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Niobium substituted magnetite as a strong heterogeneous Fenton catalyst for wastewater treatment

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ABSTRACT
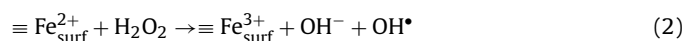
In this study, a series of Nb substituted magnetites; $Fe_{3-x}Nb_xO_4$ ($x = 0.0$, 0.022, 0.049, 0.099, and 0.19) were prepared and characterized by XRD, BET surface area, TEM, VSM, XPS, and chemical experiments. The magnetite inverse spinel structure and magnetic property were maintained in all the synthetized samples. A significant decrease in crystal size ($\approx$two times) and increase in specific surface area ($\approx$three times) were observed with increased Nb content, resulting in higher adsorption capacity of the samples. In addition, the reactivity of the synthetized samples was examined through degradation of methylene blue solution using Fenton-like reaction. It was found that the incorporation of niobium significantly improved the degradation of methylene blue of which total MB removal was achieved within 180 min at higher molar ratios of Nb ($x = 0.19$). This could be attributed to the generated oxygen vacancies on the surface of catalysts, the contribution of the introduced Nb cations in Fenton oxidation cycle for regeneration of Fe^{2+} cations, and increase in adsorption capacity of the samples due to larger surface area. The MB degradation through $Fe_{2.79}Nb_{0.19}O_4/H_2O_2$ system was well described by the pseudo-first-order equation in kinetics. All samples showed good stability under the studied pH conditions. The amount of niobium leached was not detectable in neutral and basic solutions and the samples could be reused in oxidation process for several times without a significant decrease in their catalytic efficiency. The results proved that incorporation of niobium into magnetite significantly improved the characteristics and effectiveness of the heterogeneous catalyst for Fenton treatment of recalcitrant effluents.

1. Introduction

Fenton oxidation process is a potent catalytic reaction used for environmental remediation. In this iron catalyzed Haber–Weiss reaction, hydroxyl radicals ($^\bullet$OH) are generated in situ through decomposition of hydrogen peroxide (Eq. 1). Hydroxyl radicals are highly active ($E_{ox} = 2.8$ V) and capable to destroying almost all organic pollutants unselectively. Recently, the homogeneous ferrous ion is replaced with heterogeneous iron compounds in Fenton oxidation (Eq. 2) mainly because of their easy separation, applicability for a wide range of pH, feasibility for repeated use and elimination of ferric hydroxide sludge [1]. This is specifically

reported for magnetite $[(Fe^{3+})_{tet}(Fe^{2+}Fe^{3+})_{oct}O_4]$ that has shown better performances due to presence of Fe^{2+} cations in its structure which is responsible for initiating H_2O_2 activation in Fenton oxidation [2,3]. However, magnetite application in Fenton reaction in its pure form is restricted due to its lower oxidation rate compared to soluble iron in homogeneous Fenton reaction [4,5]. In this regard, recent studies have focused on various modifications in magnetite structure to improve the adsorption and degradation of organic pollutants through Fenton reaction [6]. Application of chelating agents [2,7], pillared clays, activated carbon, and alumina as support to increase the adsorption capacity of the magnetite [8,9] and introduction of other transition metal/metals into the magnetite structure [3,10] are number of examples, so far reported in literature. Amongst them, transition metal substituted magnetite has been introduced as a promising Fenton catalyst for treatment of recalcitrant wastewater.

$$H_2O_2 + Fe^{2+} \rightarrow Fe^{3+} + {}^-OH + {}^\bullet OH \tag{1}$$

$$\equiv Fe^{2+}_{surf} + H_2O_2 \rightarrow \equiv Fe^{3+}_{surf} + OH^- + OH^\bullet \tag{2}$$

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In this category, iron is substituted isomorphically by other transition metal/metals that enhance its catalytic activity. There are some factors that contribute to higher activity of modified magnetite compared to pure magnetite. Costa et al. [3] proposed the synergistic effect of surface oxygen vacancies (OVs) on hydrogen peroxide decomposition in Co and Mn substituted magnetite catalyzed Fenton reaction. These OVs serve as active sites on the surface of catalyst and are generated via adjustments for unequal charge substitutions or cationic deficiency in the magnetite structure. On the other hand, conjugation of redox pairs of iron species and imported active ion in hydroxyl radical production cycle was suggested by Magalhães et al. [10] as a possible mechanism for the participation of incorporated transition metal in Fenton reaction. Other factors such as increased surface area and consequently, higher adsorption capacity, and increased surface hydroxyl for adsorption of probe molecules have also been proposed by other researchers [11]. The role of imported ions in prohibiting recombination of photo-generated electrons (e^-) and holes (h^+) on catalyst surface in photo-Fenton degradation of contaminants, has also been proposed [12].

Most of the previous studies have dealt with introduction of the transition metals of period 4 in the periodic table and were evaluated the effect of these transition metals on the activity of the magnetite in Fenton reaction [10,13–16]. Based on the literature review, there have not been any comprehensive studies on the assessment of the effects of the incorporation of transition metals from period five on the structure, physico-chemical properties, surface characteristics, and the activity of magnetite in Fenton oxidation process. Niobium was chosen from this period because it has similar ionic radius to iron species (Nb^{+4} (68 pm) and Nb^{+5} (64 pm) vs. Fe^{2+} (61 pm) and Fe^{+3} (55 pm)); therefore, it can theoretically replace iron in magnetite structure. In addition, both Nb and Fe have the same crystal structure (body centered cubic structure). On this basis, a series of niobium substituted magnetite nano-particles were synthetized and characterized. Subsequently, the effects of this modification on the structure, adsorption capacity, and catalytic activity of magnetite in Fenton-like reaction were investigated. Methylene blue (MB) is usually chosen as a model contaminant in the similar studies due to its extensive application in textile industry, recalcitrant nature, and strong adsorption onto the surface of magnetite [17–19]. Besides, the possible environmental impacts of heavy metal-constituents contained in catalysts must be investigated. In this respect, a series of leaching tests were performed to assess the stability of the synthetized catalysts. This was to evaluate the durability of the samples for their practical applications for several runs without significant decrease in their catalytic activity. In addition, It was to ensure that the degradation level of Fenton reaction with the synthetized catalysts have proceeded through heterogeneous route and the instability of the samples or the leaching of niobium into the solution, has not had a considerable role in the oxidation process and in wider picture, no impact on the receiving environment.

2. Experimental

2.1. Materials

All the chemicals were of reagent grade and used without further purification and the solutions were prepared with deionized water. Iron (II) chloride tetrahydrate ($FeCl_2 \cdot 4H_2O$), ammonium niobate (V) oxalaten hydrate ($C_4H_4NNbO_9 \cdot xH_2O$), and hydrazine were purchased from Sigma–Aldrich. Methylene blue (MB), hydrogen peroxide (H_2O_2, 30% w/w), sodium hydroxide (NaOH), sulfuric acid (H_2SO_4), hydrochloric acid (HCl), and sodium chloride (NaCl) were purchased from Merck.

2.2. Preparation of Nb substituted magnetites ($Fe_{3-x}Nb_xO_4$)

The method adopted here is modified version of work reported by Liang et al. [18]. Prior to use, all water samples and solutions were deoxygenated by nitrogen bubbling. For Fe_3O_4 synthesis, $0.90 \, mol \, L^{-1}$ of $FeCl_2 \cdot 4H_2O$ was dissolved in an HCl solution. A few drops of hydrazine was added into the mixture and the pH was set below 1.0 to prevent Fe^{2+} oxidation and hydroxide precipitation. This solution was then heated up to 100 °C. Equal volume of a solution containing $4.0 \, mol \, L^{-1}$ NaOH and $0.90 \, mol \, L^{-1}$ $NaNO_3$ was added drop-wise into the heated iron solution and the reaction was maintained at 90 °C for 2 h, while mechanical stirring at a rate of 500 rpm. Then, the solution was cooled to room temperature. During the reaction, N_2 flux was passed through to prevent Fe^{2+} oxidation. The particles were then separated by centrifugation at 3500 rpm for 5 min and washed with boiling deionized water, followed by an additional centrifugation. After 3–4 washings, the particles were collected and dried in a vacuum oven at 100 °C for 24 h. The preparation of $Fe_{3-x}Nb_xO_4$ (x = 0.025, 0.05, 0.1, and 0.2) samples followed the above procedure, except that predetermined amount of $C_4H_8N_2NbO_{11}$ was dissolved in basic solution. All the samples were ground and passed through a 200 mesh screen.

2.3. Characterization

The synthetized samples were analyzed with powder X-ray diffraction (XRD) to determine their crystalline phase using a PANalytical Empryean (DY 1032) diffractometer with Cu Kα radiation (k = 0.15418 nm). The XRD data were collected from 20° to 80° (2θ). The surface area of the samples was determined using Brunauer–Emmett–Teller BET-surface area method (Micromeritics, tristar II 3020). The pore volumes and pore sizes were also measured. The surface characteristics of the samples were investigated by X-ray photoelectron spectroscopy (XPS). The XPS measurements were performed with a PHI Quantera II with Spherical Capacitor Analyzer (SCA) and a monochromatic Al Kα (1486.6 eV) source. The C 1s line of spurious carbon located at binding energy of 284.8 eV was used as a reference to correct binding energies for the charge shift. Transmission electron microscopy (TEM) was used to investigate surface morphology and particle sizes of the samples. TEM micrographs were obtained from a FEI Tecnai G2 electron microscope. Vibrating sample magnetometer (VSM) (Lakeshore VSM, 7400 Series) was used to study the magnetic properties of the prepared samples. The point of zero charge (pH_{PZC}) of the samples was determined by the solid addition method. 45 mL of $0.1 \, mol \, L^{-1}$ NaCl solution was transferred to a series of 250 mL conical flasks. The initial pH values (pH_i) of the solutions were adjusted from 4.0 to 11.0 by adding either $0.1 \, mol \, L^{-1}$ HCl or $0.1 \, mol \, L^{-1}$ NaOH. The total volume of the solution in each flask was made exactly 50 mL by adding the NaCl solution. Then, 0.05 g of each sample was added into each flask and the mixtures were agitated at 170 rpm. After 24 h, the final pH values (pH_f) of the solutions were measured. The difference between the initial and final pH values ($^*pH = pH_i - pH_f$) was plotted against pH_i. The point of intersection of the resulting curve with abscissa, at which $^*pH = 0$, gave the value of pH_{PZC} [17].

2.4. Adsorption experiments

The studies on MB adsorption by modified magnetite samples were carried out in a batch system at 25 °C. The initial pH of the dye solution was adjusted to 7.0 by using NaOH solutions. $1 \, g \, L^{-1}$ of each sample was added to dye solutions of different concentrations (12.5, 50, 75, and $100 \, mg \, L^{-1}$) and constantly stirred mechanically at 170 rpm for 120 min, to achieve sorption equilibrium. Then, the adsorbent was separated from the solution by centrifugation at