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Research Article

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Investigation of Photocatalytic Reduction of Cr (VI) from Aqueous Solutions by using SiO_2 Nanoparticles: A Laboratory Study

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Abstract In this laboratory study, the effects of nanoparticle dose (0.2-1 g/L), reaction time (5-60 min), initial Cr (VI) concentration (5-200 mg/L) and lamp power (8-40 w) were assessed on Cr (VI) removal efficiency in a batch photocatalytic reactor. The disappearance of original Cr (VI) concentration with irradiation time was monitored by using spectrophotometer. The results indicate that this photoreaction is a pseudo first order reaction according to the Langmuir, Hinshelwood relationship. The optimum obtained SiO_2 nanoparticle dose was 0.6 g/L. In this study, at the optimum reaction time of 20 min, by increasing the concentration of Cr(VI) the removal efficiency increased. Under optimal conditions of concentration, the removal efficiency was 99.2% Also it has been observed that the increase of light intensity leads to the increase of Cr (VI) removal rate.

Keywords Photocatalytic reduction, Hexavalent chromium, SiO_2 nanoparticles

Introduction

Contamination of water is a worldwide problem due to agricultural, non-agricultural, and industrial pollution [1, 2]. Various toxic heavy metal ions discharged through different industrial activities, constitute one of the major causes of water pollution [3, 4]. Heavy metal residues in contaminated habitats may accumulate in microorganisms, aquatic flora and fauna, which in turn, may enter into the human food chain and result in health problems [5, 6]. Heavy metal ions arise from both natural and anthropogenic sources pose serious environmental risks and, therefore, should be removed from wastewaters [7].

Wastewater from industries such as chrome leather tanning, metallurgy, chrome plating, textiles, ceramics, photography, and photoengraving contains moderate to excessive amounts of hexavalent chromium compounds beyond the conventional statutory limit of 0.1 mg/L [8]. Remediation of these effluents is necessary because in humans Cr (VI) causes lung cancer, ulcers, nasal septum perforations, and damage to the kidneys [9]. With the rapid development of the galvanization industry in Iran recently, the amount of hexavalent chromium Cr (VI) containing wastewater generated by the industry has increased dramatically [10]. The regulated tolerance values are 0.1 and 0.05 mg/L for discharge into the inland surface and potable waters, respectively [11].

Different methods can be used for removing metals, including filtration, chemical precipitation, coagulation, solvent extraction, electrolysis, ion exchange, membrane process and adsorption [12-14]. Chemical precipitation is the most common conventional method of treatment for heavy metals containing effluents, but large amount of sludge produced during the treatment poses disposal problems [15, 16]. Activated carbon for adsorption process has undoubtedly been the most popular and widely used adsorbent in wastewater treatment applications throughout the world and has been successfully utilized for the removal of diverse types of pollutants including

metal ions [17, 18]. However, the high capital and regeneration cost of the activated carbon limits its large-scale applications for the removal of metals and other aquatic pollutants [19].

The AOP divided in to two categories (heterogeneous and homogenous catalysis), heterogeneous catalysis has been successfully employed for the degradation of various families of hazardous materials [20]. The photocatalytic oxidation is one of the most promising technologies for eliminating pollutants because it is highly efficient in mineralization and it can utilize sunlight as energy source [21]. Among all the semiconductors, SiO_2 has been proved to be the promising Photocatalyst for widespread environment applications due to its electric properties, nontoxicity, biological and chemical inertness, cost effectiveness, strong oxidizing power, and long-term stability against chemical corrosion and photocorrosion.

Materials and Methods

A stock solution of Cr (VI) was prepared by dissolving by dissolving 0.5657 g (±0.0001) $K_2Cr_2O_7$ in a 1000 ml volumetric flask with deionized water. Before performing the experiment, the Cr (VI) concentration in the stock solution was measured. All the chemicals in this study were of extra pure or analytical grade. The Silicon dioxide (SiO_2) used was purchased of US Research Nanomaterials, Inc. which is mostly anatase and has a BET (Brunauer-Emmett-Teller) surface area of 65 m^2/g and an average particle diameter of 15 nm. 0.1 N HCl or 0.1 N NaOH was used to adjust the pH solution.

This study was performed at laboratory scale. The reactors consisted of three parts: UV source, reaction cell and mixing chamber. The 15 W low-pressure Hg UV-lamps were used as the radiation source. A glass reactor (1L) was the major photoreactor used in this study, except when otherwise specified. This reactor consisted of two compartments, the outer for containing wastewater and the inner for housing a UV lamp. The experiments were carried out in a batch and continuous reactor for synthetic wastewater. The concentration of Cr (VI) was 200 mg/L in all experiments throughout the work. In this study, the effect of pH solution, SiO_2 dose, contact time reaction, Effect of Cr (VI) Concentration and Effect of intensity of light on Cr (VI) removal efficiency were investigated. At the end of each experiment, cellulose nitrate membrane (0.45 µm) was used to separation of SiO_2 particles. All experiment was conducted at room temperature (23 ± 2°C).

Results and Discussion

Effect of concentration of Cr (VI) was studied by taking different concentrations of Cr (VI). The results are reported in Figure 1. It was observed that the rate of photocatalytic bleaching increases with an increase in the concentration of the Cr (VI). It may be due to the fact that as the concentration of heavy metals increases more Cr (VI) molecules are available for excitation and energy transfer and hence, an increase in the rate of photocatalytic degradation of the Cr (VI) were observed [21, 22]. The rate of photocatalytic degradation was found to be fixed with further increase in the concentration of the Cr (VI) i.e. above 100 mg/L.

The amount of semiconductor is also likely to affect the rate of photocatalytic bleaching of Cr (VI) hence; different amounts of Photocatalyst were used. The results are reported in Figure 2. It was observed that the rate of photocatalytic degradation of Cr (VI) increases with an increase in the amount of semiconductor but ultimately, it became almost constant after a certain amount i.e. 0.6 g/L. This may be attributed to the fact that as the amount of semiconductor was increased, the exposed surface area increased, which absorb more number of photons and as a result the rate of photocatalytic degradation of the Cr (VI) increased [23, 24].

To observe the effect of intensity of light on the photocatalytic degradation of the Cr (VI), the light intensity was varied. The results obtained are reported in Figure 3. The data indicate that an increase in the light intensity increases the rate of reaction. It may be explained on the basis that as the light intensity was increased, the number of photons striking per unit area also increased, resulting into a higher rate of degradation [25]. Further increase in the intensity beyond the maximum limits result in decrease in the rate of reaction. It may be probably due to thermal side reactions [26, 27].

Photocatalytic degradation rate constant (K) of the Cr (VI) was calculated using Langmuir-Hinshelwood (L-H) first order kinetics. According to L-H model, when initial concentration Co is very small the following pseudo-first order rate equation is followed [28-30].

$\text{Ln } C_0/C_t = K.t$

Where k is pseudo- first order rate constant and t is time. A plot of Ln (C_0/C_t) versus time represents a straight line, the slope of which upon linear regression equals the pseudo-first order rate constant k. The Ln (C_0/C_t) values were calculated and plotted with respect to time as shown in Figure 2. The plotted data was best fitted by straight line of different slopes which indicate that the reactions followed pseudo-first order kinetics according to the L-H law. The pseudo-first order reaction rate constants were determined from the slopes of the plot Ln (C_0/C_t) versus time.

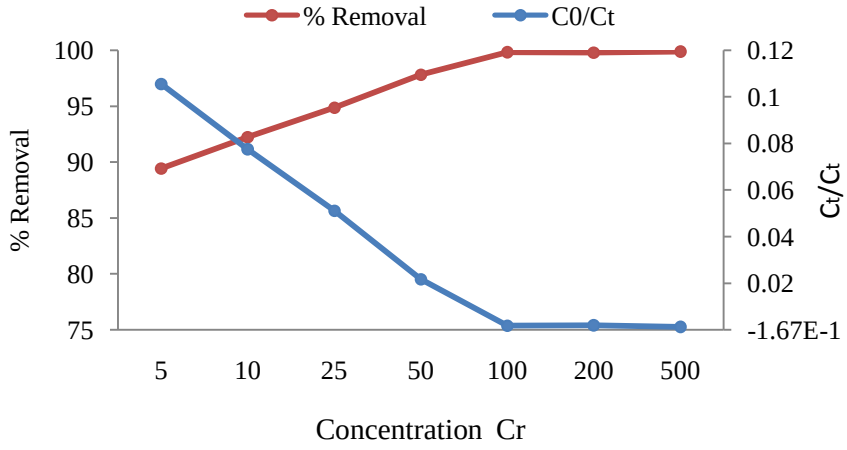

Figure 1: The diagram showing the effect of initial Cr (VI) concentration on photocatalytic degradation

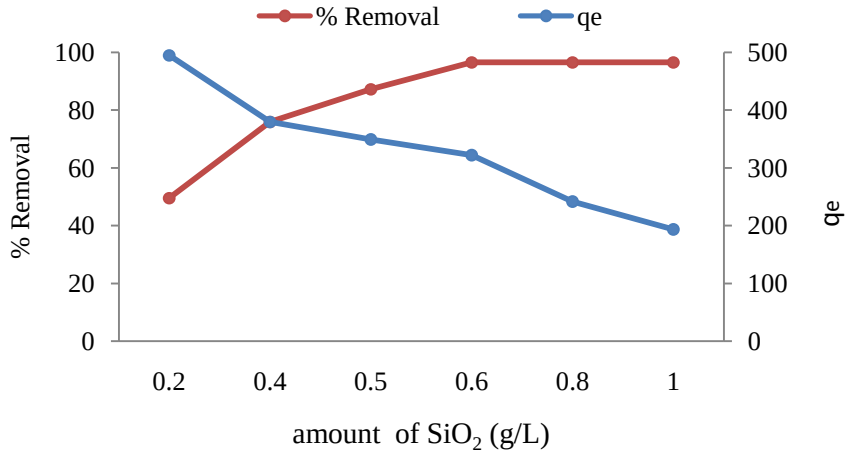

Figure 2: Effect of amount of nanoparticle on degradation rate of Cr (VI)

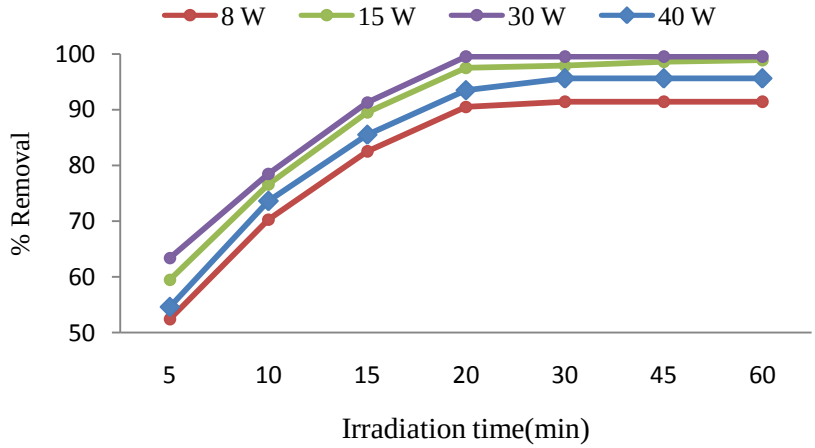

Figure 3: The change of removal rate with irradiation time at different light intensity

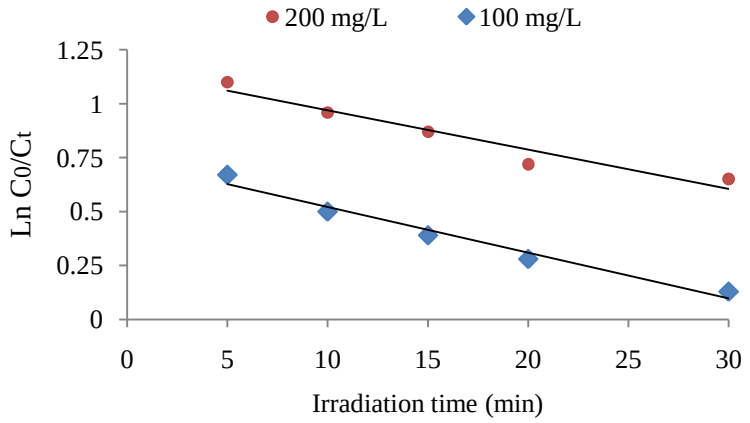

Figure 4: Kinetics of the photocatalytic degradation of Cr (VI)

Conclusions

The results of this study accurately show that a Cr (VI) ion has been not degraded in case of absent of catalyst. The compound has been successfully degraded when used the catalyst with the light. The optimum condition for the Photocatalytic of Cr(VI) ions equal 0.6 g/L mass of SiO_2 and 100 mg/L concentration of Cr (VI) and 30 W.

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