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PHOTOCATALYTIC REDUCTION OF COBALT (II) IN THE PRESENCE OF BIMUTH VANADATE

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ABSTRACT

Photocatalytic reduction of cobalt (II) has been carried out in the presence of bismuth vanadate as a reductant. The reaction was monitored spectrophotmetrically. The effect of various parameters on the rate of reduction was observed. It was observed that cobalt (II) was reduced to cobalt metal.

Key words: Cobalt, Photocatalytic, Reduction, Bismuth vanadate

INTRODUCTION

Environmental contamination with metal ions represents a potential threat to human, animals and plants. The metal ions do not undergo bioreduction and many of them are soluble in aqueous solutions and therefore, become more available for living systems and accumulate in the environment. Cobalt (II) compounds are essential in many industries. Their applications in nuclear power plants, metallurgy, mining, pigments, paints and electronics are only few examples where the presence of cobalt in waste waters represents a major environmental problem.

Conventional methods for removing dissolved metal ions from aqueous media include chemical precipitation, oxidation, reduction, ion exchange and activated carbon adsorption. However, these processes have significant disadvantages, such as incomplete removal of metal ions, high quantities of toxic sludge, required additional reagents and have high operation cost. In recent years, considerable attention has been received by the utilization of adsorption technique, where the adsorbents are natural material or industrial and agricultural wastes, to passively remove metal ions from aqueous effluents. Thus, the utilization of peat, living and dead biomass or clay and related minerals offers an efficient and cost effective alternative compared to traditional chemical, physical remediation and decontamination techniques.

Aşçı and Kaya[1] studied the removal of Co (II) ions from aqueous solutions using an ion-exchange resin (Lewatit Mono Plus SP 112). Batch adsorption studies were carried out with various parameters such as pH and contact time. The Langmuir and Freundlich isotherm models were applied to analyze the

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experimental data. The best interpretation for the experimental data was given by the Langmuir isotherm and the maximum adsorption capacity was found to be 21.93 mg/g. The kinetic data were tested using pseudo-first-order, pseudo-second-order, liquid film diffusion, and intraparticle diffusion kinetic models. In addition, diffusion models were applied to explore the rate determining step in cobalt diffusion behavior.

Cobalt can be found in wastewater coming from advanced semiconductor fabrication plants. It can be easily treated using conventional methods similar to copper precipitation. Musapatika et al.[2] reported that agricultural wastes can cause environmental problems, if not well managed. There is a lot of potential to use these wastes as raw material in other processes. Pine sawdust was evaluated as an adsorbent in the treatment of wastewater containing cobalt ions. A two-level three-factor full-factorial experimental design with centre points was used to study the interactive effect of the operating parameters in order to achieve the best conditions for the batch adsorption of cobalt ions. A response surface analysis was also conducted to further understand the interactions amongst the factors such as adsorbent dose, solution pH and initial concentration. Adsorption isotherms, like Freundlich and Langmuir, were used to characterize the removal of cobalt from the wastewater. It was observed that the combined effect of low adsorbent dose, high pH and high initial concentration of wastewater resulted in the highest adsorption capacity. The Freundlich isotherm provided a better fit to the experimental data than the Langmuir isotherm. Moreover, pine sawdust showed adsorption capabilities for cobalt, and hence, it could be an option in the quest to use waste to treat wastewater.

EXPERIMENTAL

A stock solution of cobalt (II) was prepared in doubly distilled water and it was divided in four parts:

(i) First beaker containing cobalt (II) solution was kept is dark,

(ii) Second beaker containing cobalt (II) solution was exposed to light,

(iii) 0.1 g of bismuth vanadate was added to the third beaker containing the cobalt (II) solution and it was kept in dark, and

(iv) 0.1 g bismuth vanadate was added to the fourth beaker containing the cobalt (II) solution and it was exposed to light.

It was observed that there was no or negligible change in the optical density of the solution in the first three beakers, while the solution in fourth beaker showed a reasonable decrease. It indicates that the reduction of cobalt (II) is photocatalytic in nature and not chemical (thermal) or photochemical. Photocatalytic removal of copper (II) was studied by taking 50.0 mL solution (1.0×10^{-4} M) in a 100 mL beaker and 0.10 g of photocatalyst was added to it. Then this solution was exposed to a tungsten lamp (Light intensity = 50.0 $\mathrm{mWcm^{-2}}$). 2.0 mL of this solution was taken out and the change in optical density with time of exposure was observed spectrophotometrically at λ_{max} = 510 nm. It has been observed that a plot of log (optical density) v/s time is linear; thus, it may be concluded that this photocatalytic reduction follows pseudo-first order kinetics. The rate constant of this reaction has been calculated by the expression (1).

$$k = 2.303 \times \text{Slope} \quad ...(1)$$

The results for a typical run are given in Table 1.

Table 1: A typical run

[Cobalt (II)] = 5.0×10^{-3} M pH = 4.0
Intensity of light = 50.0 $mWcm^{-2}$ $BiVO_4$ = 0.10 g

Time (min.)	Optical density (O. D.)	1 + log O. D.
0.0	0.560	0.7482
5.0	0.447	0.6503
10.0	0.376	0.5752
15.0	0.316	0.4997
20.0	0.266	0.4249
25.0	0.224	0.3503
30.0	0.178	0.2504
35.0	0.150	0.1761
40.0	0.126	0.1004

Rate constant (k) = 6.23×10^{-4} sec^{-1}

RESULTS AND DISCUSSION

Effect of pH

Photocatalytic reduction of cobalt (II) may be affected by the pH values and, therefore, the effect of pH on this photocatalytic reaction has been investigated. The results are reported in Table 2.

Table 2: Effect of pH

[Cobalt (II)] = 5.0×10^{-3} M Intensity of light = 50.0 $mWcm^{-2}$
$BiVO_4$ = 0.10 g

pH	Rate constant (k) × 10^4 (sec^{-1})
3.0	2.33
3.5	3.24
4.0	**6.23**
4.5	5.16
5.0	2.85
5.5	1.50

It has been observed that this reaction proceeds smoothly in acidic range up to pH = 4.0, above which, precipitation of cobalt hydroxide was obtained, even under ordinary conditions and therefore, the effect of variation was observed in the pH range for 3.0 to 5.5. The reaction rate was found to increase as the pH was increased and an optimum value was obtained for pH = 4.0. This pH dependence can be explained on the basis that hole can generate H^+ ions in solution from water whereas these protons are utilized by dissolved oxygen (in solution).

$$2\,h^+ + H_2O \xrightarrow{\qquad} \tfrac{1}{2}O_2 + 2\,H^+ \qquad ...(2)$$

$$2\,H^+ + O_2\ (\text{in solution}) + 2\,e^- \xrightarrow{\qquad} H_2O_2 \qquad ...(3)$$

These two reactions counter balance each other to a particular extent. Now, it is known that processes at the semiconductor electrolytic interface depend on the surface properties of the semiconductor. Therefore, the surface charge on the semiconductor will play a major role in deciding the fate of this photocatalytic reaction, because it controls the driving force for electron transfer. This surface charge depends on the pH of the solution being positive in acidic media and negative in alkaline media. The pH, where the net charge on the surface of the semiconductor is zero, is called the point of zero charge. It corresponds to the point, where no change of pH was observed after adding the semiconductor.

The value of point of zero change can be lowered, if anions are adsorbed on the surface of the semiconductor. Reverse may be true, if cations are adsorbed. The data indicate that the photocatalytic reduction of cobalt (II) proceeds smoothly, when the surface is slightly positively charged as the reaction rate in maximum at pH = 4.0. It may also be concluded that for pH > 4.0 equation (3) starts dominating the equation (2), so that there will be an additional decrease in the amount of H^+ ions and hence, the decrease in rate of photocatalytic reduction of Co(II) species. The reduction of Co(II) to its lower oxidation states will also adversely affect the value of p_zc and thus, it will add to the lowering in the rate of the reaction.

Effect of cobalt (II) concentration

The effect of the concentration of cobalt (II) on the rate of photocatalytic reduction was observed, by keeping all other factors identical. The range of concentration investigated in the present case is 2.50 - 150.0 × 10^{-3} M. The results are reported in Table 3.

Table 3: Effect of cobalt (II) concentration

pH = 4.0 $BiVO_4$ = 0.1 g

Intensity of light = 50.0 $mWcm^{-2}$

[Cobalt (II)] × 10^3 M	Rate constant (k) × 10^4 (sec^{-1})
2.50	4.33
5.00	**6.23**
10.00	4.67
25.00	4.07
50.00	2.94
100.00	0.82
150.00	0.60

It was observed that as the concentration of cobalt (II) was increased, there was an increase in the rate of the reaction. This may be explained on the ground that as the number of substrate ions increases, there will be a corresponding increase in the rate of the reaction. On the other hand, if the concentration of Co(II) was increased above 5.0 × 10^{-3} M, the coloured solution will absorb the major portion of the incident light and it may not permit the desired light intensity to fall on the semiconductor powder in the limited time and hence, decrease in the rate of photocatalytic reaction is expected.

Effect of amount of photocatalyst

The effect of amount of photocatalyst on the rate of reduction of Co(II) was also observed by taking different amounts of semiconductor, keeping all other factors identical. The results are tabulated in Table 4.

Table 4: Effect of amount of photocatalyst

[Cobalt (II)] = 5.0×10^{-3} M pH = 4.0

Intensity of light = 50.0 mWcm^{-2}

$BiVO_4$ (g)	**Rate constant (k) × 10^4 (sec^{-1})**
0.02	1.65
0.04	2.92
0.06	3.67
0.08	4.46
0.10	**6.23**
0.12	6.20
0.14	6.30

As it is clearly indicated from the data that initially the rate of photocatalytic reduction of cobalt (II) increases with increasing amount of photocatalyst. This increase was observed up to the amount 0.10 g; thereafter, there was no appreciable increase in the rate of this reaction on increasing the amount of photocatalyst further. Here, a plateau was observed, which may be considered as a saturation point.

This variation can be explained on the basis that as the amount of semiconductor was increased, more particles were available for excitation and there is a greater possibility of electron-hole pair generation on exposure to light. This will result into a corresponding increase in the rate of photocatalytic removal of cobalt (II). After a certain value is reached (0.10 g in this case), then the bottom of the reaction vessel is almost covered and now, any addition of semiconductor will not increase the exposed surface area, rather it will only add to the thickness of the layer of semiconductor at the bottom of the reaction vessel. Hence, saturation like behavior was observed.

It was further confirmed by using vessels of different dimensions, where the saturation point was shifted to higher values for larger vessels and shows a downward shift for smaller vessels. It was further supported by the observation that this point shifts to higher side, when the solution was stirred. This increase is due to the greater probability of each particle for exposure in all directions, which was otherwise not possible in an unstirred solution.

Effect of light intensity

The effect of light intensity on the rate of photocatalytic reduction of Co(II) has been observed by varying the distance between the exposed surface of the photocatalyst and the source. The results are summarized in Table 5.

It has been observed that the rate of photocatalytic reaction increases with increasing the light intensity. It may be attributed to the fact that more electron-hole pairs will be generated due to an increase in number of photons striking the semiconductor surface with an increase in intensity of light. Now more electrons will be available for reducing the substrate and hence, the rate of photocatalytic reaction will be enhanced.

Table 5: Effect of light intensity

[Cobalt (II)] = 5.0×10^{-3} M pH = 4.0

$BiVO_4$ = 0.10 g

Light intensity ($mWcm^{-2}$)	Rate constant (k) × 10^4 (sec^{-1})
20.0	1.11
30.0	2.06
40.0	3.64
50.0	**6.23**
60.0	5.12
70.0	3.35

Mechanism

On the basis of the observed experimental data, the following tentative mechanism has been proposed for the photocatalytic reduction of cobalt (II) ions.

$$SC \xrightarrow{\quad} e^-(CB) + h^+(VB) \quad \text{... (4)}$$

$$2\,h^+ + H_2O \xrightarrow{\quad} \tfrac{1}{2}O_2 + 2\,H^+ \quad \text{... (5)}$$

$$2\,H^+ + O_2\ \text{(in solution)} + 2\,e^- \xrightarrow{\quad} H_2O_2 \quad \text{... (6)}$$

$$Co(II) + 2\,e^- \xrightarrow{\quad} Co \quad \text{... (7)}$$

In the first step, semiconductor is excited by the absorption of light of an appropriate wavelength. An electron from the valence band of the semiconductor will jump into its conduction band; thus, leaving behind a hole. This hole may be utilized by the water molecules to generate oxygen and H^+ ions. These H^+ ions and dissolved oxygen in solution can be reduced by two electrons to form hydrogen peroxide, which may slowly degrade. In the last step, cobalt (II) may accept two electrons from the semiconductor and will reduce to its metallic state. This reduction of Co (II) is clearly indicated by the grey deposit on the semiconductor bismuth vanadate.

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