Mössbauer spectroscopy also supported the above findings. X-ray photoelectron spectroscopy was employed to identify oxidation states and bonding between the elements present in the composites. MHT experiments for the F-127 based ferrofluids of these MNPs indicate an optimum values of SLP and ILP to be 49 W/g and 0.548 nHm^2/kg respectively for FOC sample at 23 mT and 261 kHz field. Further, the *in-vitro* study of bare particles of N3FOC with

A549 cells suggests that a concntration up to 0.5 mg/mL was compatible. The optical properties of the composites were examined by UV-visible spectroscopy, which indicates band gaps suitable for photocatalytic activity. Further, two dyes methyl orange and p-nitrophenol were utilized to check the performance of catalytic degradation under Fenton and photo-Fenton conditions. The optimum apparent catalytic reaction rate constant for $Fe_3C/Fe_3O_4/C$ with p-nitrophenol and methyl orange were ~1.48 x10^{-2} and 3.36 x 10^{-2} mol. $lit^{-1}min^{-1}$ respectively.

Chapter-6 describes the synthesis of Fe_3C/C and Mn-substituted (Fe_3C and Fe_3O_4)/C nanocomposites using the process cited earlier. Their structural, magnetic and biological characteristics for the samples are described in detail. The magnetization value as well as heating ability of M2FOC sample were optimum. The biocompatibility of bare particles of this nanocomposite was also evaluated with human lung adenocarcinoma A549 cells after 48 h of treatment and found to be compatible up to 0.1 mg/mL. Further, the nanocomposites of Fe_3O_4 or Fe_3C or Fe_3O_4/Fe_3C with carbon were explored as anode material for Li-ion batteries due to their higher theoretical capacities. Therefore, the charging capacity of the nanocomposites of Fe_3C or $Mn_rFe_{3-r}C/Mn_sFe_{3-s}O_4$ (where $0.2 \leq r + s \geq 0.7$) with carbon are also evaluated. Moreover, specific charge capacities and coulombic efficiencies with respect to cycle numbers at room temperature were also evaluated. The optimum specific capacity ~1261 mAh g^{-1} was observed for the M7FOC (i.e. $r + s = 0.7$), whereas the reversible specific lithiation capacity was found to be around 841 mAh g^{-1} after the initial cycle at the rate of C/20.

Chapter-7 provides the summary and major conclusions drawn from the present investigation and also suggestions for future work for further materials understanding and applications of iron carbide based materials.