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Photo-Catalytic Activity of ZnO Supported on H-ZSM-5 Zeolite to Reduce Cr(VI) from Aqueous Solutions

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ABSTRACT

Aims The application of photocatalytic processes to remove heavy metals in aqueous solutions and industrial wastewater are regarded as extremely effective, clean and without producing waste methods. The goal of the present study was to investigate the photocatalytic activity of ZnO based on H-ZSM-5 zeolite support.

Materials & Methods ZnO/H-ZSM-5 composite synthesized by impregnation method successfully, and photo-reduction of Cr(VI) was investigated via this composite in present of UV light irradiation. The prepared composite was characterized by X-ray Diffraction (XRD) and Field Emission Scanning Electron Microscopy (FESEM). Data was analyzed by repeated measurement statistical test.

Findings ZnO/H-ZSM-5 (79.5%) had better removal photo-reduction activity than pure H-ZSM-5 (8.7%; p=0.003) zeolite and ZnO (58.8%; p=0.003). The initial concentration of Cr(VI) was a highly influential factor in photo-reduction of Cr(VI); In the way that when the initial concentration increased from 10 to 40mg/l, the photo-reduction percentage decreased from 92.5 to 57.7% in constant operational conditions (p=0.001).

Conclusion ZnO/H-ZSM-5 composite has higher removal photo-catalytic activity than pure ZnO and HZSM-5 zeolite. Photo-reduction of Cr(VI) by ZnO/H-ZSM-5 composite is an efficient technology for the treatment of water and wastewater containing high concentration of Cr(VI).

Keywords Oxidation-Reduction; Hexavalent Chromium; Metals, Heavy

CITATION LINKS

[1] Enhanced hexavalent chromium removal from aqueous solution using a sepiolite-stabilized zero-valent iron nanocomposite: Impact of operational parameters and artificial neural ... [2] Rapid reduction of Cr (VI) coupling with efficient removal of total chromium in ... [3] Facile synthesis of polypyrrole decorated reduced graphene oxide–Fe 3 O 4 magnetic composites and its application for ... [4] Adsorption of Cr (VI) from aqueous solution by hydrous ... [5] Photo-reduction of hexavalent chromium in aqueous solution in the presence of zinc oxide as semiconductor ... [6] A novel chitosan functional gel included with multiwall carbon nanotube and substituted polyaniline as adsorbent for efficient removal of chromium ... [7] Iron (Fe+3) oxide/hydroxide nanoparticles-based agglomerates suspension as ... [8] Ozone-assisted photocatalytic oxidation of gaseous ... [9] Photocatalytic reduction of Cr(VI) on nanosized Fe2O3 supported on natural Algerian clay: Characteristics, kinetic and ... [10] Photocatalytic reduction of Cr (VI) to Cr (III) in solution containing ZnO or ZSM-5 zeolite using oxalate as model ... [11] Nano sized ZnO composites: Preparation, characterization and application as photocatalysts for degradation of ... [12] Enhanced photocatalytic performance of Bi 2 O 3/H-ZSM-5 composite for rhodamine B degradation under UV light ... [13] An easy and efficient use of TiO2 supported HZSM-5 and TiO2+HZSM-5 zeolite combinate in the photodegradation of aqueous phenol and ... [14] Photocatalytic activity of ZnO impregnated Hβ and mechanical mix of ZnO/Hβ in the degradation of monocrotophos in ... [15] UV-assisted photocatalytic synthesis of ZnO–reduced graphene oxide composites with enhanced photocatalytic activity in reduction of ... [16] Microwave-assisted synthesis of TiO 2-reduced graphene oxide composites for the photocatalytic reduction of ... [17] Characterizations of nano-TiO2/diatomite composites and their photocatalytic reduction of ... [18] Conventional hydrothermal synthesis of nanostructured H-ZSM-5 catalysts using various templates for light olefins production from ... [19] Photocatalytic reduction of hexavalent chromium over ZnO nanorods immobilized on ... [20] Sensitization of CdS nanoparticles onto ... [21] A survey of photocatalytic materials for environmental ... [22] Photocatalytic reduction of hexavalent chromium with ... [23] Removal of mercury (II) and chromium (VI) from ... [24] Photocatalytic reduction of Cr (VI) in ... [25] Photocatalytic reduction of Cr(VI) with TiO2 film under visible ...

Introduction

In the present era, the growth of different kinds of industries and the increasing of population has led to the production of high amounts of industrial wastewater, which contains various contaminants, especially heavy metals [1].

Heavy metals, due to their high toxicity and non-biodegradability, have very harmful impacts on human health and environment [2, 3]. As a carcinogenic and mutagenic pollutant, hexavalent chromium (Cr(VI) or Cr^{6+}) is the most dangerous and significant pollutant of wastewaters and increasing in the concentration of Cr(VI) in water resources can cause spoiling of sperm in males and breast cancer in females [1, 4].

Industrial sources, e.g. metallurgy, wood processing and electronic, release Cr(VI) in effluent streams. These effluents must be purified before discharge to surface water [5]. A variety of conventional techniques has been developed to remove Cr(VI), e.g. ion-exchange, membrane separation and chemical precipitation [6]. These techniques have significant disadvantages and limits due to high operation costs, large amounts of sludge production and incomplete Cr(VI) removal [7]. Hence, due to its simplicity and manageability of system, the photocatalytic process, which is also known as a green technique, has proved to be functional in the conversion of heavy metals into non-toxic forms [8, 9].

Many semiconductor catalysts, such as TiO_2, ZnS and WO_3 have been used for photocatalytic reduction of Cr(VI) to Cr(III) [10]. ZnO is one of the most effective semiconductors because of its specific properties; anti-toxicity, low cost, high ultraviolet adsorption and lack of creation of hazardous by-products [11]. Despite many advantages of photocatalysts, low adsorption ability of semiconductors and low quantum yields in reaction are the limitations of their application. Therefore, suitable supports are needed to increase the efficiency of photocatalysts. When a semiconductor is dispersed over supports the band gap energy increases and the rate of electron-hole recombination decreases that increases the efficiency of the catalyst reaction [12]. Zeolites like H-ZSM-5, among various supports, have unique structure, strong adsorption ability and stable nature; so, it seems that ZnO supported on this zeolite has an improved efficiency [12, 13].

In last decade, several studies have been conducted in this filed. Anandan *et al.* have studied the activity of ZnO impregnated Hβ in degradation of monocrotophos in aqueous solutions [14], Liu *et al.* have investigated ZnO-reduced graphene oxide composites for reduction of Cr(VI) [15], Liu *et al.* in another research have studied photocatalytic reduction of Cr(VI) in solution containing TiO2/reduced grapheme [16] and Sun *et al.* have used TiO2/diatomite composite for Cr(VI) reduction [17].

The goal of the present study was to investigate the photocatalytic activity of ZnO based on H-ZSM-5 zeolite support.

Materials & Methods

This experimental study was conducted in laboratory scale bath. Potassium dichromate ($K_2Cr_2O_7$; 99.9%) was used as Cr(VI) source and zinc acetate dehydrate (Ph. Eur.; USP grade) was used as ZnO source and ZnO/H-ZSM-5 photocatalysts were prepared by the following method. Initially, H-ZSM-5 zeolite was added into 50ml of distilled water and continuously stirred (for 1 hour) at room temperature, then 4.04g of zinc acetate dehydrate was added into solution with constant stirring at 80℃ until dried. Finally, obtainned material was kept at 100℃ overnight and was calcined at 300℃ for 2h. The stock Cr(VI) solution (500mg/l) was made by dissolving 1.417g of 99% potassium dichromate in 1l of distilled water. Synthetic solutions of different concentration of Cr(VI) were obtained by diluting the stock solution.

X-ray diffraction (XRD) was applied for structural identification and verification of proper crystalizing of the prepared catalysts. It was done via D-5000 diffract meter (Siemens; Germany) in 2-90° 2θ range with mono-chromatized Cu-Ka radiation coupled with X-ray tube operated at 30mA and 40kV. The phase identification was made by comparison to the joint Committee on Powder Diffraction Standards (JCPDSs) database [18]. The morphology and particle size of catalysts were investigated by S-4160 Field Emission Scanning Electron Microscopy (FESEM) apparatus (HITACHI; Japan).

Photocatalytic reaction of Cr(VI) was carried out in a 300ml cylindrical reactor (Figure 1).

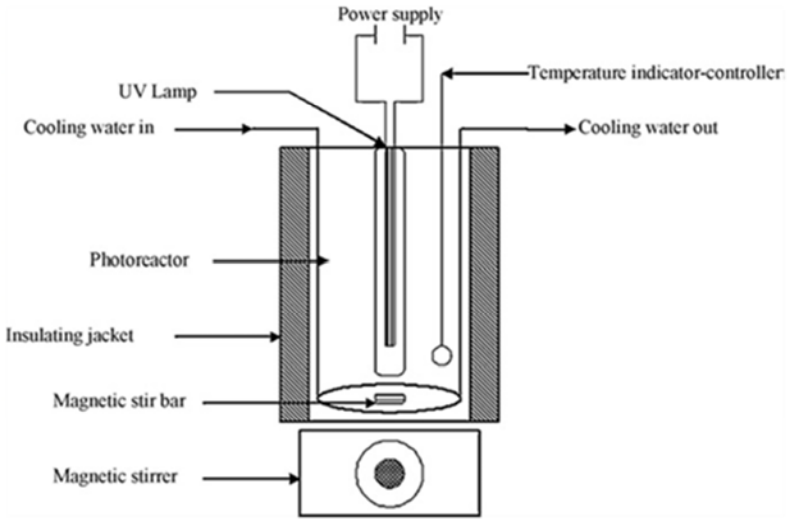

Figure 1) Schema of the cylindrical reactor used for photocatalytic reduction of Cr(VI)

The reactor was equipped with a high-pressure 125W mercury lamp (Philips; The Netherlands) that generated 300-400nm wave-length; also the reactor was covered with aluminum foil followed by a black cloth to prevent UV light leakage. The reactor temperature was controlled and maintained constant at 20±1°C by circulating air flow. A 200ml solution of Cr(VI) was introduced in the reactor and its pH value was adjusted by H_2SO_4 solution (0.1M). Before to irradiation, suspensions were magnetically stirred for 30min in dark conditions to ensure substrate-surface equilibration, and then it was irradiated under continuous magnetic stirring for 1h. After the run, the samples were separated from photocatalyst particles by centrifugation (Noavaran Tajhiz; Iran). The concentration of the Cr(VI) was determined by colorimetry at 540nm using the 1,5-diphenylcarbazide (Merck; Germany) as color agent. Cr(VI) removal percentage after photo-reduction was calculated by $C_0-C_e/C_0\times100$mg/l (C_0=initial concentration of Cr(VI); C_e=residual concentration of Cr(VI) in solution).

The repeated measurement test was applied for statistical analysis using SPSS 16 software.

Findings

X-ray diffraction (XRD) patterns of the ZnO, H-ZSM-5 and ZnO/H-ZSM-5 samples showed that all samples were formed correctly. Although, a comparison of XRD patterns exhibits that the intensity of the H-ZSM-5 peaks decreased after ZnO coated on the H-ZSM-5 (Figure 2).

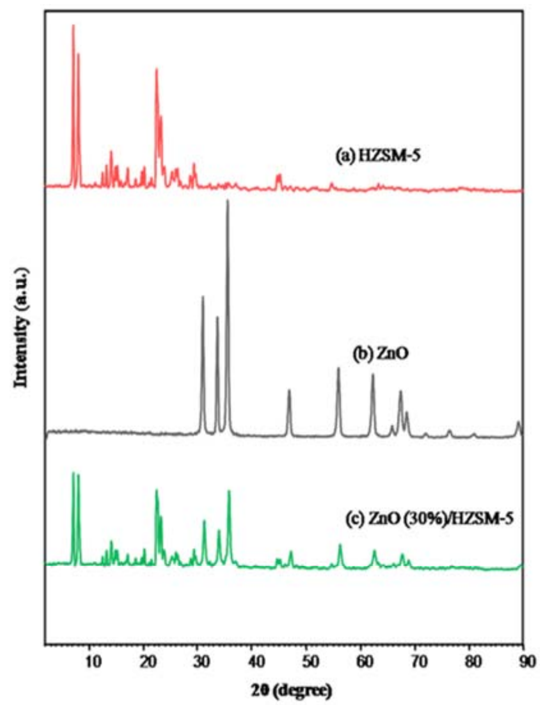

Figure 2) XRD patterns of H-ZSM-5 (a), ZnO (b) and synthesized ZnO/H-ZSM-5 composite (c).
The characteristic lines especially in the 2θ range between 30 and 40° can be indexed to the known wurtzite hexagonal phase of ZnO (JCPDS: 00-079-0206). Moreover reflection peaks of ZnO are sharp which indicate the crystalline character of ZnO. The XRD patterns in 2θvalues of 7.9, 8.9, 23.1 and 23.9° can be indexed to H-ZSM-5 orthorhombic structure (JCPDS: 00-042-0024) as reported previously [18].

The surface micrograph clearly exhibited that H-ZSM-5 sample synthesized in hexagonal shape crystals with different sizes. Additionally, no irregular-shaped particles could be observed in the mesoporous H-ZSM-5. As can be seen, our synthesized ZnO sample has narrow size and rod-like shape. So, the particles have homogeneous and uniform surface. Also, the figures illustrated that ZnO particles well dispersed on the H-ZSM-5 and ZnO coated particles seemed like clog. No significant changes were observed in zeolite crystallites (Figure 3).

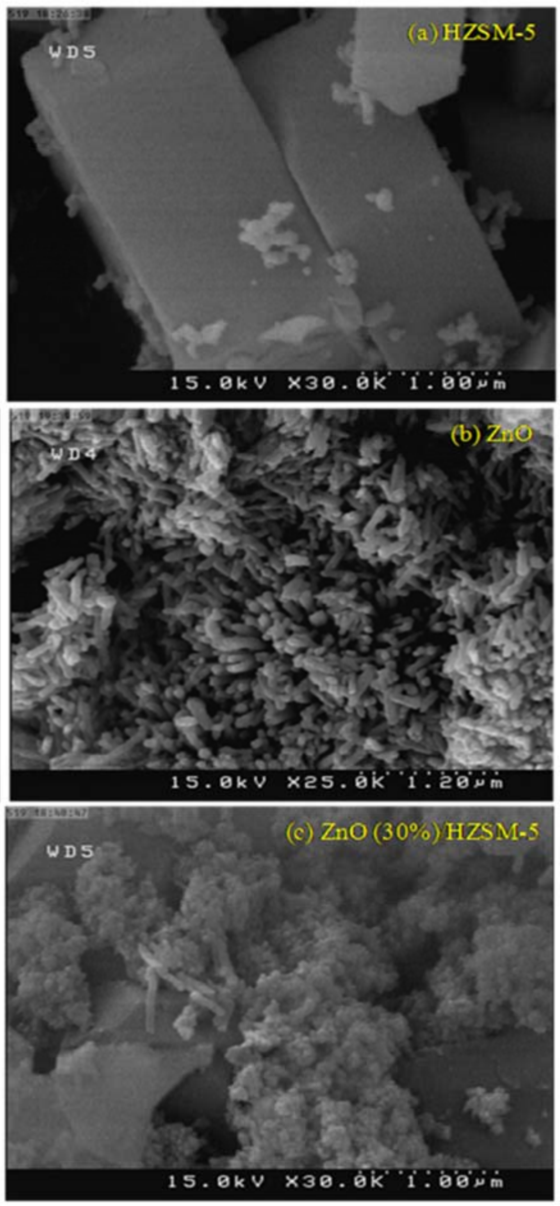

Figure 3) FE-SEM images of H-ZSM-5 (a), ZnO (b) and synthesized ZnO/HZSM-5 composite (c)

ZnO/H-ZSM-5 (79.5%) had better removal photo-reduction activity than pure H-ZSM-5 (8.7%) zeolite and ZnO (58.8%; $p=0.003$). The initial concentration of Cr(VI) was a highly influential factor in photo-reduction of Cr(VI); In the way that when the initial concentration increased from 10 to 40mg/l, the photo-reduction percentage decreased from 92.5 to 57.7% ($p=0.001$) in constant operational conditions (pH=3; UV=125W; time=60min).

Discussion

In the present study, the effect of H-ZSM-5 supported on ZnO for reduction of Cr(VI) in aqueous solution was investigated. Also, XRD and FE-SEM analyses were carried out on the samples. The FESEM and XRD results confirmed the correctly formation of ZnO/H-ZSM-5 composite.

The results displayed that ZnO/H-ZSM-5 had better activity than pure H-ZSM-5 zeolite and ZnO. It can be attributed to synergic effect between ZnO and H-ZSM-5 zeolite. On other hand the results indicated that after 60min in the dark condition only insignificant amount of Cr(VI) was absorbed by ZnO/H-ZSM-5 composite. Thus, it can be deduced that this process is mainly photocatalytic reduction than physical adsorption that is consistent with other studies such as Shirzad-Siboni *et al.* that have investigated the photocatalytic reduction of hexavalent chromium over ZnO immobilized on kaolin [19] and Pawar & Lee that have examined the activity of CdS/reduced graphene for effective removal of Cr(VI) [20].

The photo-reduction of Cr(VI) carries out following two main steps; first, Cr(VI) adsorbed on H-ZSM-5 reaction occurs on its surface and then, Cr(VI) molecules transfer to the ZnO surface to carry on photocatalytic reaction. According to the mentioned steps, various factors can be important in photo-reduction of chromium by ZnO/H-ZSM-5 nanocomposite:

(a) The large specific area of adsorbent which adsorbs Cr(VI) molecules and creates active sites for photocatalytic reaction;

(b) Quick transfer of adsorbed molecules from H-ZSM-5 to ZnO, which accelerates with increasing the surface of adsorbent; and

(c) The performance of ZnO in photocatalytic reaction [8, 12].

On other hand, the high performance of the ZnO/H-ZSM-5 composite in photo-reduction of Cr(VI) can be attributed to the coordination between H-ZSM-5 and ZnO that H-ZSM-5 has large specific area and ZnO, due to its position of valence band, has strong photogenerated holes as well as preventing of recombination [12, 21].

The increasing of Cr(VI) concentration results in more adsorption of Cr(VI) ions on ZnO/H-ZSM-5 composite which can cause the total available adsorption sites to be limited. Also, increasing in the initial concentration of Cr(VI) plays inhibitory role in reaching UV light to the catalyst. Hence, the reduction of Cr(VI) is reduced [22, 23]. This claim has been confirmed by Ku & Jung [24] and Wu *et al.* [25].

There was no limitation on implementation of this study. We suggest that effect of other cheaper zeolites such as Clinoptilolite be investigated.

Conclusion

ZnO/H-ZSM-5 composite has higher removal photo-catalytic activity than pure ZnO and HZSM-5 zeolite. Photo-reduction of Cr(VI) by ZnO/H-ZSM-5 composite is an efficient technology for the treatment of water and wastewater containing high concentration of Cr(VI).

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Conflicts of Interests: We certify that there is no conflict of interest in this manuscript.

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