



REMOVAL OF NICKEL (II) OVR BISMUTH VANADATE POWDER

DEEPIKA SOLANKI, RAKSHIT AMETA, ANUGYA PORWAL^a and
MAMTA AHUJA^{*,b}

Department of Chemistry, PAHER University, UDAIPUR – 313003 (Raj.) INDIA

^aDepartment of Chemistry, Guru Nanak Girls P. G. College, UDAIPUR – 313001 (Raj.) INDIA

^bDepartment of Chemistry, Meera Govt. P. G. College, UDAIPUR – 313001 (Raj.) INDIA

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ABSTRACT

Nickel is a toxic element and pollutes water. Nickel ions were removed by photocatalytic reduction over bismuth vanadate powder. The effect of different variables like pH, metal ion concentration, amount of bismuth vanadate, light intensity, etc. on the rate of removal was investigated and conditions for removal were optimized. A tentative mechanism for this reaction has been proposed.

Key words: Nickel(II), Bismuth vanadate, Photocatalytic reduction.

INTRODUCTION

Any human activity that impairs the use of water as a source may be called water pollution. With exploding population, rapidly increasing industrialization, urbanization, agriculture, municipal and industrial wastes have been responsible for water pollution and it has become a major concern for the welfare of the mankind. The indiscriminate disposal of water after use in the form of waste water is going to create havoc in coming years.

Water pollution is a major global problem, which requires ongoing evaluation and revision of water resource policy at all levels. It has been suggested that it is the leading worldwide cause of deaths and diseases, and it also accounts for the deaths of more than 14,000 people daily. According to an estimation, 580 people in India die of water pollution related illness every day. Millions of people lack access to safe drinking water.

The purpose of waste water treatment is to remove the contaminants from water to make it usable for industrial and domestic purposes. The entire waste water treatment processes can be broadly classified as physical, chemical and biological processes.

Nickel is not a common element. It is being only twenty-fourth in order of abundance, but even then it is ubiquitous in the environment. Only 0.008% of the Earth's crust is composed of nickel, which is not evenly distributed. The silver white metal is frequently found in plated objects and several nickel salts are

used as dyes. It is also used to form certain alloys that are strong and resistant to corrosion also. It is used in diverse commodities as batteries, coins, utensils, automobiles, surgical implants, inks, varnishes, costume jewellery etc.

The biosorption process for the removal of Ni(II) by loofa sponge-immobilized biomass of *Chlorella sorokoiniana* (LIBCS), a newly developed immobilized biosorbent was characterized¹. Ni(II) removal by LIBCS was found to be influenced by pH of the solution, initial metal concentration and biomass concentration 20 mg/L. It was observed over a pH range of 4.0 to 10.0. The suitable pH for treating Ni plating industry waste water was also tested².

Ni is found in plating metal pickling and metal cleaning waste water. Ion exchange can be used to remove Ni and other heavy metals from waste water. Wastech ion exchange systems are designed to treat plating rinse water with trace amounts of metals. Heavy metals into water as a result of industrial activity may pose a serious threat to the environment. The effect of condition on the removal process such as initial concentration of Ni²⁺ ions, temperature and adsorbent mass were investigated³. NiSO₄ is extensively used in electroplating, organic chemical synthesis, metal coloring, dye mordant, manufacturing other nickel salts and Ni-Cd battery. Nickel catalysts used in various operations become spent after several cycle of use and for that, a very simple and innovative process was developed for recovery of nickel.

In the environment, nickel occurs in divalent and tetravalent forms. Comparative to tetravalent, divalent nickel is more hazardous to the environment. Electroplating industry, which commonly use nickel metal for plating process, discharges the effluents into the environment containing nickel in excess of the maximum permissible limits. For bio-removal of nickel from waste water, *Staphylococcus* cultured was used. Nickel removal was higher in the presence of nitrate anions followed by sulfate and chloride anions. In Watt type electroplating solution, the nickel was effectively removed by combining precipitation and ion exchange but the best results were obtained with ammonium dinoptilolite⁴. The photocatalytic removal of Ni(II) using UV-irradiated TiO₂ suspension has been carried out⁵. The photocatalytic reaction was shown to be electron-mediated, and occurs both via direct electron transfer from the photo-excited TiO₂ particles to Ni(II) and an indirect route.

The ability of Na-activated bentonite for removal of Ni²⁺ from aqueous solution at room temperature was studied under various experiment conditions⁶. Ni in aquatic systems is due to discharge of chemicals and pesticides from agricultural lands to the nearby water bodies. Removal of nickel from water samples using low cost and abundant plant materials as adsorbents has been studied⁷.

A man normally takes about 0.10-0.15 mg of nickel daily, but daily requirement for an average man is 10 mg. The sources of nickel in human diet include fats, egg, milk, vegetable, whole grain cereals, etc. Since, nickel is present in soil and water, it is available for consumption by man not only in primary sources, such as drinking water, but also as the results of incorporation directly into plants from the soils and indirectly into animals through their foodstuffs.

EXPERIMENTAL

A stock solution of nickel sulphate was prepared in doubly distilled water and it was divided in four parts:

- (i) First beaker containing nickel sulphate solution was kept is dark,
- (ii) Second beaker containing nickel sulphate solution was exposed to light,
- (iii) 0.1 g of bismuth vanadate was added to the third beaker containing the nickel sulphate solution and it was kept in dark, and

- (iv) 0.1 g bismuth vanadate was added to the fourth beaker containing the nickel sulphate 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 nickel(II) is photocatalytic in nature and not chemical (thermal) or photochemical. Photocatalytic removal of nickel(II) was studied by taking 50.0 mL solution (1.0×10^{-4} M) in a 100 mL beaker and 0.1 g of photocatalyst was added to it. Then this solution was exposed to a tungsten lamp (Light intensity = 50.0 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 $\lambda_{\text{max}} = 350 \text{ nm}$. It has been observed that a plot of $\log(\text{optical density})$ 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).

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

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

Table 1: A typical run

[Ni(II)] = 1.0×10^{-2} M		pH = 6.0
Intensity of light = 50.0 mWcm^{-2}		BiVO ₄ = 0.05 g
Time (min.)	Optical Density (O. D.)	1 + log O. D.
0.0	0.500	0.6989
10.0	0.398	0.5998
20.0	0.313	0.4955
30.0	0.237	0.3747
40.0	0.188	0.2741
50.0	0.156	0.1931
60.0	0.121	0.0827
Rate constant (k) = $3.94 \times 10^{-4} \text{ sec}^{-1}$		

Effect of pH

Photocatalytic reduction of nickel(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.

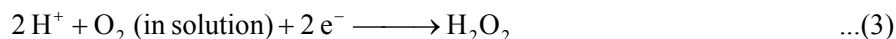
Table 2: Effect of pH

[Ni(II)] = 1.0×10^{-2} M		Intensity of light = 50.0 mWcm^{-2}
BiVO ₄ = 0.05 g		
pH	Rate constant (k) $\times 10^4 (\text{sec}^{-1})$	
3.0	1.14	
3.5	1.75	
4.0	2.38	

Cont...

pH	Rate constant (k) × 10 ⁴ (sec ⁻¹)
4.5	3.16
5.0	3.47
5.5	3.74
6.0	3.94
6.5	3.12
7.0	2.84
7.5	2.25
8.0	2.10
8.5	1.74

It has been observed that this reaction proceeds smoothly in acidic range upto pH = 6.0, above which, precipitation of nickel hydroxide was obtained, even under ordinary conditions and therefore, the effect of variation was observed in the pH range for 3.0 to 8.5. The reaction rate was found to increase as the pH was increased and an optimum value was obtained for pH = 6.0. 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).



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 (p_{zc}). It corresponds to the point, where no change of pH is 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 available indicate that the photocatalytic reduction of nickel(II) proceeds smoothly, when the surface is slightly positively charged as the reaction rate in maximum at pH = 6.0. It may also be concluded that for pH > 6.0 equation (3) starts dominating the equation (2), so that there will be an additional decrease in the amount of H⁺ ions. Hence, the decrease in rate of photocatalytic reduction of Ni(II) species. The reduction of Ni(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 nickel(II) sulphate concentration

The effect of the concentration of nickel(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 0.25-10.0 × 10⁻² M. The results are reported in Table 3.

Table 3: Effect of nickel sulphate concentration

pH = 6.0		BiVO ₄ = 0.05 g
Intensity of Light = 50.0 mWcm ⁻²		
[Nickel (II)] × 10 ² M	Rate constant (k) × 10 ⁴ (sec ⁻¹)	
0.25	0.57	
0.35	0.77	
0.50	1.06	
0.75	2.43	
1.00	3.94	
1.50	2.80	
2.50	1.92	
3.50	1.54	
5.00	1.30	
6.50	1.09	
7.00	0.97	
10.00	0.88	

It was observed that as the concentration of nickel (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 increase, there will be a corresponding increase in the rate of the reaction. On the other hand, if the concentration of Ni(II) was increased above 1.0×10^{-2} M, the colored 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 photocatalyst removal of nickel (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

[Ni(II)] = 1.0×10^{-2} M		pH = 6.0
Intensity of light = 60.0 mWcm ⁻²		
BiVO ₄ (g)	Rate constant (k) × 10 ⁴ (sec ⁻¹)	
0.02	2.15	
0.03	2.81	
0.04	3.22	
0.05	3.94	
0.06	3.85	
0.07	3.97	
0.08	3.93	

As, it is clearly indicated from the data that initially the rate of photocatalytic removal of nickel (II) increases with increasing amount of photocatalyst. This increase was observed upto the amount 0.05 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 nickel (II). After a certain value is reached (0.05 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 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 removal of Ni(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.

Table 5: Effect of light intensity

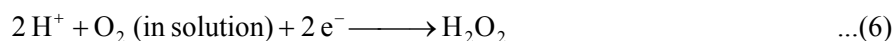
[Ni(II)] = 1.0×10^{-2} M		pH = 6.0
BiVO ₄ = 0.05 g		
Light intensity (mWcm ⁻²)	Rate constant (k) × 10 ⁴ (sec ⁻¹)	
20.0	1.20	
30.0	1.55	
40.0	2.80	
50.0	3.94	
60.0	2.99	
70.0	2.89	

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.

Mechanism

On the basis of the observed experimental data, the following tentative mechanism has been proposed for the photocatalytic reduction of nickel ions.





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. Ni(II) may accept two electrons from the semiconductor and it will reduce to its metallic state. The reduction of Ni(II) is indicated by grey deposit (with shine) on the semiconductor.

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