Laser-induced efficient reduction of Cr(VI) catalyzed by ZnO nanoparticles

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ABSTRACT

The present study demonstrates the complete removal of Cr(VI) in aqueous suspensions of zinc oxide nanoparticles using a novel laser-induced photocatalytic process without the use of any additive. The study showed that ∼95% Cr(VI) was removed within short time (60 min) of laser exposure in the presence of ZnO. However, the removal of chromium using conventional setup under identical conditions was found to be negligible. Effect of critical parameters, such as laser energy, catalyst concentration, chromium concentration, and added electron donor and acceptor on the photocatalytic reduction process was also investigated. The data regarding temporal behavior of metal removal was fitted to first-order kinetic and reaction rate was computed.

1. Introduction

The increase in concentration of toxic metal ions in the environment has been a great concern to the societies and regulation authorities around the world. Chromium has been extensively used in several industries, like steel manufacturing, metal plating, military purposes, and leather tanning, as well as in the pigment and refractory industries [1,2]. The toxicity and carcinogenic properties of chromium(VI) have been known for many years [3] and it is included in the list of priority pollutants in many countries of the world [4]. Conventional methods for treatment of industrial waste contaminated with heavy metal include biological treatment, ion exchange, liquid–liquid extraction, precipitation, reverse osmosis, and activated carbon adsorption [5]. However, these techniques often utilize potentially hazardous or polluting materials and can only transform the pollutants from one phase to another [6]. Most of these methods require pretreatment process, their by-products are often considered hazardous and disposal requires extra cost.

Heterogeneous photocatalysis involving semiconductors has attracted considerable attention in recent years for the remediation of undesirable pollutants both in aqueous [7–11] and gaseous phase [12–14] using solar or artificial light. Heterogeneous photocatalytic oxidation processes have been discussed extensively in

the literature [15,16]. Briefly, when a photocatalyst absorbs a photon of energy equal to or greater than its band gap, an electron may be promoted from the valence band to the conduction band (e^-cb) leaving behind an electron vacancy or "hole" in the valence band (h^+vb). If the charge separation is maintained, the electron and hole may migrate to the catalyst's surface where they participate in redox reactions with adsorbed species. It has been shown that the Cr(VI), highly toxic species, can be reduced to Cr(III), non-toxic species, with the help of semiconductors and light [17–21].

Most of the studies for removal of metals from water using photocatalytic process have been performed using organic additives like salicylic acid, oxalate, phenols, dye, humic acid [22–25], and some electron donors such as methanol and formate ions [5,26]. It is worth mentioning that all the previous works dealing with the removal of heavy metals from water have been carried out with broad spectral radiation sources such as lamps and TiO$_2$ as a photocatalyst. Several problems are associated with the use of lamps emitting over broad spectral wavelength range. For example, the long term power stability due to over heating of lamps during the operation, low photonic efficiency, longer exposure time (hours) for complete removal of pollutants are the major drawbacks associated with UV lamps as a source of irradiation. It is of great interest to use laser radiations as an excitation source to study the activity of photocatalysts because laser light has unique properties like mono-chromaticity, high intensity, and low beam divergence. Due to these properties, laser beam can transmit over long range in water and could expose a longer column which is not possible with broad spectral lamps. Due to these reasons, lasers are excellent tools to build a tandem facility. However, the initial cost of laser

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based systems will be much higher than lamp based systems. It is worth mentioning that currently tunable lasers in the UV and visible range are commercially available at modest costs. The use of lasers, therefore, in heterogeneous photocatalysis for the removal of pollutants will be useful in achieving the high efficiency as compared to conventional setup. Even if laser based system will not be viable solution for building up ultimately large scale facilities, the purpose of this work is to test the efficiency of ZnO catalyst for the reduction of chromium using fast and selective laser induced photocatalysis process at laboratory scale.

To the best of our knowledge, no study has been reported so far showing a complete and efficient photocatalytic reduction of Cr(VI) without the use of any additive. The present investigation deals with the chromium(VI) removal from water system in aqueous suspensions of ZnO using a 355 nm laser irradiation. The dependence of the metal removal on laser irradiation energy, catalyst and pollutant concentration, electron donor and acceptor was investigated. For a comparative study, the photocatalytic reduction of metal was also performed using conventional setup under identical conditions. The reaction rate was estimated following first-order reduction kinetics.

2. Experimental

2.1. Chemicals

Zinc nitrate and ammonium carbonate of analytical grade were obtained from Sigma–Aldrich. Potassium dichromate ($K_2Cr_2O_7$) was obtained from Sigma–Aldrich. The other chemicals H_2O_2 and methanol were obtained from Merck.

2.2. Synthesis of ZnO nanoparticles

ZnO nanoparticles were synthesized following precipitation method. An appropriate molar ratio of $[Zn(NO_3)_2]\cdot 6H_2O$ and $(NH_4)_2CO_3$ were dissolved in deionized water to prepare the respective solutions. Zinc nitrate solution was dripped slowly into the solution of ammonium carbonate and stirred for 2 h to allow complete precipitation. The resulting precipitate from the reaction between $Zn(NO_3)_2$ and $(NH_4)_2CO_3$ solutions were collected by filtration using a 0.2 μm membrane filter and washed several times with deionized water and ethanol followed by drying in the air at 100 °C overnight. The powder obtained after drying was calcined at a temperature of 500 °C for 3 h to obtain nanoparticles of zinc oxide.

2.3. Characterization

Characterization of the synthesized ZnO nanoparticles was carried out employing Field Emission Electron Microscope (FESEM), X-ray Diffractometer (Shimadzu 6000 using Cu–K radiation, with operating voltage of 40 kV and current of 30 mA). The absorbance of the samples was monitored by measuring the absorbance on a UV–vis spectrophotometer (JASCO).

2.4. Evaluation of photocatalytic activity

Stock solutions of the potassium dichromate containing desired concentrations were prepared in distilled water. For irradiation experiments, 100 mL solution of desired concentration of the model pollutant was taken into the pyrex cell/reaction vessel and the required concentration of photocatalyst was added. The suspension was stirred for at least 15 min in the dark to allow equilibration of the system so that the loss of compound due to adsorption can be taken into account. The pH of the reaction mixture was adjusted to ∼7 by adding a dilute aqueous solution of HNO_3 or NaOH. The zero

a

1. Nd:YAG Laser (1060nm)
2. Third harmonic generator (355 nm)
3. Beam splitter
4. Laser energy meter
5. Mirror
6. Beam diameter controller
7. Quartz window
8. Dead volume of cell
9. Effective volume of cell
10. Megnatic stirrer
11. Megnatic plate
12. Gas inlet
13. Liquid sampling valve
14. Gas sampling valve
15. Gas outlet
16. Pyrex cell

b

cooling water
Oxygen
UV- lamp
Purging unit
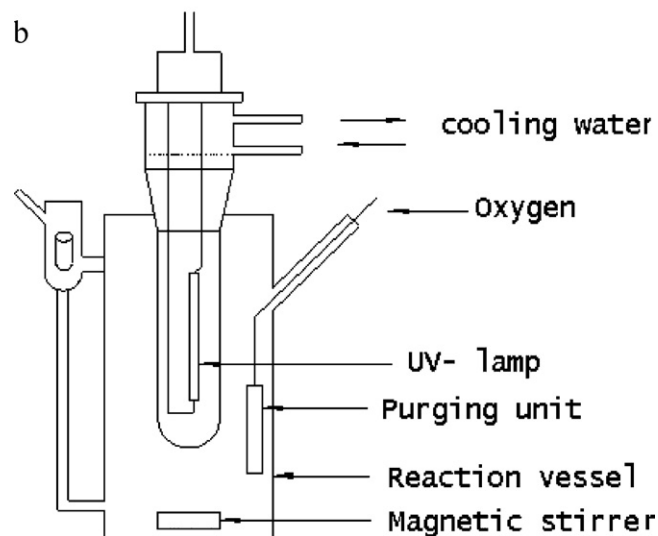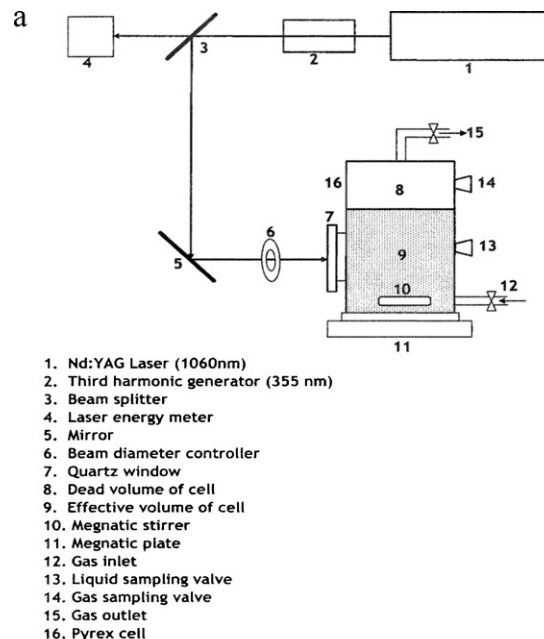Reaction vessel
Magnetic stirrer

Fig. 1. (a) A schematic of the experimental setup used for the removal of Cr(VI) using laser induced photo-catalysis process. (b) A schematic of the conventional setup used for the removal of Cr(VI) using lamp induced photo-catalysis process.

time reading was obtained from a blank solution kept in the dark but otherwise treated similar to the irradiated solution. Irradiations were carried out using a 355 nm wavelength high power laser beam generated from the third harmonic of the Spectra Physics Nd:YAG laser (Model GCR 250), with a pulse width of ∼8 ns. The band gap energy of ZnO is around 3.1 eV and absorbs the photons of equal to or less than 380 nm wavelength. The laser light, therefore, with wavelength around 355 nm corresponds to optimal wavelength for the excitation of ZnO because the excitation energy at this wavelength is higher than band gap energy to pump an appreciable amount of ZnO. In order to avoid the destructive effect of radiation, laser beam diameter was expanded to 1.0 cm. A schematic of the experimental setup has been given in Fig. 1. Samples (3 mL) were collected before and at regular time intervals during the irradiation. ZnO particles were removed by filtration using Nylon membrane with 0.45 μm pore size, with graduated glass fiber prefilter (Millex-HPF LCR Filter Unit, Millipore) before the analysis.
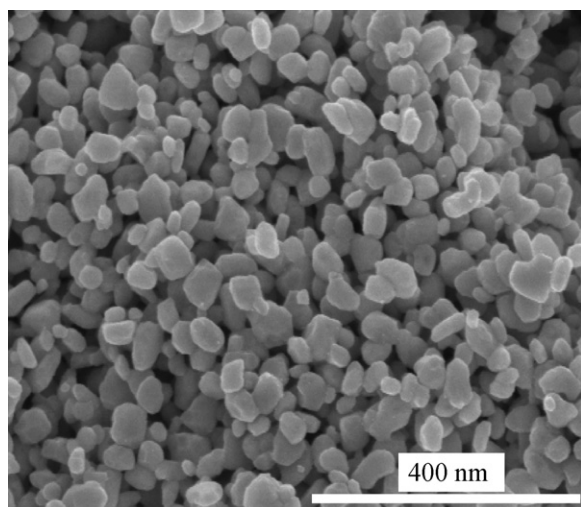
Fig. 2. FESEM image of ZnO nanoparticles calcined at 500 °C for 3 h.

Fig. 3. XRD patterns of ZnO nanoparticles calcined at 500 °C for 3 h.

The photocatalytic reduction of Cr(VI) was also evaluated with conventional setup involving lamp and immersion well photochemical reactor. The reactor was made of Pyrex glass equipped with a magnetic stirring bar, a water circulating jacket and an opening for supply of gases. The photochemical reactor was consisted of two vessels; the vessel containing the irradiation lamp was immersed into the other part containing chromium solution. A schematic of the photochemical reactor is shown in Fig. 1b. A predetermined volume (140 mL) of chromium solution was taken into the photoreactor and ZnO (1.0 g/L) was added. The solution was stirred for at least 15 min in the dark for homogenization. Irradiation was carried out using a 125 W medium pressure mercury lamp. Samples were collected before and at regular intervals during the irradiation. The catalyst was removed through filtration before the analysis using aforementioned filter.

Various experimental conditions, such as chromium concentration = 75 mg/L, ZnO concentration = 1.0 g/L, laser energy = 200 mJ and irradiation time = 60 min, were kept constant in most of the reactions presented here unless stated otherwise.

2.5. Analysis

The removal of Cr(VI) was monitored by measuring the absorbance on a UV–vis spectrophotometer. The absorption maxima of the potassium dichromate were found to be 372 nm. Therefore, the removal of the metal was estimated at this wavelength as a function of irradiation time. For each experiment, the rate for the removal of the model pollutant was calculated from the initial slope obtained by linear regression from a plot of the natural logarithm of absorbance of the metal as a function of irradiation time, i.e. first order removal kinetics.

2.6. Structural and morphological characterization of ZnO nanoparticles

Fig. 2 illustrates the FESEM micrograph of zinc oxide nanoparticles calcined at 500 °C for 2 h. The image indicated that most of the particles were spherical in shape and were in the wide range of size (10–70 nm). The XRD patterns of ZnO nanoparticles has been shown in Fig. 3 and all the diffraction patterns could be assigned to hexagonal lattice structure of ZnO.
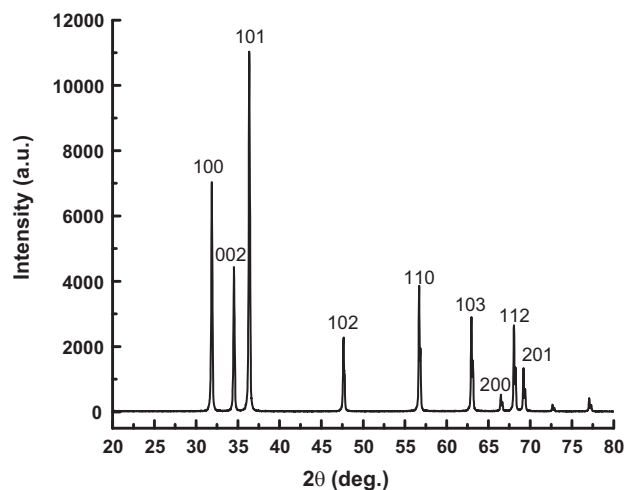
2.7. Photolysis of ZnO suspensions containing potassium dichromate

Fig. 4a depicts typical UV absorption spectrum representing the trend of removal of Cr(VI) in the presence of ZnO with respect to time under laser irradiation using pyrex cell shown in Fig. 1a. All the experiments in this study were carried out in pyrex cell under laser irradiation unless stated otherwise. It can be seen from the figure that more than 95% removal was achieved within short laser exposure time (60 min) using 355 nm laser radiations. In order to determine the role of photocatalyst in the reduction process, blank experiments were also carried out by irradiating the aqueous solution of the potassium dichromate under laser light in the absence of ZnO where about 5% removal was observed. For each experiment, the rate constant was calculated from the plot of natural logarithm of pollutant concentration as a function of irradiation time. A typical plot of $-\ln A/A^0$ (for Fig. 4a) versus time is depicted in Fig. 4b for Cr(VI) removal. The least square fit $R = 0.98$.

3. Results and discussion

3.1. Effect of incident laser energy on the photocatalytic reduction process

The effect of incident laser energy on the removal of Cr(VI) was investigated and obtained results are presented in Fig. 5. It is obvious from the figure that the removal of metal was significantly influenced by the laser energy and removal was found to increase almost linearly with the increase in laser energy within the range studied. This phenomenon may be explained in terms of the fact that when higher laser energy is employed, incident photon flux increases in the solution exciting more and more catalyst particles which in turn increases the photocatalytic reduction process. It is pertinent to mention here that the maximum energy we can get with the laser we have is about 240 mJ and hence the effect of laser energy more than 240 mJ could not be investigated in the present study. In contrast to the conventional photocatalytic systems where one has to change the lamp to control the energy, the laser equipment furnishes very easy access as well as a range of energy to control the photonic efficiencies, according to the requirements, during the photocatalytic reactions. It has been observed in this study that the removal of chromium metal can be significantly enhanced (almost complete removal within the 60 min of irradiation time) by simply increasing the laser energy. The observed improvement in the removal trend of Cr(VI) as a function of laser
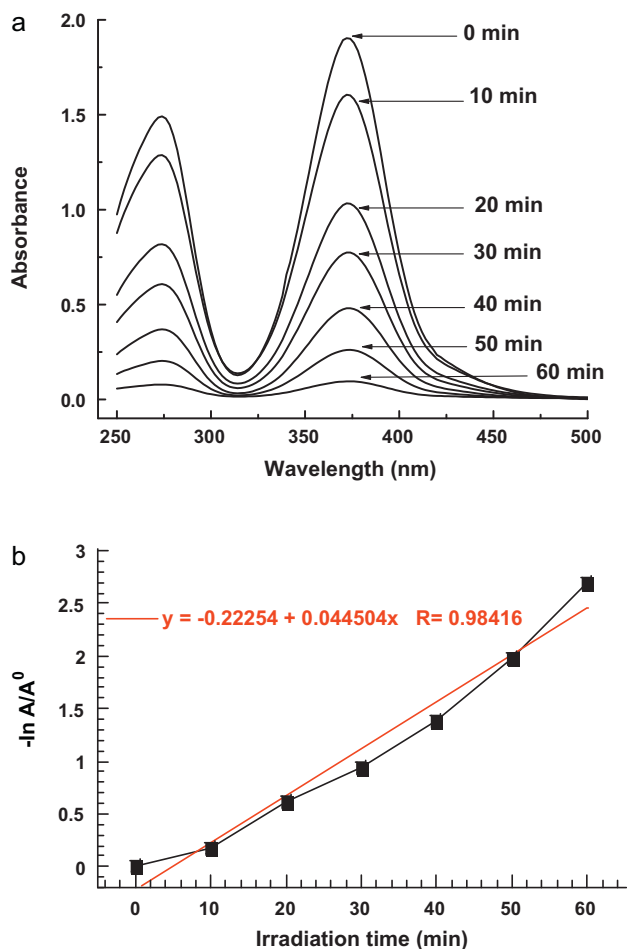
Fig. 4. (a) Typical UV–vis spectra showing the change in absorption intensity of $K_2Cr_2O_7$ in aqueous suspensions of ZnO as a function of laser irradiation time. Experimental conditions: chromium concentration = 75 mg/L, ZnO concentration = 2.0 g/L, laser energy = 200 mJ, irradiation time = 60 min. (b) A plot of $-\ln A/A^0$ versus the reaction time (for the (a)) for Cr(VI) removal showing the first-order kinetics. Experimental conditions: chromium concentration = 75 mg/L, ZnO concentration = 2.0 g/L, laser energy = 200 mJ, irradiation time = 60 min.
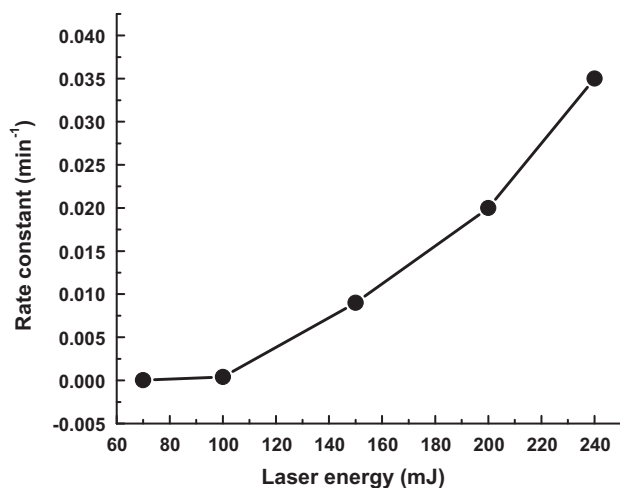

Fig. 5. Dependence of removal of Cr(VI) on the incident laser energy. Experimental conditions: chromium concentration = 75 mg/L, ZnO concentration = 1.0 g/L, laser energy = 70, 100, 150, 200 and 240 mJ, irradiation time = 60 min.
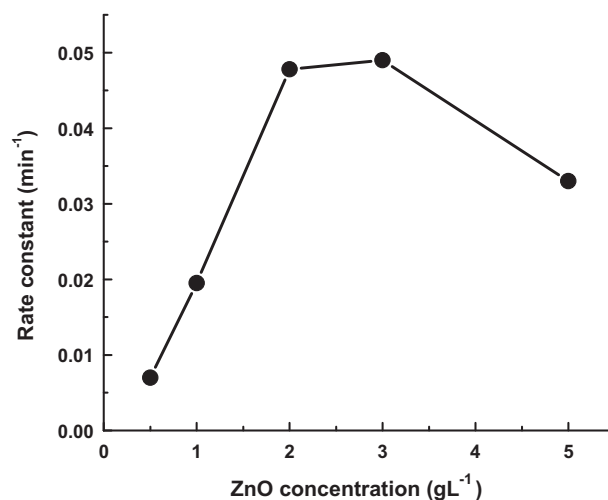

Fig. 6. Dependence of removal of Cr(VI) on the ZnO concentration. Experimental conditions: chromium concentration = 75 mg/L, ZnO concentration = 0.5, 1.0, 2.0, 3 and 5 g/L, laser energy = 200 mJ, irradiation time = 60 min.

energy is more significant than that obtained using different conventional UV lamps [27].

3.2. Effect of catalyst concentration on the photocatalytic reduction process

The dependence of chromium removal on the photocatalyst concentration is shown in Fig. 6. ZnO concentration was optimized by exposing the aqueous suspensions of potassium dichromate containing ZnO ranging from 0.50 g/L to 5.0 g/L while keeping other parameters constant. As the concentration of ZnO was increased from 0.50 to 2.0 g/L, the reaction rate was much faster and a further increase in catalyst concentration (from 2.0 to 3.0 g/L) was not found to be much beneficial for the photocatalytic reduction of metal. When the catalyst concentration was increased above 3.0 g/L, the reduction rate was decreased. As the other parameters, such as exposure to a constant photon flux, beam diameter, stirring rate, metal concentration, irradiation time etc. were kept constant, further increase in particle density beyond optimum density fails to contribute significantly to the reduction process. When the catalyst concentration is very high, after traversing a certain optical path, turbidity impedes further penetration of laser light in the reactor (incidence of the combined phenomena of particle masking and scattering) lowering the efficiency of the catalytic process.

3.3. Effect of Cr(VI) concentration on the photocatalytic reduction process

It is important both from mechanistic and application points of view to study the dependence of the photocatalytic reaction rate on the chromium concentrations. Hence, the influence of metal concentration varying from 25 mg/L to 130 mg/L on the photocatalytic reduction process was studied and the obtained results are presented in Fig. 7. It can be seen from the figure that the removal increased with the increase in substrate concentration from 25 to 50 mg/L and a further increase in the concentration of the metal led to a decrease in the reaction rate. The decrease in reduction process at higher metal concentration may be rationalized by the fact that the higher pollutant concentration requires higher photocatalyst surface. Since the availability of photocatalyst surface remains constant in this experiment, the reduction rate of metal decreases when the pollutant concentration increases. On the other hand, at pollutant concentration below 50 mg/L, the pollu-
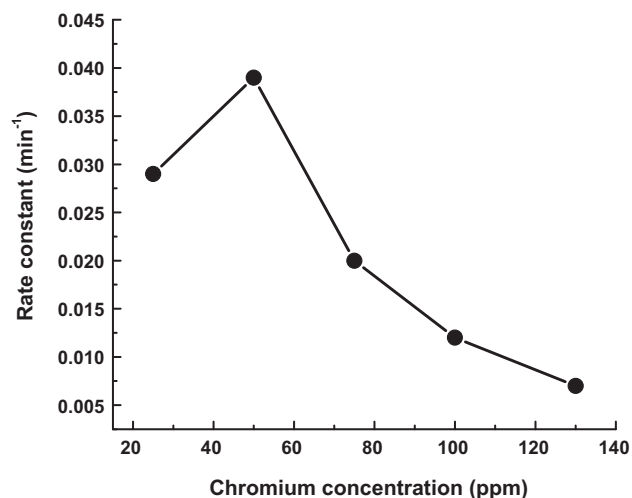
Fig. 7. Dependence of removal of metal on the $K_2Cr_2O_7$ concentration. Experimental conditions: chromium concentration = 25, 50, 75, 100 and 125 mg/L, ZnO concentration = 1.0 g/L, laser energy = 200 mJ, irradiation time = 60 min.

Fig. 8. Effect of electron donor and acceptor on the photocatalytic reduction/removal of Cr(VI). Experimental conditions: chromium concentration = 75 mg/L, ZnO concentration = 1.0 g/L, laser energy = 200 mJ, irradiation time = 60 min.

tant concentration is limited with regard to the available surface of photocatalyst.

3.4. Effect of added electron donor and acceptor on the photocatalytic reduction process

One practical problem in photocatalytic reactions using semiconductors is the undesired electron/hole recombination, which, in the absence of proper electron acceptor or donor, is extremely efficient and hence represents the major energy-wasting step thus limiting the achievable quantum yield. One strategy to inhibit electron–hole pair recombination is to add other (irreversible) electron acceptors or donor to the reaction. They could have several different effects such as (1) to increase the number of trapped electrons and, consequently, avoid recombination, (2) to generate more radicals and other oxidizing species, and (3) to increase the reduction rate of metals. It is pertinent to mention here that in highly toxic wastewater where the removal of heavy metal is the major concern, the addition of additives to enhance the photocatalytic process may often be justified. In this connection, we studied the effect of electron acceptor and donor such as hydrogen peroxide and methanol respectively on the photocatalytic reduction of chromium and the results obtained are illustrated in Fig. 8. The enhancement in reduction rate of Cr(VI) in the presence of methanol may be ascribed to current-doubling effect [28]. The methanol scavenges the generated holes and get oxidized producing the electron-donating species $^\bullet CH_2OH$ (E^0 ($^\bullet CH_2OH/CH_2O$) = −0.95 V). Due to its large negative potential, the methanol radical then injects an electron into the semiconductor particles thereby increasing the total number of electrons on the catalyst's surface. The effect of methanol on the metal reduction process, in the absence of photocatalyst, under identical conditions was also investigated. The metal removal was found to be more or less similar as observed in the case of blank experiment which indicates that the presence of methanol in the absence of catalyst is not effective for the removal of metal. We also investigated the removal of metal in the presence of ZnO and methanol but in the absence of light. The analysis did not indicate any change in chromium concentration. Conversely, the addition of hydrogen peroxide affected the reduction process negatively as evident from Fig. 8. Hydrogen peroxide can pick up the excited electrons making the reduction process slow; it was clearly indicated by the retardation of chromium reduction rate. Another process that may occur
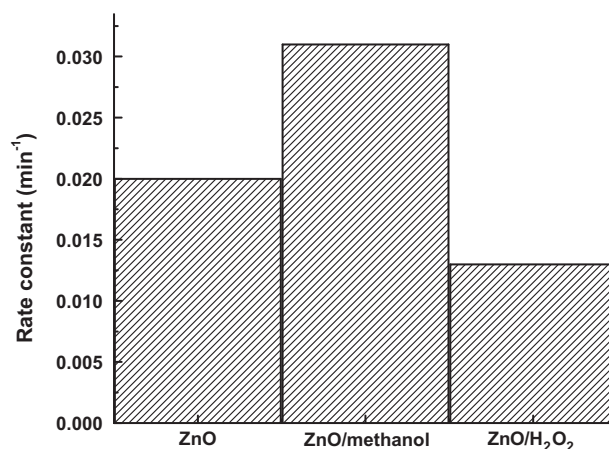
simultaneously and may contribute negatively in the reduction process is the formation of $^\bullet OH$ radical from H_2O_2 under irradiation. These radicals may reoxidize Cr(III) to Cr(VI) making the reduction process slow.

For the comparison, the photocatalytic reduction/removal of Cr(VI) was also investigated using conventional setup consisting of a UV-lamp coupled to a photochemical reactor. Other conditions such as chromium and ZnO concentrations, irradiation time were kept identical for comparison. The schematic of the photoreactor was described in Section 2.4 and shown in Fig. 1b. The obtained results are shown in Fig. 9. It can be seen from the figure that after 60 min of irradiation using lamp, about 5% removal of Cr(VI) was observed. The efficient reduction in the presence of laser could be ascribed to different properties of laser because laser is a coherent, monochromatic and strong source of light. In case of laser, there is high absorption of photons of particular laser emission wavelengths by photocatalysts. However, in case of broad spectral sources like lamps, most of the emission wavelengths lie outside the band gap energy of catalyst.
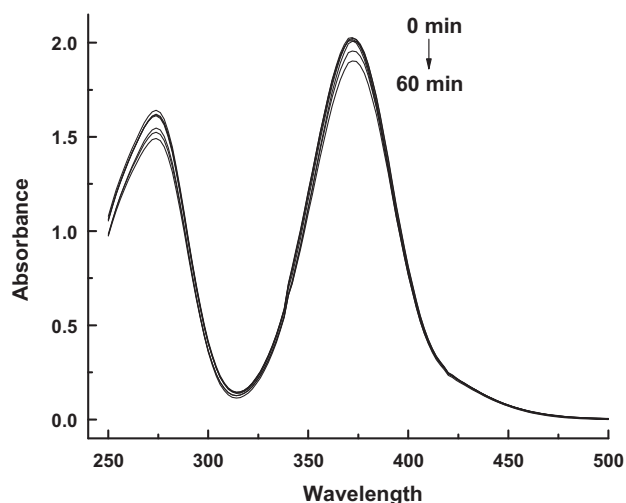

Fig. 9. UV–vis spectra showing the change in absorption intensity as a function of irradiation time under conventional setup for an aqueous solution of $K_2Cr_2O_7$ in the presence of ZnO. Experimental conditions: chromium concentration = 75 mg/L, ZnO concentration = 1.0 g/L, irradiation time = 60 min.

4. Conclusions

The present study showed that complete and efficient removal of Cr(VI) in aqueous suspensions of zinc oxide nanoparticles can be achieved using a novel laser-induced photocatalytic process. The study showed that ~95% Cr(VI) was removed within short time (60 min) of laser exposure without the use of any additive. A linear dependence of chromium removal was found on the incident laser energy. The maximum removal of chromium was achieved using catalyst concentration = 2–3 g/L and laser energy = 240 mJ (355 nm). From this starting condition, the maximum chromium(VI) concentration that reduced in 60 min was about 50 mg/L. The addition of electron donor such as methanol enhanced the metal reduction process. This study clearly demonstrates that the laser-induced photocatalytic process could be applied as an effective method to remove the heavy metals present in wastewater in shorter time duration without incorporation of any additives. The optimization of various operational parameters demonstrates the significance of selection of the optimum experimental conditions to obtain a high removal rate.

Acknowledgement

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