Applied Surface Science xxx (2014) xxx–xxx

Contents lists available at ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

Modified Fe_3O_4- hydroxyapatite nanocomposites as heterogeneous catalysts in three UV, Vis and Fenton like degradation systems

S. Valizadeh[1], M.H. Rasoulifard*, M.S. Seyed Dorraji[2]

Department of Chemistry, Faculty of Science, University of Zanjan, Zanjan, Iran

ARTICLE INFO

Article history:
Received 1 June 2014
Received in revised form 15 July 2014
Accepted 24 July 2014
Available online xxx

Keywords:
Hydroxyapatite
Magnetite
Modification
Metal ions
Degradation
Dye pollution

ABSTRACT

The magnetite-hydroxyapatite (M-HAP) nanocomposites were prepared by a chemical co- precipitation procedure and characterized by Fourier transform infrared spectroscopy (FT-IR), X-ray diffraction (XRD), scanning electron microscopy (SEM) and diffuse reflectance spectra (DRS). The ability of the synthesized catalyst for photocatalytic degradation of Acid Blue 25 (AB25), as an organic dye, under UV irradiation was studied. The catalyst was modified employing transition metals (Mn, Fe, Co, Ni, Cu and Zn) trying to improve the catalytic performance of HAP in absence of UV irradiation and in the presence of hydrogen peroxide i.e. a Fenton like reaction. The best results obtained for Cu and Co modified M-HAPs and the effect of operational parameters such pH, amount of catalyst and hydrogen peroxide concentration was studied. In order to investigate the performance of HAP based photocatalyst in visible light region, M-HAP was modified with silver ions. At the end, Langmuir-Hinshelwood kinetic expression used to evaluate and compare the catalytic systems. The strongest degradation activity was observed for Ag-M-HAP/Vis system because of Ag_3PO_4 formation. Apparent reaction rate constant (K_{app}) by Ag-M-HAP/Vis was 63, 36 and 19 times faster than Cu-M-HAP(II)/H_2O_2, Co-M-HAP(II)/H_2O_2 and M-HAP (I)/UV systems, respectively.

1. Introduction

Over the few decades, rapid industrialization has led to discharge into environment a large quantity of wastewater containing dyes, phenol and its derivatives and other organic pollutants. These compounds are toxic to humans and aquatic lives. Therefore, the wastewater containing these compounds must be treated before their discharge into the water streams [1,2]. Recently, hydroxyapatite has been employed as a photocatalyst for degradation of organic contaminants under UV irradiation [3]. HAP with structural formula of $Ca_{10}(PO_4)_6(OH)_2$ is the major inorganic component of human bones and teeth[4,5]. It is abundant in nature, easily available, low in cost and has minimal environmental impact for restoration or remediation of natural resources [6]. It was shown that the surface of the HAP was slightly changed by UV irradiation and active $O_2^{\bullet-}$ species generated on the surface of HAP. Electron spin resonance and FTIR studies of H. Nishikawa [3,7] showed that $O_2^{\bullet-}$ species generated on HAP is in connection with the changes of PO_4 group. The X-ray photoelectron spectroscopy studies cleared that the surface of HAP gets a negative electric charge by UV irradiation. This result would prove indirectly the formation of radical species on HAP by UV irradiation. ESR spectrum obtained by subtracting the spectrum of HAP before UV irradiation from that after UV irradiation showed the signal assigned to electron trapped on vacancy. The changes of surface PO_4 group and the generation of trapped electron suggest the appearance of oxygen vacancy by UV irradiation. The activation of oxygen due to the electron trapped on the vacancy in HAP would occur followed by formation of the labile $O_2^{\bullet-}$ species. The radicals are very active and are able to oxidize organic compounds [3,7]. Because of complicated structure of HAP many kind of cations can be induce into the apatite crystal structure. Thereby, substituting cations in HAP can be done easily [8]. Up to now HAP has been used for removal of numerous metal and transition metal ions from wastewater [9,10]. On the other hand, activation of H_2O_2 as Fenton reaction oxidant has been reported by transition metal ions such as manganese, copper, cobalt, nickel and etc. for degradation of organic dye pollutants at room temperature [11–18]. Because of many disadvantages of homogeneous Fenton systems such as the requirement of further treatments for metal ions and sludge, the acidification of effluents before decontamination and neutralization of treated solution before disposal, several

---

* Corresponding author. Tel.: +98 24 33052591; fax: +98 24 33052477.
E-mail addresses: valizadehsolmaz@yahoo.com (S. Valizadeh), m_h_rasoulifard@znu.ac.ir (M.H. Rasoulifard), dorraji@znu.ac.ir (M.S.S. Dorraji).
[1] Tel./fax: +98 24 33052477.
[2] Tel./fax: +98 24 33052477.

http://dx.doi.org/10.1016/j.apsusc.2014.07.139

Please cite this article in press as: S. Valizadeh, et al., Modified Fe_3O_4- hydroxyapatite nanocomposites as heterogeneous catalysts in three UV, Vis and Fenton like degradation systems, Appl. Surf. Sci. (2014), http://dx.doi.org/10.1016/j.apsusc.2014.07.139

studies have been made to find efficient heterogeneous Fenton like systems [19–21]. Therefore, modified HAP with metal ions can be a favorable candidate for heterogeneous Fenton like reactions. Recently silver ions modified HAP showed photocatalytic activity in visible light [22]. The source of photocatalytic activity of modified HAP with silver ions was formation of Ag_3PO_4 nanoparticles on the surface of HAP. Ag_3PO_4 identified as novel alternative photocatalyst for visible light and has a large dispersion of conduction band which facilitate the separation of electron–hole pairs [23,24].

In the present work, to obtain a direct and comprehensive understanding of the catalytic activity of HAP in degradation of organic pollutant, three different catalytic systems were investigated. For facilitating the recovery of the catalyst, hydroxyapatite synthesized along with magnetite (Fe_3O_4), which synthesized nanocomposite easily recovered by an external magnet. Acid blue 25 was selected as a model of organic dye pollutants. Study of degradation of AB25 under UV irradiation by HAP was the first catalytic system. In order to eliminate the UV irradiation from photocatalytic system, modifying of HAP with transition metal ions were performed and degradation properties of modified catalyst in Fenton like system as second system were studied. In third catalytic system for the sake of removing oxidant reagent used in Fenton like system, modification of HAP with silver ions was carried out and photocatalytic properties in the presence of visible light were investigated. To the best of our knowledge, comparison study of catalytic properties of HAP in various catalytic systems was not reported in the literature.

2. Experimental

2.1. Materials

Calcium nitrate tetra hydrate ($Ca(NO_3)_2{\cdot}4H_2O$), cobalt chloride hexahydrate ($CoCl_2{\cdot}6H_2O$), manganese chloride dihydrate ($MnCl_2{\cdot}2H_2O$), iron sulfate heptahydrate ($FeSO_4{\cdot}7H_2O$), zinc sulfate heptahydrate ($ZnSO_4{\cdot}7H_2O$) were obtained from Merck and Ammonium hydrogen phosphate ($(NH_4)_2HPO_4$), cupric sulfate pentahydrate ($CuSO_4{\cdot}5H_2O$), nickel nitrate hexahydrate ($Ni(NO_3)_2{\cdot}6H_2O$), were supplied by Fluka. Magnetite (Fe_3O_4) nanoparticles and silver nitrate ($AgNO_3$) were purchased from Pishgaman Mashhad Co. (Iran) and Applichem Co. (Germany), respectively. All of the chemicals were analytical grade and used without further purification.

2.2. Synthesis of M-HAP nanoparticles

Fifty ml aqueous solution containing 1.77 g $Ca(NO_3)_2{\cdot}4H_2O$ adjusted to pH 10, was added drop wise into a 50 ml aqueous solution with 1.74 g $(NH_4)_2HPO_4$ and 0.048 g Fe_3O_4 over 30 min with continuous mechanical stirring (1100 rpm). The resultant solution was heated to 90 °C, after 2 h; the mixture was cooled to room temperature and aged overnight. The dark brown precipitation was filtered and washed twice with deionized water until neutral pH. The resultant solid was dried at 90 °C for 2 h. Finally, the as-prepared sample was calcinated at 400 °C for 3 h [25]. The synthesized magnetite-hydroxyapatite was named M-HAP (I).

Also M-HAP (II) was synthesized by co-precipitation procedure [26]. At first calcium nitrate solution (1.77 g $Ca(NO_3)_2{\cdot}4H_2O$ in 50 ml of distilled water) was immediately poured into diammonium hydrogen phosphate solution (1.74 g $(NH_4)_2HPO_4$ in 50 ml of distilled water) contained 0.048 g Fe_3O_4. pH of the solution was adjusted to 7 by ammoniac solution. After a mild agitation for about 2 h, the suspension was filtered on a large Buchner funnel and washed with distilled water subsequently dried at 70 °C for about 48 h.

Pure HAP (I) and HAP (II) synthesized for supplementary experiments according mentioned procedures without additional of Fe_3O_4 nanoparticles.

2.3. Modification of M-HAP nanoparticles

The M-HAPs (1 g) was treated with a solution of $CoCl_2$ (200 ml of 20 mM) at ambient temperature for 24 h and then dried at 70 °C for 3 h. This process repeated for $CuSO_4$, $ZnSO_4$, Ni $(NO_3)_2$, $FeSO_4$, $MnCl_2$ and $AgNO_3$ solutions. In the case of $AgNO_3$, only M-HAP (II) was used and drying process done at room temperature. The modified catalysts were named Co-M-HAP (I), Co-M-HAP (II), Cu-M-HAP (I), Cu-M-HAP (II), Zn-M-HAP (I), Zn-M-HAP (II), Ni-M-HAP (I), Ni-M-HAP (II), Fe-M-HAP (I), Fe-M-HAP (II), Mn-M-HAP (I), Mn-M-HAP (II) and Ag-M-HAP. Metal content of modified catalysts were calculated with concentration subtracting of modifying solution before and after modification.

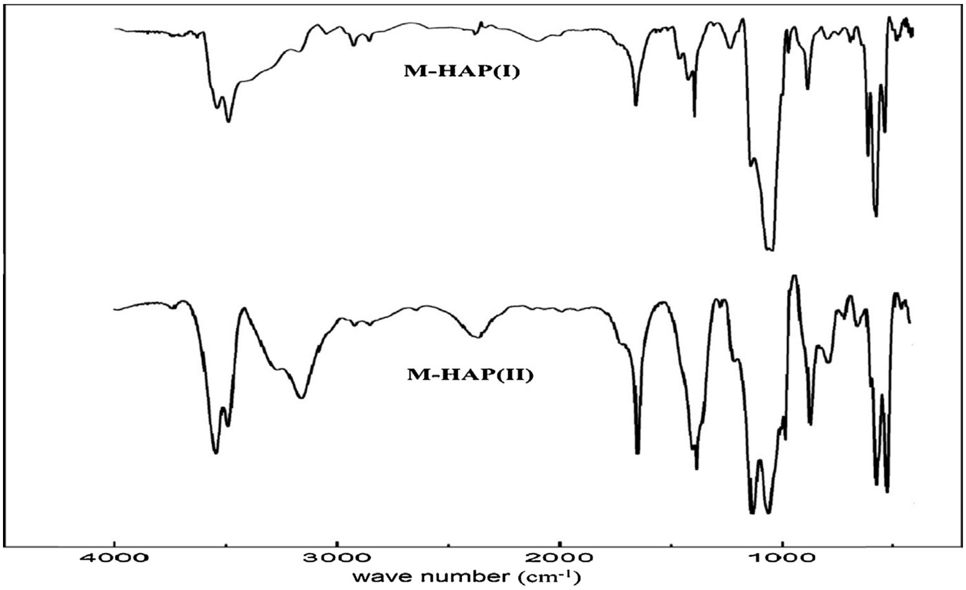

Fig. 1. FT-IR spectra of M-HAP (I) and M-HAP (II).

Please cite this article in press as: S. Valizadeh, et al., Modified Fe_3O_4- hydroxyapatite nanocomposites as heterogeneous catalysts in three UV, Vis and Fenton like degradation systems, Appl. Surf. Sci. (2014), http://dx.doi.org/10.1016/j.apsusc.2014.07.139