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Application of Fe_3O_4 Sphere Doped with Zn for Enhanced Sonocatalytic Removal of Cr (VI) From Aqueous Solutions

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ABSTRACT

Fe_3O_4 sphere doped Zn were successfully prepared by the simple one-pot solvothermal method. Morphology and structure of the as-synthesised products was checked through the XRD, SEM, HRTEM techniques. The Fe_3O_4 hollowsphere doped showed the high photocatalytic activity for degradation of hexavalent chromium under visible light irradiation. The effects of reaction conditions such as initial pH, photocatalyst dosage and hexavalent chromium contratentation were also studied systematically. The stability of the catalsyts and and possible catalytic mechanism was also proposed. The results indicate that Fe_3O_4 sphere doped Zn can be promising catalyst for photo-reduction of hexavalent chromium.

KEYWORDS: Fe_3O_4 sphere doped Zn hexavalent chromium; hollowsphere; photo-reduction reaction

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I. INTRODUCTION

Intense development of global industrial and economic is resulting in the great amount of heavy metal pollution in water such as Cd, As, Hg, Cr… Among of these heavy metals, hexavalent chromium is considered as one of reasons for carcinogenic and toxic, while trivalent chromium is friendly-environment and one of trace elements for animal and human. Specially, Cr(III) can be precipitated and separated from solution by adjusting alkaline or neutral pH. Therefore, transformation of Cr(VI) into Cr(III) should be conducted before getting rid of effluents on surface water sources. The traditional routes to eliminate wastewater polluted by Cr(VI) are adsorption by adsorbent[1], precipitation and ion exchange[2], reduction of Cr(VI) with zero-valent aluminum.[3] Recently, using photocatalytic materials for reducing Cr(VI) are getting the great attention due to its low-cost, high efficiency and friendly-environment. The different photocatalysts as TiO_2[4], ZnO[5], Ti-Fe kaolinite[6] have been employed to reduce Cr hexavalent. However, some problems is still remaining while using semiconduction catalyts to photo-reduce Cr(VI) such as low potential adsorption light, low efficiency, complexity in preparing and separation and recycling.

Recent years, metal doped oxide, spinel oxide nanopartlicles have attracted much more attention due to their enhanced electrical conductivity, interesting magnetic properties and high photocatalyst activities. Among the spinel oxides, Fe_3O_4 nanoparticles with a cubic spinel structure where a half of Fe^{3+} ions occupy in all the tetrahedral sites, a half of the Fe^{3+} ions and all the Fe^{2+} ions local on the octahedral sites, are considered as promising materials in many fields owing to its abundant, low-cost, friendly-environment, easy controllable synthesis and interesting magnetic properties.

Herein, we successfully synthesised uniform Fe_3O_4 hollowpheres doped Zn via a simple solvothermal route in absence of any surfactants. The as-obtained products indicated porosity hollow properties. The catalytic property of the as-obtained products in

photo-reduction Cr(VI) was evaluated by under visible light irradiation.

II. EXPERIMENTS

2.1. Materials

All chemicals used in this work were from Sinopharm Chemical Reagent Co., Ltd, China without further treatment and purification. De-ionized water was used in the whole experiments.

2.2. Mesocrystal preparation

Fe_3O_4 spheres dopoed Zn were prepared by a simple solvothermal approach.[7] Typically, 0.372 g of $Zn(NO_3)_2$ and 1.08 g of $Fe(NO_3)_3$ and 2.412 g of amoniacetate dissolved in 100 ml ethylene glycol while stirring kept for 0.5h. Sequentially, the solution was transferred into the 100 ml autoclave and heated at 180 °C for 24h after ultrasonic treatment (at 59 Hz) for 30 minutes. After naturally cooled until room temperature, the resulting product was collected by a magnet, washed with ethanol and deionized water for several times. Finally, product powder was dried at 80 ºC in an electric oven for 12h before further use.

2.3. Characterization

X-ray diffraction (XRD) analysis was carried out using a X-ray powder diffractometer with Cu Kα radiation at 40 kV and 50 mA. The morphology and internal structure of the prepared samples were further checked by transmission electron microcopy (TEM), high-resolution transmission electron microcopy (HRTEM) using a JEOL JEM-2010 HR electron microscope operated at a voltage of 200 kV and equipped with a Gatan GIF Tridiem system.

2.4. Photo-Reduction Cr(VI) activity

The photocatalytic activity of the as synthesized product was investigated by the Cr(VI) photo-reduction from aqueous solution under the visible light irradiation (300W Dy lamp with a 400 nm cut-off filter). In a typical experiment, 2 mg of the as-prepared photocatalyst was dispersed in 100 mL of 50 mg/L Cr(VI). During irradiation, 2 mL of sample was taken at different time intervals and centrifuged immediately to remove the composite particles. The residual concentration of Cr(VI) in the supernatant was measured by UV-Vis spectrophotometry at 540 nm after complexation with DPC.

III. RESULTS AND DISCUSSION

3.1. Characterization of hollowsphere Zn-doped Fe_3O_4

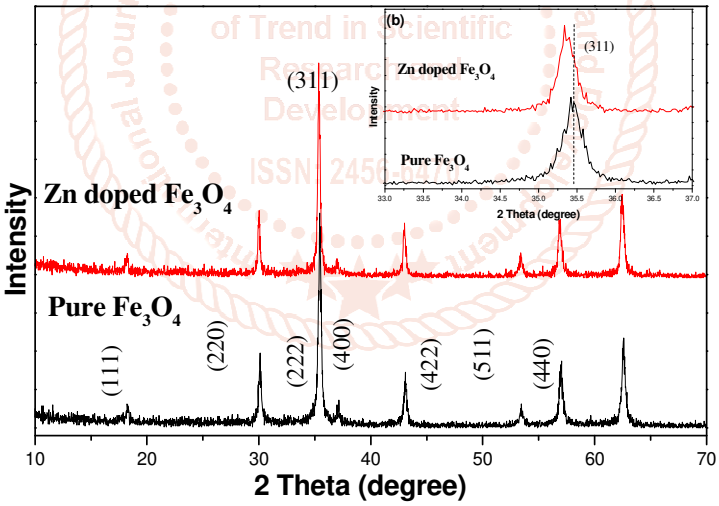

Fig. 1. XRD pattern of pure Fe_3O_4 and Fe_3O_4 sphere doped Zn at 180 °C for 24 h; the highlighted (311) diffraction peak of pure Fe_3O_4 and Fe_3O_4 sphere doped Zn at 180 °C for 24 h (inserted).

The XRD patterns of the pure Fe_3O_4 and Fe_3O_4 sphere doped Zn are showed in Figure 1. Both the patterns indicate that all reflection peaks could be indexed to magnetite with cubic spinel structure (JCPDS 77-1545). No diffraction peaks of zinc oxide were observed, suggesting that crystalline zinc oxides did not form during the synthesis process. However, it can be learned from patterns inserted in Fig.1 that the (311) crystal plane of Fe_3O_4 sphere doped Zn slightly shifted to smaller angle and the corresponded lattice constant increased from 0.8395 nm to 0.8406 nm, which could be ascribed to the substitution of a small amount of Fe^{2+} (ion radius =0.61 nm) and Fe^{3+} (ion radius = 0.49 nm) in the magnetite by Zn^{2+} with a larger ion radius of 0.74 nm. The results suggest that Zn has been successfully doped into the crystal structure of Fe_3O_4 sphere, in which doped Zn^{2+} ion may tend to substitute Fe^{3+} ion in tetrahedral sites and a small amount Fe^{2+} ion located on octahedral sites.[8,9]

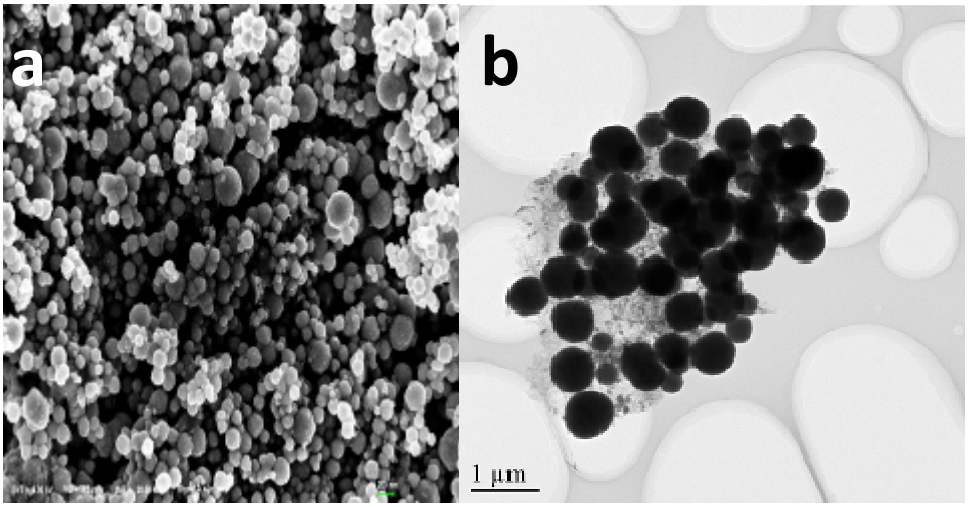

Fig. 2. (a) SEM, (b) TEM images of the as-synthesized sample

Morphology and crystalline structure of the as prepared products were investigated by SEM, TEM and HRTEM. As depicted in Figure 2a-b, the products exposed uniform submicrosphere shape with an average size of 450 nm. The TEM image of the products in Figure 1b confirms the sphere high structure.[10] From the results, it can see that uniform Fe_3O_4 sphere doped Zn was prepared successfully.

3.2. Photocatalytic reduction of Cr(VI)

3.2.1. Cr(VI) adsorption isotherms

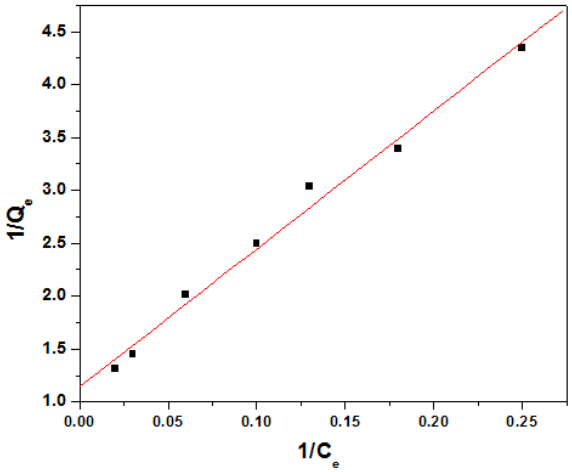

Fig. 3. Lnear plot of $1/Q_e$ versus $1/C_e$.

As well-known, in heterogeneous systems, the catalytic sites often occupy on the surface of catalysts. Therefore, the adsorption of reactants on the surface plays a very important role in the hetero-catalytic reaction. It was reported that most of photocatalytic reactions followed Langmuir–Hinshelwood model in which the adsorption capacity of photocatalysts could significantly effect on the reaction efficiency[4]. To address further the photocatalytic performance of the as-prepared Fe_3O_4 sphere doped Zn, Cr(VI) adsorption isotherms at pH 3,5 and room condition are conducted, which used the well-known isotherms Langmuir model as shown in Fig. The isotherms models can be describe in linear form by following equations:

$$\frac{C_e}{q_e} = \frac{1}{bQ_m} + \left(\frac{1}{Q_m}\right)C_e$$

Q_e: the equilibrium adsorption amount (mg/g); C_e: the equilibrium concentration of Cr (VI) (mg/l); Q_m: the maximum adsorption amount (mg/g); b: the adsorption constant (l/mg)

The plot of $1/Q_e$ values versus $1/C_e$ is presented in the Figure 3. The results were well fitted on the basis of high R^2 value (0.98) suggesting that the Cr(VI) adsorption on the Fe_3O_4 sphere doped Zn can be well followed Langmuir-Hinshelwood model. The monolayer adsorption potential (Q_m) was 3.52 mg/g in the equilibrium at pH 3.5.

3.2.2. The photo-reduction of Cr(VI)

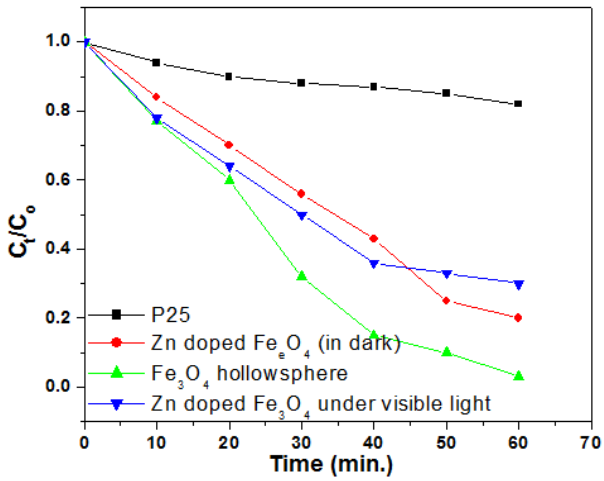

Fig.4. The photo-reduction for Cr(VI) with different photocatalysts

In the presence of Fe_3O_4 sphere doped Zn under visible light irradiation, Cr(VI) can be reduced to Cr(III) by the exicited electrons. The overall parthway of Cr(VI) photo-reduction could be expressed as the following reactions:[11]

Photocatalyst + hγ→ Catalyst (e_{cb}, h_{vb}) (1)

$Cr_2O_7^{2-} + 14\ H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$ (2)

$2H_2O + 4h^+ \rightarrow O_2 + 4H^+$ (3)

To further demonstrate the excellent photocatalytic activity in the removal Cr(VI) under visible light, P25 and pure Fe_3O_4 sphere are also employed in this experiment. The photo-reduction of Cr(VI) with different catalysts and conditions are shown in the Fig.4. It can see that Cr(VI) removal efficiency reached 95,8% with Fe_3O_4 sphere doped Zn under visible light, while only reached at 52% in dark. The results also indicated that Fe_3O_4 sphere doped Zn showed the highest photo-removal Cr(VI) compared to Fe_3O_4 spheres and P25. The enhanced photo-reduction of Cr(VI) activity of Fe_3O_4 sphere doped Zn could be ascribed to the uniform sphere structure as well as metal doping effect of the as-prepared sample. The sphere structure will improve visible-light photoresponses.[12] Furthermore, the improvement of the photo-removal of Cr(VI) in the present of Fe_3O_4 sphere doped Zn could be attributed to that metal doping can make the electron transfer process amore accelerated.[13,14]

3.3. Effect of pH

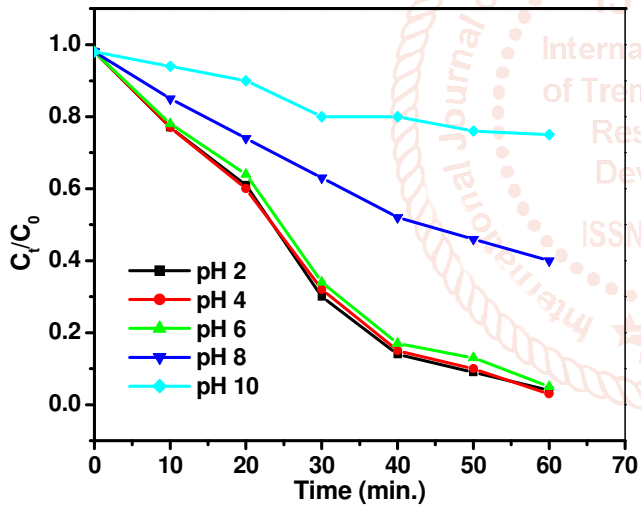

Figure 5 Effect of pH on the photo-reduction Cr(VI).

The pH of initial solution usually plays an important role in controlling the performance of contaminant removal. Therefore, the effect of initial pH on the efficiency of the photocatalytic degradation Cr(VI) also was studied. The reaction was carried out by varying pH from 2 to 10, whereas other parameters are constant. The Figure 5 illustrates the variation of the degradation of Cr(VI) at different pH. The results show clearly that the pH distinctly influence on the reaction rate whereas get higher rates in the region 2.0±6.5 It can see that at pH 4.5, the reaction rate is highest. This was due to the fact that the removal of Cr(VI) both strongly dependent on the solution pH and favorable at lower pH[3]. The Cr(VI) exist in solution as $HCrO^-_4$ and $Cr_2O_7^{2-}$, at acidic pH the $HCrO^-_4$ is the dominant specie. Moreover, higher pH also can leads to the precipitation of Cr and Fe in the form of $Cr(OH)_3$ and $Fe(OH)_3$, which may cover surface active sites and resulting in decreased photocatalytic activity.[15]

3.4. Effect of catalyst dosage

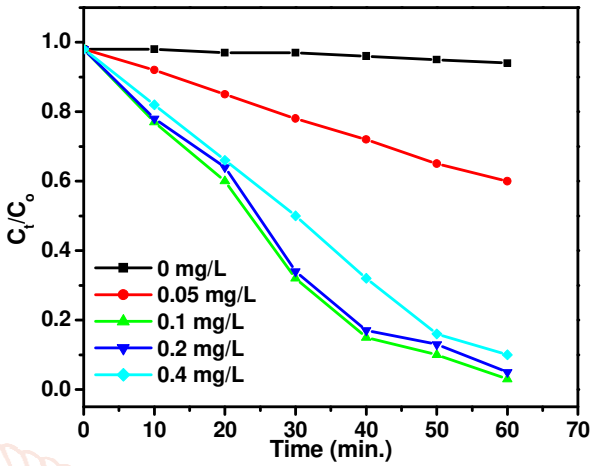

Figure 6. Effect of catalyst contents on the photo-reduction reaction of Cr(VI)

Catalyst content introduced in the photo-reduction Cr(VI) reaction is considered as one of the important parameters. The influence of catalyst dosage on the heterogeneous photo-degradation of Cr(VI) by Fe_3O_4 sphere doped Zn is shown in Figure 6. Catalyst dosage of 0.05, 0.1, 0.2 and 0.4 mg/L was studied while keeping other parameters constant. The results reveal that the photo-degradation of Cr(VI) increased with Fe_3O_4 sphere doped Zn concentration from 0g/L to 0.2 mg/L. However, when the catalyst dosage was beyond 0.2 mg/L the rate of reaction decreased. The similar trend of this effect has studied by other authors.[16] At Zn doped Fe_3O_4 concentration increasing from 0 to 0.2 mg/L leaded to increase in the rate of degradation, which can be attributed to more active sites and the free reactive radical generation. The rate of reaction reduced at the higher dosage of catalyst can be assigned to the enhanced muddiness of solution, resulting in the light harvesting reduced.[17]

3.5. The stability and reusability

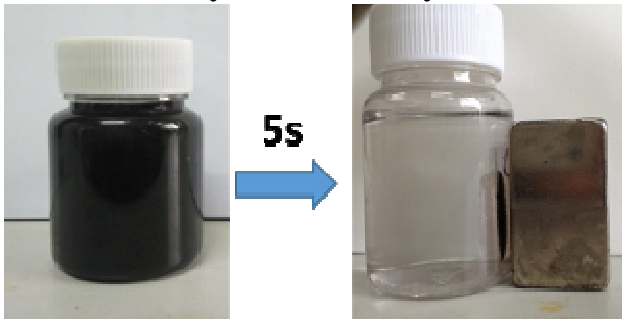

Figure 7 The recovery of the as-prepared products under an external magnetic field

In addition, the stability and reusability of Fe_3O_4 sphere doped Zn in the Cr (VI) photo-reduction process were also investigated. After the experiment, the photocatalyst was collected and then it was transferred into 50 mL aqueous solution with deionized water, 0.1 M NaCl, 0.1 M HNO_3 and 0.1 M HCl, respectively. The mixtures were shaken at room temperature overnight, and the filtrates were analyzed to determine the concentration of Cr(VI) after desorption, the same experiment was repeated for five times. The results show that the catalyst was easily separated by an external magnetic field (Figure 7) and their photo-reduction efficiency for Cr(VI) degradation has no significant change even after the five successive cycles (losing only 3%), indicating high stability of the catalyst. These properties will play a very important role in application for water treatment at industry scale.

IV. CONSCLUSION

Uniform and magnetic recyclable Fe_3O_4 sphere doped Zn were synthesised via the facile solvothermal process in EG solvent. The as-prepared products are uniform sphere with high porosity and ferromagnetic behavior. The Fe_3O_4 sphere doped indicated the high photocatalytic efficiency for degradation of Cr(VI) in water under visible light irradiation. The sphere catalyst has high stability and could be easily separated and recycled by external magnetic field. The as-prepared photocatalysts could be promising photo-reduction catalysts for the degradation of Cr(VI) in water and wastewater.

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