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Adsorption and photodegradation of methylene blue by iron oxide impregnated on granular activated carbons in an oxalate solution

Zukhra C. Kadirova [a,b,*], Ken-ichi Katsumata [b], Toshihiro Isobe [c], Nobuhiro Matsushita [b], Akira Nakajima [c], Kiyoshi Okada [b]

[a] Institute of General and Inorganic Chemistry, Academy of Sciences of the Republic of Uzbekistan, Mirzo Ulugbek Str. 77a, Tashkent 100170, Uzbekistan
[b] Materials and Structures Laboratory, Tokyo Institute of Technology, 4259 Nagatsuta, Midori, Yokohama 226-8503, Japan
[c] Department of Metallurgy and Ceramics Science, Tokyo Institute of Technology, 2-12-1 O-okayama, Meguro, Tokyo 152-8552, Japan

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ABSTRACT

The photocatalytic adsorbents BAU-OA, BAU-CL and BAU-HA with varying iron oxide content (9–10 mass%) were prepared by heat treatment at 250 °C from commercial activated carbon (BAU) impregnated with iron oxalate, chloride, tris-benzohydroxamate, respectively. The XRD patterns showed amorphous structure in the BAU-CL sample (S_{BET} 50 m^2/g) and low crystallinity (as FeOOH and Fe_2O_3 phases) in the BAU-HA and BAU-OA samples (S_{BET} 4 and 111 m^2/g, respectively). The methylene blue adsorption capacities was decreased in order of BAU-OA < BAU-CL < BAU-HA sample and the adsorption followed Langmuir model. The apparent MB photodegradation rate constant (k_{app}) was increased in same order BAU-HA < BAU-CL < BAU-OA under the standard experimental conditions (initial MB concentrations 0.015–0.025 mM; sample content – 10 mg/l; initial oxalic acid concentration – 0.43 mM; pH 3–4; UV illumination). The process included high efficiency combination of adsorption, heterogeneous and homogeneous catalysis under UV and solar lights illumination without addition of hydrogen peroxide. The detoxification of water sample containing organic dyes was confirmed after combined sorption-photocatalytic treatment.

1. Introduction

The combination of photocatalysis and adsorption processes is very promising technology for the treatment of water containing organic pollutants [1]. Whereas most studies focus on the modification and performance of activated carbon like adsorbents [2], the use of activated carbons as materials for the photocatalyst's support has many advantages because of an excellent adsorption for organic compounds, high surface areas, easy control of the surface chemistry, high porosity and ability for recovering of active metal phase by burning the carbon support. Moreover the degradation rate under UV irradiation usually attributed to the porosity of the carbon and presence of the carbon support affects the nature of mechanism for degradation of organic pollutants, suggesting an important self-photoactivity of the carbon support [3].

It is known that the photocatalytic decomposition of organic compounds is enhanced greatly by the presence of oxalic acid (OA) and also can be considered as a photo-Fenton reaction system [4]. The mechanism of catalytic oxidation is based on the processes of the formation of photoactive $[Fe(III)(C_2O_4)_n]^{(3-2n)}$ complex species, where $n = 1–3$. These complexes can be excited under UV and/or solar illumination and transformed to $[Fe(II)(C_2O_4)_{(n-1)}]^{(4-2n)}$ and oxalate radicals, initiating of organic oxidation by generation of hydroxyl radicals in the system [4,5].

The main advantages of the Fenton process are the simplicity of the pollutant destruction and using soft operating conditions (room temperature and atmospheric pressure) without specific equipment in comparison with traditional Fenton process. The Fenton process can be carried out as a homogeneous system [4,5], where the Fe-catalyst is partially dissolved in the aqueous solution, as in a heterogeneous way in the Fenton-like processes [6–18]. However, the homogeneous system is less appropriate since it leads to high metal (iron or other transition metals) concentrations in the final effluent. The homogeneous process can generate metal ion concentration about 50–80 ppm, which is much higher than the maximal allowable concentration of 2 ppm, and an additional metal recovery process would consequently rise the cost and the complexity of this process. But the application of heterogeneous catalysts for the Fenton-like process in the presence of OA under UV- and/or solar illumination can decrease high level of Fe ions leaching during the oxidation process. At present time, a number of studies have been carried out to find efficient heterogeneous

* Corresponding author at: Institute of General and Inorganic Chemistry, Academy of Sciences of the Republic of Uzbekistan, Mirzo Ulugbek Str. 77a, Tashkent 100170, Uzbekistan. Tel.: +998 71 2625660; fax: +998 71 2627990.
E-mail address: zuhra_kadirova@yahoo.com (Z.C. Kadirova).

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systems, including oxides [6–10], carbon materials [11–13], rice husk ash [14], silica SBA-15 [15,16], zeolites [17], clays [18], etc. The aqueous solutions of metal chelates are highly suitable for the production of supported metal oxide catalysts by impregnation, and various researches demonstrated that solutions of chelated metal ions provide excellent precursors for the preparation of heterogeneous catalysts by impregnation of support materials [19]. The increase in viscosity of such solutions during heat treatment lead to redistribution of the catalyst precursor due to the formation of a gel-like film over the support surface, forming upon calcination the homogeneous dispersed oxides. The average particle size as well as the particle size distribution were much smaller for the catalysts prepared with the chelated precursor in comparison with metal salts [20–22].

The aim of present work is preparation and study of low cost materials with simultaneous advantages of adsorption, heterogeneous and homogeneous catalysis in presence of oxalic acid. Besides of many studies in this field, the photo-Fenton-like heterogeneous system in presence of oxalic acid solution without hydrogen peroxide and low-cost photocatalytic adsorbents from activated carbon and iron oxides were not considered. In this study, a series of the iron oxide loaded on activated carbon (FAC) samples were prepared by an impregnation method followed by heat treatment at 250 °C. Different iron oxide bearing precursors were applied to enhance photocatalytic activity by varying Fe_2O_3 particles formed and distributed on the AC surface. The crystallinity and porous properties were characterized by X-ray diffraction and N_2 adsorption. The adsorption and photocatalytic properties of the as-prepared samples for methylene blue (MB) were investigated in the dark and under UV illumination in an OA solution. A cationic dye, MB, was chosen as a model compound because it is widely used in the textile and paper industries owing to its low price. Adsorption and photocatalytic performance of the FAC samples were also analyzed as a function of preparation method, Fe precursor and porous properties.

2. Experimental

2.1. Sample preparation

A commercially available granular AC (BAU, Russia) was used as the starting material. The granular AC was acid treated with 1 M HCl, washed with distilled water several times to remove any impurities in the pores and then dried at 105 °C for 24 h. Three kinds of the Fe-phase impregnated ACs (BAU-CL, BAU-HA and BAU-OA) samples were separately prepared by impregnation of AC in the iron chloride ($FeCl_3{\cdot}6H_2O$) (I), the iron oxalate [$Fe(C_2O_4){\cdot}2H_2O$] (II) and the iron tris-benzohydroxamate [$Fe(C_7H_6O_2N)_3{\cdot}3H_2O$] (III) solutions (Fig. 1), respectively, with the concentration of 1 M. After drying at 105 °C overnight, the samples were heat treated at 250 °C for 1 h in order to convert the impregnated Fe-salts to Fe_2O_3.

2.2. Characterization

The crystallinity of the samples was examined by X-ray powder diffraction using a LabX XRD-6100 X-ray diffractometer (Shimadzu, Japan) with monochromated Cu Kα radiation. The specific surface area (S_{BET}), pore size distribution (PSD) and total pore volume (V_P) were obtained from N_2 adsorption–desorption isotherms at 77 K (Autosorb-1, Quantachrome, USA), on samples preheated at 120 °C for 20 h in vacuum. The S_{BET} values were calculated by the Brauner, Emmett and Teller (BET) method and the PSD was determined by the Barrett, Joyner and Halenda (BJH) method using the desorption isotherms.

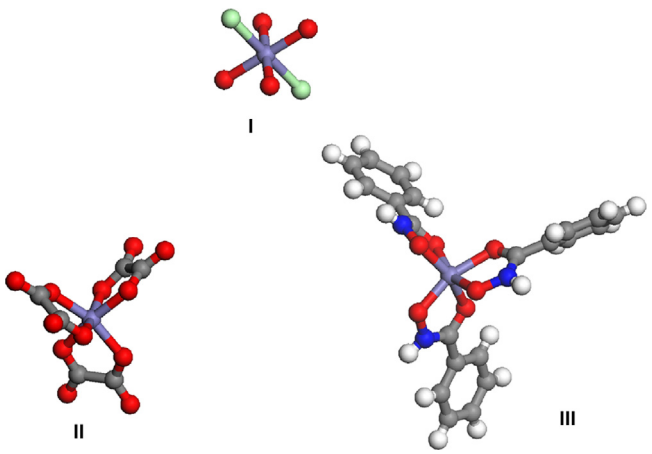

Fig. 1. Three-dimensional molecular structure of iron chloride ($FeCl_3{\cdot}6H_2O$) (I), the iron oxalate [$Fe(C_2O_4){\cdot}2H_2O$] (II) and the iron tris-benzohydroxamate [$Fe(C_7H_6O_2N)_3{\cdot}3H_2O$] (III) and (dark gray, carbon atoms; light gray, hydrogen atoms; green, chloride atoms; and blue, nitrogen atoms; red, oxygen atoms; violet, iron atoms). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

2.3. Adsorption and photodegradation of MB

Adsorption capacity of the as-prepared samples for MB was determined by dispersing the sample in an OA aqueous solution containing MB under magnetic stirring for 24 h in the dark. The equilibrium adsorption capacity (Q_e; mmol/g) of MB on the samples was calculated from the following equation:

$$Q_e = \frac{C_0 - C_e}{m} V \quad (1)$$

where C_0 and C_e are the initial and equilibrium MB concentrations in the dark (mmol/l), V is the solution volume (l) and m is the amount of sample (g).

After adsorption, the photodegradation of MB was investigated under UV illumination using three different UV lamps of 20 W power with a wavelength range of 300–415 nm and the maximum at 352 nm. The measured UV illumination power flux inside the reactor was 1.8 mW/cm^2. For each experiment, 10 mg of sample was dispersed in a 100 ml of solution containing MB with the initial concentration of 0.011–0.025 mM and OA with the initial concentration of 0.43 mM (40 ppm). The pH of the reaction mixture measured using a digital pH meter was around 2.9–3.6. The UV illumination was kept for 2 h, and 5 ml of aliquot was taken at predetermined times for analysis. The photocatalytic degradation experiments by solar radiation were performed under clear sky on sunny days using a glass flask covered by a thin transparent plastic film to suppress temperature rise under direct sunshine. The intensity of solar radiation was estimated to be about 0.080–0.094 W/cm^2 at 480 nm [23]. Since the measurement of solar radiation shows the fluctuation of sunlight intensity during the photooxidation experiment even under clear sky on sunny days, the identical sunlight intensity was maintained for a set of photooxidation experiments with different samples. The change in the MB concentration was monitored using a Lambda35 UV–Vis spectrophotometer (Perkin-Elmer, USA) with measuring the pH of the solution. The concentration of total Fe ion in the solution was analyzed by ICP-OES (Prodigy, Leeman Labs, USA).

2.4. Aquatic toxicity tests

Aquatic toxicity tests are used for complex determination and monitoring the toxic effects of water before and after adsorption–photodegradation treatment. During experiments

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