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Analysis of electrokinetic properties of $NiFe_2O_4$ nanoparticles synthesized by DC thermal plasma route and its use in adsorption of humic substances

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ABSTRACT

The paper reports the influence of electro-kinetic properties of nanoparticles of $NiFe_2O_4$ on the adsorption of humic substances (HS); with an aim of understanding their adsorption behavior. Crystalline single phase magnetic nanoparticles of $NiFe_2O_4$ are synthesized by gas phase condensation method using DC thermal plasma reactor. Due to the high temperature and steep temperature gradient this method helps in producing highly crystalline nanoparticles with sufficiently large number of surface states suitable for adsorption. These particles possessed high value of zeta potential, reducing their agglomeration and resulting into an enhanced adsorption capacity. However no significant influence of plasma parameters is observed on their zeta-potential and iso-electric values. The adsorption kinetics is studied and fitted to non-linear kinetic models and the best fit is observed for the pseudo first-order model. The analysis of adsorption isotherms suggests that the non-linear Langmuir model fits better as compared to Freundlich adsorption model. The adsorption of HS onto the nanoparticles is seen to depend on the pH value of the solution. A maximum adsorption of 5.2 mg/g is obtained at pH value of 3.64. These results suggest that plasma synthesized nanoparticles of $NiFe_2O_4$ have high colloidal stability and can be employed as efficient adsorbents for the removal of humic substances from water sources.

1. Introduction

Humic substances (HS) is natural organic macromolecule abundantly obtained from environmental systems such as soils, surface and subsurface waters and usually originates from microbial degradation of plants and animal residues [1,2]. Humic substances contains both hydrophobic and hydrophilic moieties and different functional groups such as carboxylic (—COOH), phenolic (Ar—OH), amine (—NH_2), and hydroxyl (—OH) connected with aliphatic or aromatic carbons [3]. The presence of humic substances, which possess high reactivity, cause contamination of various water resources and its removal has been a big concern. It is earlier reported that the humic substances can easily bind with heavy metal ions and other organic substances, facilitating their transportation in the water systems. They also promote bacterial growth which reacts with chlorine during water treatment and produce carcinogenic disinfection byproducts like trichloromethanes and haloacetic acids [4]. Thus the removal of HS from the water system is of major concern. Although various techniques like chemical coagulation, membrane separation, ultrafiltration, biodegradation and ion exchange are employed for the separation of HS, they have high operational cost and produce extra sludge.

Currently the method of adsorption-separation is proved to be effective in removing HA from aquatic systems. Several adsorbents like activated charcoal/carbon, clays, fullerene, zeolite, chitosan and inorganic nano-oxides like TiO_2, ZnO, SiO_2, Al_2O_3, Fe_3O_4 etc. have been employed for the effective separation of HS from the water sources [3,5–7]. The main advantages of using nanoparticle as an adsorbent are (a) high adsorption capacity due to large surface area (b) simple and rapid separation (c) no secondary pollutants are produced (d) reduction in the usage of chemicals and (e) can be easily coated with different functional groups.

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Magnetic nanoparticles are found to be more effective and are widely used for the separation technique in different fields.

Among the various magnetic nanoparticles adsorption of humic substances on iron oxide (hematite) has been widely examined and reported [2,8]. However, recently it has been reported that the $NiFe_2O_4$-nanoparticles exhibit high surface reactivity and high water adsorption capacity as compared to Fe_3O_4-nanoparticles [9]. It is, therefore, important to explore the adsorption capacity of $NiFe_2O_4$-nanoparticles which have suitable magnetic, chemical and physical properties and can be synthesized easily. The properties of $NiFe_2O_4$-nanoparticles have been widely studied and they are reported to be highly sensitive to the method of synthesis [10,11]. Thus, it would be interesting to explore the adsorption mechanism of HS on the nanoparticles synthesized by homogeneous gas phase condensation process, which is known to yield particles with high surface states. As reported earlier this method involves steep temperature gradient of 10^3 K/mm which introduces different magnetic, chemical and physical properties of the synthesized particles [12–15]. In our earlier publication [16] we have very emphatically pointed out that the surface crystallinity of the nanoparticles synthesized by high temperature gas phase routes have very unique surface crystallinity resulting into the higher surface states and further into high adsorption properties, although the chemical formula remains the same. Thus the advantages of synthesizing magnetic nanoparticles by thermal plasma method is that we get (a) highly crystalline single phase nanoparticles (b) high saturation magnetization for easy removal (c) good yield for mass application (d) organic free particles and (e) good colloidal stability.

Adsorption analysis are usually carried out in the colloidal solutions and it is known that in such solutions, the particles are hydrated and the M–OH sites on the surface react with H^+ or OH^- ions forming positive ($M–OH^{2+}$) or negative ($M–O^-$) surface charges depending upon the pH of the solution [2,17–19]. The surface charge, on the nanoparticle, is measured in terms of zeta potential; which in turn is responsible for the adsorption of various organic and bio-molecules [20,21]. The effect of adsorption of organic and biomolecules on the electro-kinetic properties of nanoparticles has been reported earlier. The polyanionic coating like citric acid (CA) and humic substances on the surface of magnetite nanoparticles and its effect on the colloidal stability has also been emphasized [22]. Thus along with the adsorption capacity it is important to understand the role of adsorption of HS on the electro-kinetic properties of $NiFe_2O_4$-nanoparticles.

It is reported that the adsorption mechanism of humic substances on the nanoparticle involves (a) electrostatic interaction (b) ligand exchange (c) hydrophobic interaction (d) entropic effect (e) hydrogen bonding and (f) cation bridging. However electrostatic interaction and ligand exchange may be favored [23,24]. Moreover the interaction mechanisms may be more complex due to the heterogeneity of humic substances and different structural and surface properties of nanoparticles. Therefore, in this paper we report the suitability of $NiFe_2O_4$ nanoparticles, synthesized by the present method, for the adsorption of HS and to understand their interaction mechanisms.

The analysis of HS adsorption onto the nanoparticles of $NiFe_2O_4$ was carried out by studying the kinetic and isotherm adsorption models. The analysis of the kinetic and the isotherm data is important because it describes the rate and quantity of adsorbate uptake respectively [25–27]. Various researchers have reported the fitting of experimental data by linear forms of kinetic and isotherm adsorption equations. However, recently, few studies have compared the linear and non-linear forms of these equations and found that the non-linear fitting leads to accurate kinetic and isotherm parameters. In this study, the non-linear equations pertaining to kinetic and isotherm models were used to fit the experimental data for the adsorption of HS onto nanoparticles of $NiFe_2O_4$ [28–30].

The particle size and morphology of the as-synthesized nanoparticles are determined by X-ray Diffraction (XRD) and Transmission Electron Microscopy (TEM) respectively. The magnetic properties were analyzed by plotting M–H curve using vibrating sample magnetometer (VSM). The adsorption of humic substances was confirmed by Fourier Transform Infrared Spectroscopy (FTIR) and zeta potential measurements. The concentration of humic substances (HS) was determined by measuring the absorption intensity at fixed wavelength using UV–vis spectrophotometer.

2. Materials and experimental method

2.1. Synthesis of $NiFe_2O_4$ nanoparticles by gas phase condensation route

The $NiFe_2O_4$ nanoparticles were synthesized by gas phase condensation method using an indigenously built transferred arc DC thermal plasma reactor. During the synthesis; the pressure inside the reactor was varied from 260 to 760 Torr, and the dc-power was varied from 4 to 8 kW. The powder synthesized under different experimental conditions was characterized using XRD, VSM and zeta potential measurements. Based on the highest values of saturation magnetization (required for the easy removal of adsorbant), further samples were prepared at 500 Torr and 6 kW and were used for adsorption analysis. Initially the pellets were prepared by mixing micron sized powders of Ni and Fe metals (Loba Chem, India) in the molar ratio of 1:2 and by applying 110 kg/cm^2 of pressure. The reactor consists of water cooled double walled stainless steel chamber. There is a water cooled movable graphite block which acts as anode and the graphite crucible is used to place the pellets made out of Ni and Fe powders. Initially the base pressure of 0.01 mbar was obtained in the reactor by using rotary pump. Then the reactor chamber was filled with oxygen so that there are sufficient oxygen molecules to react with evaporated metal ions. The argon plasma arc is initiated by 240 V and 2 MHz of rf frequency. The plasma plume of argon gas (5 Lpm) was then

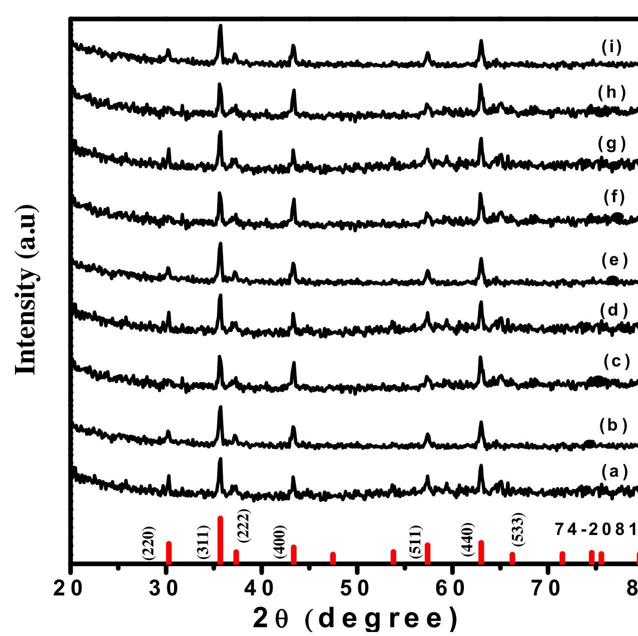

Fig. 1. XRD pattern of $NiFe_2O_4$ nanoparticles synthesized at different plasma parameters (a) 260T, 4 kW (b) 500T, 4 kW (c) 760T, 4 kW (d) 260T, 6 kW (e) 500T, 6 kW (f) 760T, 6 kW (g) 260T, 8 kW (h) 500T, 8 kW (i) 760T, 8 kW.