ECO-FRIENDLY NANOPHOTOCATALYSTS FOR DISCOLORING OF AZO DYES IN INDUSTRIAL WASTEWATERS

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ABSTRACT. The photocatalytic activity of nanostructured semiconductor TiO2 and ZnO thin films to destruct azo dye has been investigated and compared with that of Fe/FeO(OH) magnetic nanoparticles. Laboratory experiments have been carried out to evaluate the performance of applied nanomaterials by test with reactive black 5 (RBS) as a model pollutant. Special attention is focused on the possibilities for application of these materials in green Nanobiotechnology, e.g. their conjunction with microbiological processes for complete mineralization of the organic pollutants. In this report it is studied the correlation between absorbance of model dye solution illuminated with UV radiation in the presence of three types nanoparticles TiO2, ZnO and Fe/FeO(OH). Photodegradation rate constants and adsorption efficiency were determined using spectrophotometric methods.

1. Introduction

The removal of organic pollutants as azo dies in wastewater of the textile industry is an important measure in environmental protection. Nanobiotechnology is a rapidly growing field with potential technological applications for remediation of such wastewaters. However, an important challenge for its green chemistry consists in developing of appropriate chemical processes for the treatment of pollutants, which might ensure the following step of mineralization by microorganisms. A perspective solution of this requirement could be the heterogeneous photocatalysis with semiconductor ZnO and TiO2 or reduction with zero valent iron nanoparticles (ZVIN).

These three nanomaterials are eco-friendly with proven nontoxic and biocompatible properties (Matos et al. 2009).

ZnO and TiO2 nanoparticles are the most used photocatalysts that show high efficiency for the oxidative photodegradation of hazardous aromatic macromolecules in polluted water and air (Choi 2006). Photocatalytic reactions occurring on semiconductor surface have many applications, in particular for discoloring of azo dyes in contaminated wastewaters (Karkmaz et al. 2004).

Photocatalytic conversation or degradation with illuminated nanostructured oxides have been demonstrated for a huge number of substances, which are largely ascribed to the strong oxidation potential of their valence band holes and surface OH radicals (Kun et al. 2005, Ullah & Dutta 2008). ZnO powder has been demonstrated as an improved photocatalyst as compared to commercialized TiO2 one based on the larger initial rates of activities (Jung et al. 1997) its absorption efficiency of solar radiations (Sakthivel et al. 2003). However, their states of application and synthetic methods of preparation highly affect the reaction activity with pollutants. Laboratory research has established that FeO(OH) ZVIN are very effective in destroying a wide variety of common contaminants as azo dyes, halogenated organic derivatives and other polychlorinated hydrocarbons and pesticides (Zhang 2003).

ZVIN can reduce not only organic contaminants but also the inorganic anions nitrate, which is reduced to ammonia, perchlorate, selenate, arsenate, chromate, but they are also efficient in removing dissolved metals from solution.

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2. Experimental procedures

2.1. Synthesis of FeO(OH) nanoparticles by wet reduction of iron (III) chloride with sodium borohydride.

0.4 g of NaOH was dissolved in 100 ml 0.16 M solution of NaBH₄ at room temperature. Then into this solution was added dropwise 100 ml 0.1 M aq FeCl₃. The reaction is exothermic and it is accompanied with liberated hydrogen gas. The synthesis is performed with constantly mixing under ambient pressure. The formed iron nanoparticles as black precipitation were harvested by centrifugation and kept in refrigerator at 4 °C without future wishing steps (to avoid their oxidation).

2.2. Decolorization of RB5 by FeO(OH) nanoparticles.

50 mg zerovalent iron nanoparticles were suspended in distilled water and injected into 250 ml solution of RB5 with concentration 10 mg/L. The reaction mixture is stirrer (150 rounds/ min) and aliquots of 1 ml were taken at every 10 min. The tests for decolorization are performed at pH 8.5, 7.5, 5.0, 4.0 and 2.0. The absorption changing was measured with Spectrumom 410 (Hungary) at 600 nm fixed wavelength.

2.3. Preparation of thin film nanostructured ZnO and TiO₂ on glass and aluminum.

The semiconductor thin films of ZnO and TiO₂ nanoparticles were prepared by sol-gel and spray pyrolysis method (Kaneva et al. 2010, Yang et al. 2009). Some details about the conditions for sample preparation are given in Table 1 and 2.

Table 1. Conditions for sample preparation of ZnO and TiO₂ by spray pyrolysis method.

<table>
<thead>
<tr>
<th>code</th>
<th>solvent</th>
<th>precursor</th>
<th>temp. [°C]</th>
<th>pad</th>
</tr>
</thead>
<tbody>
<tr>
<td>T5</td>
<td>isopropanol : glycol (3:11)</td>
<td>0.1 M Ti(OPr)₄</td>
<td>400</td>
<td>glass</td>
</tr>
<tr>
<td>T5</td>
<td>isopropanol : butyldiglycol (3:1)</td>
<td>0.1 M Ti(OPr)₄</td>
<td>400</td>
<td>aluminum</td>
</tr>
<tr>
<td>S6</td>
<td>butanol</td>
<td>TiO₂ degussa Ti(Obu)₂</td>
<td>500</td>
<td>glass</td>
</tr>
<tr>
<td>S6</td>
<td>butanol</td>
<td>TiO₂ degussa Ti(Obu)₂</td>
<td>500</td>
<td>aluminum</td>
</tr>
<tr>
<td>BC2</td>
<td>ethanol</td>
<td>Zn(CH₃COO)₂</td>
<td>380</td>
<td>glass</td>
</tr>
<tr>
<td>BC2</td>
<td>ethanol</td>
<td>Zn(CH₃COO)₂</td>
<td>380</td>
<td>aluminum</td>
</tr>
</tbody>
</table>

Table 2. Conditions for sample preparation of ZnO and TiO₂ by sol-gel method.

<table>
<thead>
<tr>
<th>code</th>
<th>solvent</th>
<th>precursor</th>
<th>temp. [°C]</th>
<th>pad</th>
</tr>
</thead>
<tbody>
<tr>
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<td>0.34 M Ti(Obu)₂</td>
<td>400</td>
<td>glass</td>
</tr>
<tr>
<td>T5</td>
<td>ethanol + water</td>
<td>Zn(CH₃COO)₂</td>
<td>400</td>
<td>glass</td>
</tr>
<tr>
<td>BC2</td>
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<td>TiCl₄ + celulose</td>
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<tr>
<td>BC2</td>
<td>butanol</td>
<td>Zn(CH₃COO)₂</td>
<td>micro wave</td>
<td>glass</td>
</tr>
</tbody>
</table>

2.4. Design of photo-catalytic cell.

A scheme of photocatalytic cell for oxidation of RB5 is shown on Fig. 1. The distance between UV lamp and reaction tank can be controlled. In this experiment it was kept 5 cm. The volume of treated azo dye RB5 is 250 ml and concentration 10 mg/L (analogical with the described above experiment with ZVIN). The solution is constantly mixed by magnetic stirrer (150 rounds/ min) and aerated. Aliquots of 1 ml were taken at every 30 min and the absorption was measured at 600 nm.

Fig. 1. Experimental scheme of a photocatalytic cell used to test ZnO and TiO₂ activity to oxidize RB5. 1 – cell, 2 – UV lamp, 3 – stand, 4 – reaction tank, 5 – RB5 solution, 6 – magnetic stirrer

The decolorization and degradation efficiency have been calculated as: $D = [(C₀-C)/C₀]*100$, where $C₀$ is the initial concentration of dye and $C$ is the concentration of dye after irradiation in selected time interval. All photocatalytic tests were performed at room temperature (25 °C). Control experiments without UV light (the reaction system was kept in dark) were also performed.

3. Result and discussion

3.1. Structural characterization of the oxides nanoparticles.

Scanning electron microscopic (SEM) images of ZnO and TiO₂ prepared by sol gel methods and FeO(OH) nanoparticles are shown in Fig. 2. This analysis reveals that semiconductor nanoparticles are spherical as the average diameter of ZnO (Fig. 2b) is 150-230 nm in comparison with TiO₂ (Fig. 2c), which is 40-50 nm. Particle size and surface area play key effects on their photocatalytic activities. The observed difference is expected to improve the efficiency of TiO₂ nanoparticles due to their higher surface area.

Fig. 2. SEM images of (a) FeO(OH), (b) ZnO and (c) TiO₂ nanoparticles. Scale bar = 200 nm.
ZVIN possess triangle geometric shape with average size of 150-200 nm. They are composed of a core which is consists of metallic iron and magnetic shell of mixed valent Fe (II) and Fe (III) oxides. ZVIN are applied in the reaction tank as suspension. They are not immobilized in thin film as ZnO and TiO₂. This state increases their contact area with pollutant and improves the decolorization rate. However, their separation from reaction mix is possible by use of external magnetic field. Thus the harmful components can be removed from magnetic particles, which can be reused.

3.2. The UV/VIS spectra of dye solutions before and after decolorization by TiO₂ and ZVIN.

The absorbance peaks of reactive black 5 in the visible region (400 – 700 nm) were disappeared after treatment by ZnO, TiO₂ and ZVIN. The absorbance decreasing indicated that chromophore azo group (-N=N-) of dye for its visible color, was broken down. Preliminary photocatalytic experiments indicated that in the absence of TiO₂ (or ZnO) there was no noticeable change in dye concentration after prolonged irradiation (3 hours) of RB5. The results of absorption studies with TiO₂ are presented in Fig. 3.

Fig. 3. UV-VIS spectra of RB5 before and after decolorization by nanostructured TiO₂ at pH = 2.6.

Prolonged illumination (1-3 h) of air-equilibrated aqueous dye solutions containing TiO₂ resulted in substantial decolorization. The oxidation processes occurred not only in the azo-group, but also there is destroying of the aromatic structure. The benzene and naphthalene peaks are shifted to the left side of the spectrum and disappeared as it is shown on Fig. 3. In each experiment sulphate, nitrate and ammonium ions together with formate and oxalate were identified as end products by analyzing the colorless solution obtained after 20 hours irradiation. Identification of the reaction intermediates is difficult, however some references confirm the presence of naphthionic acid, 1-amino-2-naphthol, 2-naphtol, 1,2-naphthoquinone as intermediates in the photolysis of RB5 (Chatterjee et al. 2008). The destructive oxidation path is shown on Fig 4. Time course of RB5 decoloration reaction was followed at the absorption maximum at 600 nm. In each case it exhibit first-order kinetics. The rates of dye decoloration under specified reaction conditions are not markedly changed for different dye molecules used in this investigation. This suggests that at lower concentration range the rate-controlling step in the decoloration reaction is governed by the adsorption efficiency of dye molecules onto TiO₂ nanoparticle surface.

Most experiments revealed that the absorbance caused by azo group became lower after treatment by zerovalent iron as it is shown on Fig. 5. In this case only new absorbance of amino group appeared in UV-VIS chromatograph (Cao et al. 1999).

Fig. 4. Degradation of Reactive Black 5

Fig. 5. UV-VIS spectra of RB5 before and after decolorization by ZVIN at pH = 2.6

Our result confirmed that ZVIN reduced the azo linkage to hydrogenated azo structure (proved by ninhydrin test). There is no evidence for any destroying of aromatic benzene and naphthalene rings (see Fig. 6). In comparison, the aromatic peaks pointed by arrow on Fig. 5 is not changed or shifted as those on Fig. 3.

Fig. 6. Destruction of azo bond by FeO(OH) nanoparticle
3.3. Photocatalytic comparison of ZnO and TiO\textsubscript{2} decolorization efficiency

In order to understand the efficiency of different catalysts, identical experiments were carried out with ZnO and TiO\textsubscript{2} on the photocatalytic degradation of RB5 and the results are presented in Fig. 7. The results clearly indicate that TiO\textsubscript{2} is found to be more active, showing higher photocatalytic activity for decolorization under UV-VIS irradiation.

![Fig. 7. Comparison of photocatalytic activity of ZnO and TiO\textsubscript{2} catalysts prepared by sol-gel method on degradation rate of RB5: (a) decolorization changing and (b) concentration increasing](image)

The reason for greater activity of TiO\textsubscript{2} is due to the smaller nanoparticles size and the absorption of more light quanta. The method of preparation plays an important role for the nanoparticles size distribution, number of catalytic centers and oxidation efficiency. In our experiments it was found that the nanostructured oxides obtained by spray pyrolysis possess higher catalytic activity than those obtained by sol-gel methods. There is another important phenomenon, which influences the catalyst efficiency – the supporting padding. As it is shown on Fig. 8 catalysts deposited on aluminum material are more effective of those on glass. The reason is not yet elucidated, but probably it is related to the size of catalysis surface or any inhibition reactions from the glass components.

3.5. Effect of pH

The amphoteric behavior of ZnO and TiO\textsubscript{2} semiconductor oxides influences the surface charge of photocatalysts. The role of pH on the rate of degradation was studied in the pH range 2 – 8.5 at constant dye concentration (10 mg/L). The results are illustrated in Fig. 8,9. It is observed in all cases that the rate of degradation increase with decreasing of pH. It is most efficient at pH 2 and very low efficient at neutral or weak alkaline conditions. This is indicative of the significant role of the surface property of the photocatalysis. It has already been reviewed by Bahnemann (Neppolian et al. 1998) that acid-base property of the metal oxide surface can have considerable implication upon their photocatalytic activity. The best effect of pH=2 at Fig. 8 can be explained on the basis of zero point charge of TiO\textsubscript{2}. The adsorption of H\textsubscript{2}O molecules at surficial metal sites is followed by the dissociation of OH\textsuperscript{–} groups leading to coverage with chemically equivalent metal hydroxyl groups (M–OH). TiO\textsubscript{2} surface is positively charged in acidic media (pH < 6.8) whereas it is negatively charged below pH 9. RB5 is anionic dye in aqueous solution. At low pH range, electrostatic interactions between the positive catalyst surface and dye anions lead to strong adsorption of the latter on metal oxide support.

![Fig. 8. pH effect on the decolorization rate of RB5 in the presence of nanostructured TiO\textsubscript{2} prepared by spray pyrolysis method](image)

Removal efficiency RB5 by ZVIN at various pHs are shown on Fig. 9. From the results, lowering pH from 8.5 to 2 increased the removal kinetic rates.

![Fig. 9. The effect of pH on removals of RB5 by ZVIN](image)

In this experiment pH reducing to 2 and 4 for RB5 removals using synthesized nanoscale zerovalent iron particles by addition of hydrochloric acid (1.0 mol/L) resulted in the significant elevation of decolorization to more than 95 % of the original pH. Whereas, elevating the pH to 8.5 and 9 by addition...
of sodium hydroxides solution (1.0 mol/L) to dye wastewater resulted in lower decolorization efficiency. At high pH, the ferrous ions dissolved from the iron surface were collided with hydroxyl ions in alkaline solution, and ferrous hydroxides were produced and precipitated on the iron surface which led to occupy the reactive sites to hinder reaction. Degradation of the azo dye using Fe\textsuperscript{0} occurred on the surface of metal iron when effective collision between dye molecules and elemental iron happened. Fe\textsuperscript{0}, as an electron donor, loses electrons while the dye molecule, as an electron acceptor, gets electrons and combines with \textit{H}\textsuperscript{+} and turns into transitional products and finally terminal products. As a consequence, pH would strongly affect the degradations of RBS by NZVI at lower pH.

4. Conclusion

The azo dye reactive black 5 has been completely decolorized by applying of ZnO TiO\textsubscript{2} and FeO(OH) nanoparticles. In our experiment nanostructured TiO\textsubscript{2} possess better efficiency in comparison with ZnO. The method for preparation and the padding chemical contents influence significantly their photocatalytic properties. The zero-valent iron nanoparticles broke the azo bond more efficiently. Nevertheless, in the case of ZVIN the end products are aromatic amines, which are toxic for the most microorganisms. In the case of photocatalysis the obtained carboxylic acids are not toxic and easier for mineralization by most microorganisms in biotechnological reactor. The results suggest that use of TiO\textsubscript{2} in one BioNanotechnological process for industrial wastewater decontamination is better than other two types nanoparticles. In addition, TiO\textsubscript{2} is proved eco-friendly material with low solubility in aqueous environment. These properties enable to design photocatalytic reactor. However, a disadvantage of photocatalysis is that it occurs reliable at low acidic conditions. This necessitates neutralization of the sample before enter in the biotechnological reactor.

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References