Influence of pH and salinity on the photocatalytic dye degradation and heavy metal ion reduction with cobalt ferrite photocatalysts.

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Abstract. The magnetic nanoparticle assisted photocatalytic oxidation-reduction is an effective method to remove and detoxify the organic dyes and the heavy metal ions present in the industrial wastewater. In the present study, the photocatalytic degradation of Methyl Orange (MO) dye and Cr(VI) ions in the presence of cobalt ferrite (CoFe$_2$O$_4$) superparamagnetic photocatalysts under visible light illumination are investigated as a function of wide range of pH and salinity conditions. The effect of pH on the photodegradation rates and the dual effect observed in the presence of Cl$^-$ ions were discussed. The photocatalytic degradation rates in single and binary impurity systems were also examined and the synergetic effect of MO oxidation and Cr(VI) reduction were established at different salinity and pH conditions.

Keywords: Photocatalysis; cobalt ferrite catalysts; dye degradation; heavy metal ion reduction; pH; salinity; synergetic catalysis.

1. Introduction

One of the significant threats recently confronted by most developing countries is the scarcity of clean drinking water free of chemicals and pathogens[1]. Heavy metal ions and organic dyes are the chemicals usually found in industrial effluents that cause a high degree of water contamination. The bio-accumulative nature of heavy metals in biotic systems substantiates the consequences of its hazardous nature[2]. The hexavalent chromium Cr(VI) ion, which is highly toxic and potentially harmful to living organisms, is introduced in the drinking water through the effluents from electroplating activities, paper, rubber, paint, nylon and plastic factories[3]. Methyl Orange (MO) is a hazardous anionic organic dye commonly found in industrial discharges which persists together with the heavy metal ions in the surface water sources[4].

The conventional adsorption methods by activated carbon[5],[6], biomass[7] etc. are widely studied water treatment methods. Even though the pollutants are removed from the bulk liquid onto the adsorbent surface, in most cases, the detoxification of these hazardous contaminants hardly occurs[3]. Photocatalytic oxidation-reduction is an alternative that can remove and detoxify the heavy metal ions and the organic dye simultaneously in a mixed impurity system[8],[9]. A wide variety of photocatalysts has been studied so far, incredibly magnetic nanoparticle photocatalysts, one amongst is the cobalt ferrite (CoFe$_2$O$_4$) which is proved to have higher adsorption, photocatalytic and magnetic separable efficiency[4]. The superparamagnetic property and its sensitivity to visible light make cobalt ferrite an attractive catalyst for water treatment application.
To enhance the adsorption efficiency and the photocatalytic degradation rates, it is necessary to determine the optimal process parameters like solution pH, reaction temperature, the concentration of the catalysts and the concentration of the pollutants and the salts present. The pH is a critical operational variable in actual wastewater treatment. It is a parameter that plays a key role in determining the adsorption capacity of a photocatalyst since its surface properties explicitly depend on the reaction pH. It also influences the reaction mechanisms of the photocatalytic oxidation of organic dyes and the reduction of heavy metal ions [5],[7]. Sodium chloride being a primary constituent in the dye effluents coming with the sectional water of textile mills, the study of its influence on the photo mineralization efficiency is much relevant[10]. Considering the necessity for optimization of reaction parameters, this study investigates the effect of solution pH and salinity in the photocatalytic degradation of MO dye and Cr(VI) ions. This study also demonstrates the effect of the synergism of MO oxidation and Cr(VI) reduction in the photocatalytic degradation rates in acidic, neutral and alkaline medium and in the presence of Cl\(^-\) ions.

2. Materials and Methods

2.1 Materials

The Cobalt ferrite nanoparticles are synthesized from the nitrates of Co and Fe, Co(NO\(_3\))\(_2\).6H\(_2\)O (97%) and Fe(NO\(_3\))\(_3\).9H\(_2\)O (98%), respectively, in Ethylene Glycol solvent using the solvothermal route. Poly ethylene glycol -PEG, Sodium acetate and Urea were used as surfactants. Methyl Orange (MO: C\(_{14}\)H\(_{14}\)N\(_3\)NaO\(_3\)S) and potassium dichromate (K\(_2\)Cr\(_2\)O\(_7\)) are used as the organic dye and the source of heavy metal ion respectively, to study the photocatalytic experiments. The pH of the test solution is adjusted by the addition of sodium hydroxide and hydrochloric acid in required concentrations. The salinity of the test solution is varied by adding the right concentration of sodium chloride (NaCl) to it. All the chemicals are used as obtained without further purification and double distilled water is employed here in all the studies.

2.2 Methods

The salinity dependence of the photocatalytic degradation of MO and Cr(VI) was studied by varying the concentration of NaCl from 0 mM to 900 mM. The pH dependence of the same is studied in the acidic, neutral and basic pH conditions with pH values ranging from 2 to 12. The photocatalytic degradation were investigated in both single impurity systems, i.e. (i) with MO only and (ii) with K\(_2\)Cr\(_2\)O\(_7\) only and in binary impurity system, ie, a mixture of MO and K\(_2\)Cr\(_2\)O\(_7\) (10 ppm each). In each experiment, 50 mg of cobalt ferrite photocatalysts were suspended in 100 ml of the impurity solution. The photocatalytic experiments were carried out under visible light illumination using a 500 W halogen lamp with an illuminance of 70,000 lux. The detailed experimental procedure is cited elsewhere[4]. For each experiment, the absorbance spectra of methyl orange and chromium ions are studied using a UV-Vis Spectrophotometer to determine the photocatalytic reaction rate constants.

3. Results

3.1. Effect of pH

The effect of pH on the photocatalytic degradation of MO dye and chromium ion in the presence of cobalt ferrite photocatalysts are studied in the solution pH ranging from pH 2 to 12 and is shown in figure 1.
Figure 1 Effect of pH on the photocatalytic degradation of MO dye (Red Line) and Cr(VI) (Black line) in the presence of cobalt ferrite photocatalyst.

The photocatalytic dye degradation rate enhancement at strong acidic conditions may be attributed to the improved adsorption of the anionic MO dye molecules onto the protonated catalyst surface. Point of Zero charge (PZC) of a catalyst is the pH at which its surface becomes neutral. The PZC of cobalt ferrite photocatalyst is reported to be around pH ~ 6.6 [11][12]. At pH < PZC, the surface of the catalyst will be positively charged. The catalyst then strongly adsorbs the anionic dye molecules onto its surface by coulombic attraction, increasing the degradation efficiency. As pH of the solution increases below PZC, the positive charges on the catalyst surface decreases which causes a decrease in the degradation rate. When the solution pH becomes greater than PZC, ie, pH > 6.6, the degradation rate decreases markedly due to the electrostatic repulsion of the dye molecules with the surface of the photocatalyst which is negatively charged and also with the hydroxyl ions present in the solution.

The different forms of hexavalent chromium that exist in aqueous solution are HCrO$_4^-$, Cr$_2$O$_7^{2-}$, CrO$_4^{2-}$, and the stability of these forms mainly depends on the pH of the system[7]. HCrO$_4^-$, Cr$_2$O$_7^{2-}$, Cr$_3$O$_{10}^{2-}$,Cr$_4$O$_{13}^{2-}$ are the different forms of chromium ions that co-exists in the pH range of 1.0 -6.0 of which HCrO$_4^-$ predominates. As the pH of the solution increases, the predominant species are then Cr$_2$O$_7^{2-}$ and CrO$_4^{2-}$. The greater adsorption at acidic pH is due to the strong electrostatic attraction between the H$^+$ ions at the highly protonated adsorbent surface and the chromate ions. The adsorption of Cr(VI) at pH values greater than 6.0 decreases due to the dual competition of both the anions, CrO$_4^{2-}$ and OH$^-$, to get adsorbed on the surface of the adsorbent, of which OH predominates[5].

3.2. Effect of salinity
The effect of salinity on the photocatalytic oxidation of methyl orange and the reduction of chromium ions were studied in the chloride ion concentrations ranging from 0-900 mM keeping all other parameters a constant. It is noted that the photocatalytic degradation rate of both MO and Cr ion increases initially till the Cl$^-$ ion concentration reaches 100 mM and decreases on further addition of Cl$^-$ ions (100-900 mM).
The enhancement of dye degradation rate at lower Cl\(^-\) ion concentration can be attributed to a mechanism involving chloride(Cl\(^-\)) and dichloride radicals(Cl\(_2\)). The chloride and dichloride radicals are efficient in inhibiting the e\(^-\) - h\(^+\) recombination which enhances the photodegradation. The chlorine radicals involved in the degradation mechanism are formed through the following reactions:\(^{13}\), Eqs. (1) to (4):

\[
\begin{align*}
\text{Cl}^- + \text{OH} & \rightarrow \text{HOCl}^- \quad (1)\\
\text{HOCl}^- + \text{H}^+ & \rightarrow \text{Cl}^- + \text{H}_2\text{O} \quad (2)\\
\text{Cl}^- + \text{OH} & \rightarrow \text{Cl}^- + \text{OH}^- \quad (3)\\
\text{Cl}^- + \text{Cl}^- & \rightarrow \text{Cl}_2^- \quad (4)
\end{align*}
\]

The photocatalytic degradation mechanism of MO dye in the presence of Cl\(^-\) ions is illustrated in figure 3 [13-15].

**Figure 2** Effect of salinity on the photocatalytic degradation of MO dye (Red Line) and Cr(VI) (Black Line) in the presence of cobalt ferrite photocatalyst.

**Figure 3.** The proposed chlorine radical-mediated mechanism for the photocatalytic degradation of MO in the presence of Cl\(^-\) ions.
The degradation rate enhancement at lower Cl\(^–\) ion concentration can also be explained based on the PZC of the photocatalyst\[16\]. The photocatalytic experiments for the salinity dependence studies were carried out at the natural solution pH 5.75 (acidic) which is less than the PZC of the cobalt ferrite. Thus the positively charged photocatalyst surface at the reaction pH, easily adsorbs the anionic MO dye molecules through an electrostatic interaction at low Cl\(^–\) ion concentration which in turn improves the photocatalytic performance. Similar is the case of chromium ion where HCrO\(_4\)^–, the predominant form of Cr ion in acidic pH condition get easily adsorbed onto the protonated catalyst surface which undergoes further reduction.

The considerable reduction in the degradation rates observed at higher salt concentrations can be ascribed to the inhibitory effect of chloride ions. At higher salinity, there is a competitive adsorption between the chloride ions and the anionic dye molecules/ HCrO\(_4\)^– on to the protonated catalyst surface\[17\]. A higher number of Cl\(^–\) anions adsorbing onto the catalyst surface, masks and effectively block the active sites, thus decreasing the photodegradation rates notably\[15\].

3.3. Effect of Salinity and pH on the synergetic photocatalysis of Cr(VI) reduction and MO oxidation

The salinity and pH dependence of the photocatalytic experiments were studied both in single impurity systems containing either Cr(VI) ions or MO dye alone and the binary impurity systems containing both the impurities together. In both cases the concentration of Cr(VI) and MO are 10 ppm each. It is observed that the value of the rate constant, k is higher in the binary impurity system than in the single one. This enhancement can be attributed to a mutual promotion in the degradation mechanisms through a simultaneous Cr(VI) reduction and methyl orange oxidation. The hole-scavenging property of the MO dye prevents the electron-hole recombination which facilitates the utilization of the conduction band electrons by the Cr(VI) ions for undergoing reduction. In addition, the electrons are available for the Cr(VI) ions, which are transferred to them through the conduction band of CoFe\(_2\)O\(_4\) by the photoexcited MO molecules\[4\].

**Figure 4.** (a) The photocatalytic reduction of Cr(VI) in the absence (Green bar) and presence (Blue bar) of MO under different pH conditions, (b) The photocatalytic oxidation of MO in the absence (Green bar) and presence (Blue bar) of Cr(VI) under different pH conditions.
Figure 5. (a) The photocatalytic reduction of Cr(VI) in the absence (Blue bar) and presence (Red bar) of MO under different concentration of NaCl (mM), (b) The photocatalytic oxidation of MO in the absence (Blue bar) and presence (Red bar) of Cr(VI) under different concentration of NaCl (mM).

4. Conclusions

The effect of salinity and pH on the photocatalytic oxidation of Methyl Orange (MO) and reduction of Chromium(VI) ion in the presence of CoFe$_2$O$_4$ photocatalyst under visible light illumination was investigated. The adsorption of both the MO dye and Cr(VI) on the photocatalyst is highly dependent on the pH and the concentration of Cl$^-$ ions present in the waste water to be treated. The photodegradation rates of both MO dye and Cr(VI) ions are observed to be the highest at acidic pH conditions. The salinity of the test solution presented a double effect on the photodegradation rates; a promotion effect at lower salt concentrations and an inhibitory effect at higher salt concentrations. This work also demonstrated the enhancement of photocatalytic degradation rates in binary impurity system that arises from the synergistic MO oxidation and Cr(VI) reduction and proves to hold in acidic, neutral and alkaline conditions and also in the presence of salt.

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