PHOTOCATALYTIC TREATMENT OF WASTEWATER USING COO NANOPARTICLES

Udit A. Kanoi[1], Nadeem M. Ahamed[2], Prasad Parulekar[3]
[1]Department of Chemical Engineering, Thadomal Shahani Engineering College, Mumbai, India)
Email: prasadjparulekar@gmail.com[3]

ABSTRACT

In recent years, photocatalytic oxidation using semiconductor photocatalyst nanoparticles (NPs) has gained a lot of research potential as a method for wastewater treatment in presence of UV/visible spectra. The cobalt oxide (CoO) NPs were synthesized by one step thermal dehydration method. The CoO were synthesized by mixing aqueous $CoCl_2.6H_2O$ solution with sodium hydroxide (NaOH) in the presence of glycerol as capping agent. The reaction mixture was heated for a total time of 2 min. The size of synthesized NPs was in the range of 50-60 nm as revealed by Scanning Electron Microscopy and showed distinct absorbance in the visible region when characterized by UV-Visible Spectroscopy. The photocatalysis was carried at room temperature and high intensity discharge (HID) lamp of 1000 watt was used to irradiate wastewater-NP mixture for treatment. Different wastewater samples were collected and analyzed for parameters such as Chemical Oxygen Demand (COD), solid content, color and pH. The COD and Total Dissolved Solids (TDS) reduced effectively, confirming that CoO NPs can reduce the pollutants in wastewater.

KEYWORDS: Cobalt Oxide (CoO) Nanoparticles (NPs), Thermal Dehydration, Wastewater, Oxidation, COD, Solid Content

INTRODUCTION

In the last few years, a lot of interest has been devoted in the field of nanotechnology as it has many applications in material science, chemistry, biochemistry, etc. In the nanoscale dimensions, the properties of materials change when compared to their bulk element. Various metal oxides have been studied by researchers in their nanoscale dimensions, for example, TiO_2, ZnO, SnO_2, etc. The NPs find their applications in various fields like battery applications[1], as photocatalysts[2], solid state sensors[3], pigments and magnetic data storage[12]. The prominent ones among them being photocatalysis and as self-cleansing materials[4][5]. There are several methods to synthesize metal oxide NPs such as hydrothermal method[6], solvo-thermal method[7], thermal dehydration of metal nitrates and hydroxides[8], sol-gel method[9], etc. Cobalt oxide exists in various forms such as CoO and Co_3O_4[10] out of which Co_3O_4 is thermodynamically more stable form as CoO reduces to Co metal[11]. CoO absorbs in the visible region of the electromagnetic spectrum[4] and hence it shows photocatalytic activity in the visible range. So, it can be used for water splitting[2] in visible light thus making it applicable for oxidation of organic pollutants in WW.

We report one step synthesis of CoO NPs by thermal dehydration of cobalt (II) hydroxide.

Cobalt (II) hydroxide was prepared by mixing cobalt chloride hexahydrate ($CoCl_2.6H_2O$) and sodium hydroxide (NaOH) in presence of glycerol as a capping agent. Different water samples from sources such as reactor washing, effluent treatment plant discharge were used for treatment and analysis. For photocatalytic oxidation of waste, high intensity discharge lamp of 1000 watt was used as light source. Since, the synthesis of NPs is simple and cost effective in makes the whole treatment process more feasible.

MATERIALS AND METHODS

Glycerol was purchased from S D Fine-Chem Ltd. and used without further purification. The hydrated cobalt (II) chloride-hexa hydrate ($CoCl_2.6H_2O$) and sodium hydroxide (NaOH) were obtained from S D Fine-Chem Ltd. and Loba Chemie respectively and used as received. All reagents used were of analytical grade. Deionized (DI) water was used for the entire synthesis.

UV-Visible studies were carried out on Perkin-Elmer Lambda-25 spectrophotometer and SEM measurements were performed on ZEISS Ultra plus FESEM instrument.

SYNTHESIS OF NANOPARTICLES

10 mL of 1 M NaOH solution was taken in a test tube, 2 mL of glycerol was added to it with constant stirring. Further 2mL of 0.01M $CoCl_2.6H_2O$ was added to the above solution. This solution was then heated in a glycerol bath at 90°C for 2 min. Appearance of black-brown color to the solution indicates the formation of CoO nanoparticles as shown in Figure 1. These nanoparticles were further characterized by UV-Visible spectroscopy and Scanning Electron Microscopy (SEM).

Figure 1: Colloidal Dispersion of CoO NPs in water.

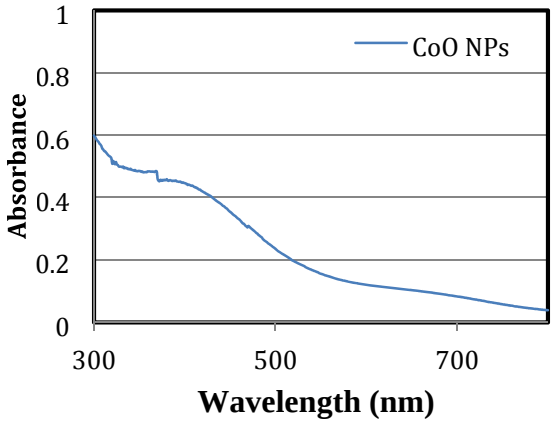

Figure 2: UV-Visible spectra of CoO NPs in water.

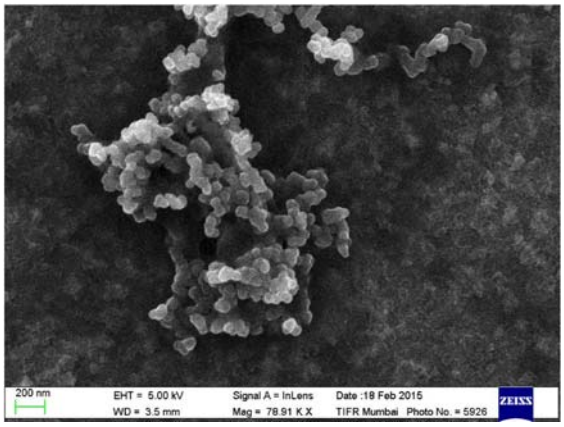

Figure 3: SEM image of CoO NPs

EXPERIMENTAL SETUP

The wastewater samples were collected from reactor washing and effluent treatment plant discharge. The sample taken from the reactor washing stream was allowed to rest for 5 to 6 months and hence the COD increased from 3,56,450 mg L^{-1} to 58,46,400 mg L^{-1}. The sample was then filtered using ordinary filter paper. Here, the filtration pre-treatment removed the suspended particles and thus, the turbidity in the effluent. Thereby, the working load of the CoO catalyst was reduced and the transparency of the medium was increased, such that the visible light could pass through easily. Since, the increase in intensity of light increases the activity of the photocatalyst this step is essential. The 100 ml sample from the filtered effluent was analyzed before treatment for solid content. The filter paper used for solid content analysis was Whatman filter paper grade 1.

The filtrate was studied for colour using Lovibond PFX995 Tintometer and subsequently for pH. The 50 ml of the sample was heated in the oven at 105^{o}C for 20 mins for total solids (TS) in the wastewater sample. The filter paper after passing the 50 ml of filtrate was dried to account for total suspended solids (TSS) and 0.1 ml of the filtered sample was taken for the COD analysis. The 30 ml of the WW after TSS analysis was mixed with CoO nanoparticle photocatalyst which was centrifuged for 4 hours at the speed of 4000 rpm. The FTIR analysis of the centrifuged revealed that glycerol is precipitated and the CoO remains in the colloidal solution. The mixture was treated under the HID of 1000 watt at room temperature of 30^{o}C for 5 min using a magnetic stirrer as seen in the Figure 4.

Cold water in the outer beaker was added so that the temperature of the reactant does not rise due to heat generated from HID lamp, as the increase in the temperature increases the activity of the NPs[13] and hence error in the readings would affect the optimization of the treatment process. After treatment similar procedure was followed for analysis where in 0.1 ml of the treated sample was taken for COD and the rest of the 30 ml for solid content, colour and pH after treatment. The setup for the photocatalytic treatment is shown in the Figure 4.

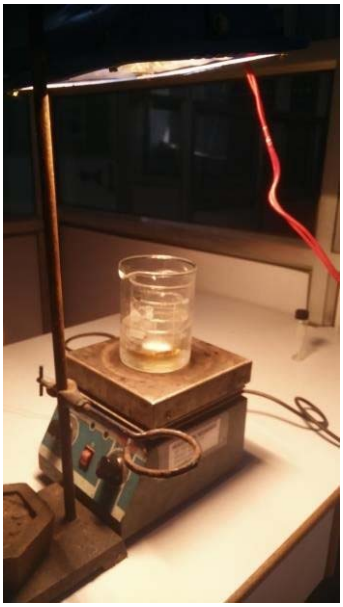

Figure 4: Photocatalytic oxidation under HID lamp.

RESULTS AND DISCUSSION

The CoO NPs synthesized at laboratory scale were characterized by UV-Visible spectroscopy and SEM. The analysis revealed that CoO NPs also show absorbance in the visible spectrum. The morphology of the synthesized NPs was found to be spherical and sizes in the range of 50-60 nm as seen in Figure 3 of the SEM image. These characterizations are consistent with the existing literature[1].

As discussed in the above experimental setup the COD of WW from reactor washing stream increased to 58, 46, 400 mg L^{-1} whereas, the initial COD of the water sample from the effluent treatment plant discharge was 56,441 mg L^{-1}. After treatment of WW sample with CoO NPs at different process times it was found that with increase in time the COD of the WW increased when compared to the COD with shorter process time. For example, the COD of 30 ml WW sample treated with the 1 ml of nanoparticle photocatalyst for 5 minutes shows greater reduction in COD when compared to the same 30 ml sample treated with 1 ml of nanoparticle photocatalyst for 10 minutes. The initial COD was 58, 46, 400 mg L^{-1} which reduced to 6, 96, 800 mg L^{-1} in 5 mins. of treatment time whereas, after 10 mins with same amount of 30 ml of WW and 1 ml of NPs reduced to 14,61,600 mg L^{-1}.

When 50 ml of sample is treated with 2 ml of nanoparticle photocatalyst shows greater reduction in COD when compared to 0.5 ml or 1 ml. The initial COD of WW from effluent treatment plant discharge was 56441 mg L^{-1} which after treatment for 5 mins. with 50 ml WW and 0.5 ml of CoO NPs reduced to 31356 mg L^{-1}. Similarly, treating with 2 ml of NPs reduces the COD to 28536 mg L^{-1}. Also, further analysis of increased volume of CoO NPs does not reduce the COD to the extent where the process could be cost effective.

The solid content analysis of WW sample from the reactor washing, before treatment with CoO NPs helps us in understanding amount of solids to be removed from the WW after treatment of 30 ml WW with 1 ml of CoO NPs. The total solids (TS) in the sample before treatment was 42.262 g L^{-1}

which increased to 54.785 g L^{-1} as we leave the CoO NPs in the solution after treatment, thus adding to the TS. The total suspended solids (TSS) increases from 14.532 g L^{-1} to 28.1 g L^{-1} which suggests that the majority of CoO NPs associated with suspended organic matter is of a size larger than the pore size of the CoO NPs present in colloidal dispersion with water seen in Figure 1. The total dissolved solids decreased from 27.73 g L^{-1} before treatment to 26.685 g L^{-1} after treatment which is consistent with the literature[14].

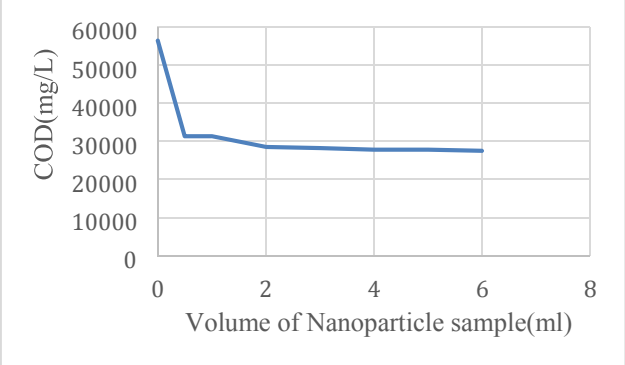

Figure 5: Relation between COD in mg L^{-1} and Volume of CoO NPs in ml for constant treatment time of 5 mins.

Table 1: Change in COD with different volumes of CoO NPs for constant treatment time of 5 mins.

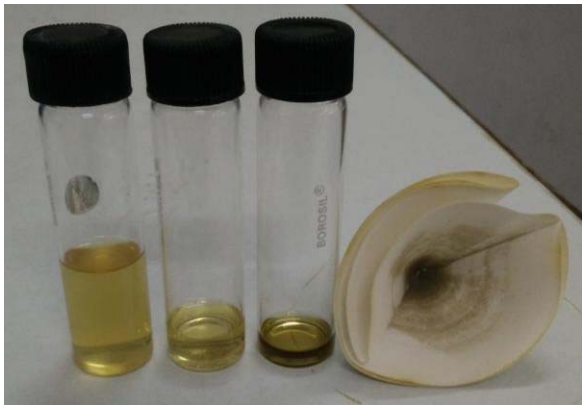

Figure 6: Bottle 1- WW sample before treatment, bottle 2- WW sample after treatment, Bottle 3- CoO NPs, Filter paper showing the TSS before treatment.

The colour as seen from the Tintometer analysis shows that the yellowness of the water before addition of NPs was 4.2 on the Gardner Scale which increased to 5.1 after treatment. As, the CoO NPs photocatalyst ranges in the higher dark yellow to red range with 10.2 on the Gardner scale, shows that the addition of NPs increases the output of the Tintometer confirming the presence of CoO which remain in the solution after treatment as seen in Figure 7.

The pH of the WW before treatment is 12.18 which shows that the WW is highly alkaline and the activity of NPs is decreases in the acidic as well as alkaline medium[13]. The NPs are most effective at neutral pH value of the solution[13]. The CoO NP sample was also found to be alkaline with pH of 12.11. After treatment the pH of the solution remained unchanged which shows that photocatalytic oxidation using CoO NPs does not affect the change in pH. Since, the WW solution before treatment was alkaline in nature it did not neutralize on addition of CoO NP sample, confirming the reduction in COD was due to the photocatalytic treatment rather than the chemical neutralization.

Sr No.	**Sample**	**Contents (ml)**		**COD mg L^{-1}**
		Vol. of WW	**Vol. of CoO NPs**	
1	Wastewater before treatment.	50	0	56441
2	Sample A	50	0.5	31356
3	Sample B	50	1	31356
4	Sample C	50	2	28536
5	Sample D	50	3	28220
6	Sample E	50	4	27872
7	Sample F	50	5	27872
8	Sample G	50	6	27524

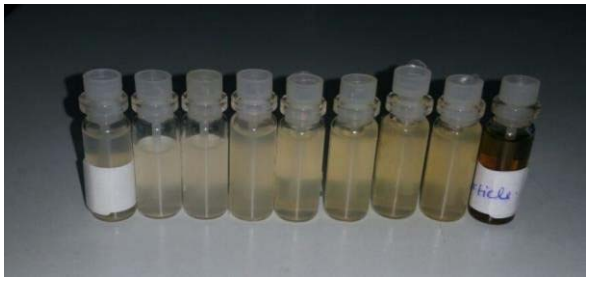

Figure 7: Change in the yellowness of the WW sample as volume of NPs added for treatment is increased from 0.5 ml to 6 ml per 50 ml of WW. Bottle 1 shows WW sample without addition of CoO NPs whereas, bottle 9 shows CoO NPs used for treatment.

CONCLUSION AND FUTURE PROSPECTS

CoO NPs were synthesized by low temperature thermal dehydration method which is simpler and cost effective than previously known methods. The CoO NPs are of the size ranging between 50-60 nm and spherical morphology as seen from the SEM results. The absorption spectrum of these nanoparticles is consistent with the existing literature.

The WW sample was successfully treated using the advanced oxidation process of photocatalysis. The results prove that CoO NPs can be used to reduce the organic pollutants in the WW similar to other metal oxide NPs like TiO_2, ZnO, etc. The setup is in crude state which can be further improved and process systems can designed. Further research can be done to recover the CoO NPs from the treated WW using different separation techniques. This would be beneficial as CoO though being highly efficient in reducing COD cannot be left in the treated WW as it is toxic in nature. Also, different dopants could be used to increase the efficiency of CoO NPs.

From the analysis of the treatment method we can conclude that, the photocatalytic treatment technology using CoO NPs is one of the most versatile modern methods that can be used for water treatment.

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