Kinetic Modeling of the Photocatalytic Reduction of Cr(VI) in the Presence of Dye Using Composite Photocatalyst

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Abstract: The photocatalytic properties of surface TiO2 supported zeolite in a semi batch reactor for the reduction of Cr(VI) in the presence of methyl orange dye were investigated. The prepared composite photocatalyst was characterized by SEM-EDS (scanning electron microscopy and energy dispersive spectroscopy). The effects of operating parameters such as the pH and concentration of Cr(VI) in the absence and presence of dye were evaluated. The Cr(VI) reduction was more efficient in the ternary system (Cr(VI)/dye/TiO2-zeolite) than that of the corresponding binary system (Cr(VI)/TiO2-zeolite). The extent of metal reduction after 210 min of irradiation was 68% at pH = 3 for the ternary system. In order to optimize the effectiveness of the composite photocatalyst on the photocatalytic reduction of Cr(VI), kinetics and isotherm models were applied. The kinetics of Cr(VI) in the presence of dye on TiO2/zeolite composite photocatalyst followed the pseudo-first-order model while the equilibrium data correlated reasonably well with Freundlich isotherm.

Key words: Composite photocatalyst, Cr(VI), dye, kinetics, isotherm.

1. Introduction

The water pollution co-contaminated with dyes and heavy metal ions is becoming increasingly problematic countrywide. Amongst the heavy metal ions, Cr(VI) often co-exist with organic compounds in wastewater. Cr(VI) complex in dyes that are extensively used in leather tanning industry are generated through the chemical reaction between Cr2O3 and a variety of azo organic compounds [1]. The increasing level of Cr(VI) toxic metal discharged into the environment as industrial wastes represents a serious threat to human health and living resources. Treatment of wastewater containing both inorganic and organic pollutants is a challenge worldwide and an environmental problem, as the two compounds need to be treated independently. In addition, Aksu [2] reported that these chemicals have shown a significant difference in molecular weight, chemical composition and toxicity. The desired treatment method is to reduce Cr(VI) to less harmful Cr(III), which can be precipitated in neutral or alkaline solutions as Cr(OH)3 [3]. With this growing demand, an alternative solution to address these problems is by heterogeneous photocatalysis using TiO2 which is one of the innovative and cost effective wastewater treatment methods. This technology is based on the generation of hydroxyl radicals that can oxidize the toxic and non-degradable pollutants in the wastewater efficiently into harmless species [4]. TiO2 is an attractive photocatalyst since it is stable, non-toxic and inexpensive, however, the cost of separating TiO2 after water treatment remains a technical challenge. The application of TiO2 in the form of slurry would need an additional process step for post-separation of the photocatalyst and this involves additional cost. To
address this problem in this work, a composite photocatalyst is prepared by supporting TiO₂ powder onto zeolite. The primary objective of this work was to investigate the kinetic studies and isotherms equilibrium modeling of Cr(VI) reduction in synthetic wastewater containing dye by TiO₂/zeolite composite photocatalyst using semi batch reactor.

2. Materials and Methods

The clinoptilolite zeolite sample used in this study, as supporting material, was supplied by Pratley after being analyzed. The methyl orange, an azo dye, TiO₂ as photocatalyst, absolute ethanol (99%) and potassium dichromate (99.8% K₂Cr₂O₇) as the source of Cr(VI) ions were purchased from Sigma Aldrich. All chemicals used were of analytical reagent grade and used as received. Stock methyl orange and Cr(VI) solutions (1,000 mg/L) were initially prepared in Mill-Q plus water (resistance = 18.2 MΩ) and preserved in tight bottle at 5 °C. Working solutions with concentrations from 0.5 mg/L to 10 mg/L of metal ions were prepared by appropriate dilutions of the stock solutions immediately prior to their use. The pH was adjusted by adding 0.1 M HCl or 0.1 M NaOH.

2.1 Preparation of the Composite Photocatalyst

The TiO₂ photocatalyst supported onto zeolite particles was prepared using the SSD (solid state dispersion) method modified by Nikazar et al [5]. Zeolite sized particle of 1-1.2 mm was at first rinsed with Mill-Q water to remove any impurities and dried. In this method, absolute ethanol as a solvent was added into the mixture of TiO₂ and zeolite which was prepared using an agate pestle and mortar. The solution was stirred until the solvent was removed by evaporation. Subsequently, the sample was dried at 110 °C and then calcined at 450 °C for 5 h to produce TiO₂ supported zeolite catalyst. By this procedure, a sample of 10 wt.% of TiO₂ onto zeolite material was prepared.

2.2 Photocatalytic Experiments

Photodegradation experiments were carried out using a Pyrex semi batch reactor with dimensions of 9 cm in diameter and 15 cm in height. Ultraviolet lamp with an irradiation intensity of 5.5mW/m² (protected by a quartz sleeve) was used as a light source. For all experiments, the solution was left to equilibrate for 30 min in the dark before the lamp was switched on. This was sufficient to reach an equilibrated adsorption as deduced from the steady-state concentrations. Samples were taken every 30 min and immediately filtered through a polypropylene syringe filter (0.45 μm) in order to remove the photocatalyst.

2.3 Chemical Analysis

The Cr(VI) ion concentration was analyzed by ICP-OES (inductively coupled plasma optical atomic emission spectrometry) model CAP6300 (Thermo Electron Corporation, USA). The adsorption capacities (qₑ) (mg/g) of TiO₂/zeolite were calculated as:

\[ qₑ = \frac{(C_i - C_e)}{m} V \]

where, \( C_i \) and \( C_e \) are the initial and the equilibrium concentrations (mg/L) of the metal ion, respectively, while \( m \) (g) and \( V \) (L) represent the mass of the composite photocatalyst and the volume of the solution, respectively.

3. Results and Discussion

3.1 Characterization

The morphology of the prepared TiO₂/zeolite was characterized by SEM (scanning electron microscopy) technique coupled with EDS (energy dispersive spectroscopy) analysis. It can be seen from Fig. 1 that the morphology was homogeneous. The EDS spectra of the zeolite alone showed the major building block of zeolite framework which is the tetrahedron, the centre occupied by a Si or Al atom increased significantly after supporting TiO₂ on zeolite surface (Fig. 2). The EDS spectra revealed that the Ti is
detected, which clearly shows that crystallites of TiO$_2$ is well dispersed on the surface of the zeolite supporting material.

3.2 Effect of pH

The effect of pH on the photocatalytic reduction of Cr(VI) by TiO$_2$-modified zeolite material was determined in the absence and presence of dye at 6.25 g/L composite photocatalyst concentration and 5 mg/L Cr(VI) concentration. As shown in Fig. 3, the reduction of Cr(VI) was much slower at pH = 6.5 and significantly increased at pH = 3. The slow reduction at pH = 6.5 was due to the electrostatic repulsion between the negatively composite photocatalyst surface and the negatively charged anions of Cr(VI). However, an opposing phenomenon was observed during the ternary system of Cr(VI)/dye/TiO$_2$-zeolite (Fig. 3).

This fact can be attributed to the oxidation of dye consuming photo-excited holes quickly, which weakens electron-hole recombination promoting the photocatalytic reduction of Cr(VI) on the photocatalyst surface directly or indirectly and was oxidized [6]. This indicates the fact that the photoreduction of Cr(VI)
was much faster in the mixed system than in the single one. The optimum pH = 3 and this was applied in further studies. Similar results were reported by Colon et al. [7] during the simultaneous photocatalytic treatment of salicylic acid and Cr(VI) over TiO₂ suspensions at pH = 2.

3.3 Kinetics Studies

Kinetics modeling was conducted by using the pseudo-first-order and pseudo-second-order models. To distinguish a kinetic equation based on the adsorption capacity of composite, the equation for the pseudo-first-order kinetics is expressed as:

\[
\ln(q_e - q_t) = \ln q_e - k_1 t
\]  

where, \(q_t\) and \(q_e\) are the adsorption capacity (mg/g) at time \(t\) and at equilibrium, respectively, while \(k_1\) represents the pseudo-first-order rate constant (min⁻¹).

The plot of \(\ln(q_e - q_t)\) vs. \(t\) is shown in Fig. 4 and its output is presented in Table 1. Fig. 4 and Table 1 show that the pseudo-first-order model correlated better with the experimental data than the pseudo-second-order model, did as indicated by their higher values of correlation coefficient \((R^2)\) of 0.9973, 0.9906 and 0.9692. The values of the pseudo-first-order model rate constants showed faster photoreduction kinetics for TiO₂/zeolite composite photocatalyst. Furthermore, the obtained rate constants \((k_2)\) were higher at all initial concentrations studied as compared to the pseudo-second-order model. This could be due to more active sites involved on composite photocatalyst, thus, enabling the metal ions to be adsorbed more quickly.

The kinetic data of metal reduction by the TiO₂/zeolite composite photocatalyst were also fitted by pseudo-second-order model. The equation of this model is given as:

\[
\frac{t}{q_t} = \frac{1}{k_2q_e^2} + \frac{t}{q_e}
\]

where, \(q_t\) and \(q_e\) (mg/g) are the adsorption capacity at time \(t\) and at equilibrium, respectively, while \(k_2\) (min⁻¹) is the pseudo-second-order rate constant. The plot of \(t/q_t\) vs. \(t\) is shown in Fig. 5 and its output is shown in Table 1. It is observed from Table 1 that the correlation factor values are high for both pseudo-first and pseudo-second-order models. However, the pseudo-second-order model was not representative enough to describe the experimental data at all initial concentrations, for instance, at 2 mg/L initial concentration a moderate fit with \(R^2\) value of 0.8902 was observed. This observation was different from the Azizian’s theory [8], which state that the sorption fits better to the pseudo-second-order model than to the first-order model when the initial concentration of the adsorbate is not excessively high. However, this observation did not deviate so much from Azizian’s theory as indicated by a moderate fit. Considering both models, the pseudo-first order predicted better the theoretical \(q_e\) values than the pseudo-second-order. With respect to the \(R^2\), the pseudo-first-order model seems to describe well the experimental data. Similar results were reported by Wang [9] for the photocatalytic reduction of Cr(VI) in both the absence and presence of the organic compounds using TiO₂.

3.4 Isotherm Studies

In addition to kinetics modelling, isotherm studies
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were undertaken to estimate the Cr(VI) uptake by composite photocatalyst in the presence of methyl orange. The isotherm modelling basically defines the interaction between substrate and composite photocatalyst until the state of equilibrium is reached. Nonlinear error functions such as the correlation coefficient ($R^2$), residual RMSE (root mean square error) sum of the ERRSQ (squares of the errors) and chi-square test ($\chi^2$) were used to evaluate the equilibrium model with the optimal magnitude. The non-linear form of the Langmuir isotherm can be expressed as:

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e}$$

(4)

where, $q_e$ and $C_e$ are the adsorption capacity (mg/g) and the equilibrium concentration of the Cr(VI) (mg/L), respectively, while $q_m$ and $K_L$ represent the maximum adsorption capacity of composite (mg/g) and the energy of the adsorption (L/mg). The plot of the Langmuir isotherm is shown in Fig. 6, while the isotherm parameters obtained, along with the mean error, $\chi^2$ test and correlation factor ($R^2$) are listed in Table 2. In spite of having correlation coefficients higher than 0.9, Fig. 6 shows that the equilibrium data did not fit well with the Langmuir isotherm. This model did not correspond to the experimentally obtained values of $q_e$ and this was reflected by high values of RMSE and $\chi^2$ in comparison to the Freundlich model. Nevertheless, it can be seen from Fig. 6 that the real $q_e$ values were over estimated. This suggests that homogeneous distribution of active sites on TiO$_2$/zeolite composite photocatalyst surface might not have occurred.

The Freundlich model suggests a heterogeneous adsorption surface with sites that have different energies of adsorption [10]. Its non-linear form can be represented as:

$$q_e = K_f C_e^{1/n_f}$$

(5)

where, $K_f$ is the Freundlich constant related to adsorption capacity, $q_e$ (mg/g), $n_f$ is a measure of the surface heterogeneity, ranging between 0 and 1. Fig. 6 illustrates the Freundlich plot of the Cr(VI) reduction, while the Freundlich constants are presented in Table 2. It is clear from Fig. 6 that the Freundlich model fitted the experimental data reasonably well. Based on the $R^2$ value, a better approximation of the experimental data were achieved for ERRSQ. This was also confirmed by the low values of RMSE and $\chi^2$ test. The
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Table 1 Kinetic parameters for Cr(VI) reduction in the presence of methyl orange dye on TiO$_2$/zeolite.

<table>
<thead>
<tr>
<th>$C_0$ (mg/L)</th>
<th>$q_e$ (mg/g)</th>
<th>$q_e$ (mg/g)</th>
<th>$K$ (min$^{-1}$)</th>
<th>$R^2$</th>
<th>$q_e$ (mg/g)</th>
<th>$K$ (min$^{-1}$)</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>0.2295</td>
<td>0.2618</td>
<td>0.0149</td>
<td>0.9973</td>
<td>0.3560</td>
<td>0.00999</td>
<td>0.8902</td>
</tr>
<tr>
<td>5</td>
<td>0.5424</td>
<td>0.6012</td>
<td>0.0140</td>
<td>0.9906</td>
<td>0.2169</td>
<td>0.00187</td>
<td>0.9805</td>
</tr>
<tr>
<td>10</td>
<td>1.5687</td>
<td>1.2736</td>
<td>0.0139</td>
<td>0.9692</td>
<td>0.3933</td>
<td>0.00375</td>
<td>0.943</td>
</tr>
</tbody>
</table>

$C_0$—denotes initial concentration of Cr(VI).

Table 2 Fitting results of Langmuir and Freundlich isotherms for the reduction of Cr(VI) on composite photocatalyst.

<table>
<thead>
<tr>
<th>Composite photocatalyst</th>
<th>Langmuir isotherm</th>
<th>Freundlich isotherm</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$Q_m$</td>
<td>$K$</td>
</tr>
<tr>
<td>TiO$_2$/zeolite</td>
<td>1.951</td>
<td>0.013</td>
</tr>
</tbody>
</table>

$\chi^2$—denotes chi-square test; $\chi^2$—RMSE—denotes residual root mean square error.

Fig. 6 Photodegradation isotherms of Cr(VI) on TiO$_2$/zeolite: experimental (□); Langmuir model (---) and Freundlich model (•••).

Estimated values were very close to the experimentally obtained maximum Cr(VI) uptake. Moreover, the value of Freundlich parameter ($n$), related to the degree of system heterogeneity, was found to lie between 0 and 1, which again confirmed that Freundlich model could be the adequate model for the Cr(VI) reduction. From the isotherm studies, it is evident that the application of the Freundlich model is a suitable model to describe the equilibrium data for the photoreduction of Cr(VI) by TiO$_2$/zeolite composite photocatalyst. This implies that heterogeneous adsorption has occurred at the surface of the applied composite photocatalyst. However, Asuha et al. [11] reported that the adsorption data for Cr(VI) in the presence of methyl orange fit well with Langmuir model. These observations can be due to different treatment processes applied.

4. Conclusions

In this study, the TiO$_2$ supported zeolite was applied for the photocatalytic reduction of Cr(VI) in the presence of methyl orange dye. From SEM-EDS results, TiO$_2$ was well supported on the surface of zeolite. A significant enhancement of the photocatalytic efficiency was observed for the ternary system than in the binary component system, indicating a synergistic effect. The experimental data fitted the Freundlich isotherms model better than the Langmuir isotherms model. This implies the heterogeneous distribution of activesites on the TiO$_2$/zeolite surface. The kinetics of Cr(VI) photocatalytic reduction in the presence of methyl orange dye by the prepared composite photocatalyst followed pseudo-first-order model. The values of the pseudo-first-order rate constants showed faster photocatalysis kinetics for TiO$_2$/zeolite than that of the pseudo-second-order model. The results revealed the viability and the effectiveness of using TiO$_2$/zeolite as composite photocatalyst for the heterogeneous photocatalytic reduction of Cr(VI) in the presence of organic pollutants such as methyl orange.
Acknowledgments

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References


