Int. J. Chem. Sci.: 9(1), 2011, 421-428
ISSN 0972-768X

PHOTOCATALYTIC TREATMENT OF POLLUTED WATER CONTAINING CRESOL RED

RICHA TIWARI, MOHAN KUMAR SHARMA[a] and SURESH C. AMETA[*]

Department of Chemistry, M. L. Sukhadia University, UDAIPUR – 313002 (Raj.) INDIA
[a]Department of Chemistry, M. S. J. College, BHARATPUR – 321001 (Raj.) INDIA

ABSTRACT

The photocatalytic degradation of cresol red was studied using ZnO as semiconductor. Sunlight was used as the source of energy. ZnO is an extensively used photocatalyst because of its chemical stability, nontoxicity, and low cost. Parameters like pH, BOD, COD, DO, conductivity, TDS, alkalinity, hardness, calcium, magnesium, chloride, fluoride, sulphate, nitrate and turbidity were observed in present experiments. It was observed that photocatalytic degradation mainly affects the parameters like COD, BOD, nitrate, sulphate and hardness. Increased BOD, conductivity, decreased COD, pH, hardness, alkalinity and significant release of SO_4^{2-} confirm the mineralization of the polluted water during this treatment process.

Key words: Cresol red, ZnO, Quality parameters, BOD and COD.

INTRODUCTION

The textile processing industries are putting a severe burden on the environment, through the release of heavily polluted wastewaters[1]. Current methods used to remove these substances involve filtration, extraction by organic solvents or biological treatments. Often these methods are unable to remove the pollutants completely; however, these may reduce their levels.

In recent years, there has been a growing interest in using semiconductors as photosensitizers for complete oxidative mineralization of pollutants. As an example, purification of water by semiconducting photocatalyst has attracted a great deal of interest,

[*]Author for correspondence; E-mail: ameta_sc@yahoo.com, richatiwari06@gmail.com

not only from researchers but also from manufacturers of water purifiers[2]. The field of photocatalysis has been excellently reviewed by Ameta *et al.*[3,4]

The focus of the present work is to analyze the changes occurring in quality parameters of water after photocatalytic treatment of polluted water (containing dye). Evaluation of quality improvement of waste water was done on the basis of certain parameters like pH, BOD, COD, DO, conductivity, TDS, alkalinity, hardness, calcium, magnesium, chloride, fluoride, sulphate, nitrate and turbidity of canal water, polluted water (in the presence of cresol red) and treated water (photocatalytically).

The canal water was collected from the Sujan Ganga of Bharatpur District in Rajasthan.

EXPERIMENTAL

Materials

Cresol red, ZnO, EDTA, murexide indicator, potassium chromate indicator, silver nitrate, phenol disulfonic acid, zirconyl- acid reagent and SPADNS solution.

Apparatus

Systronics spectrophotometer 104, Systronics water analyser 371, Digital pH meter, Systronics spectrophotometer Model 106 and Solarimeter CEL Model 211.

Methods

Cresol red (CDH) and ZnO (Merck) were used in the present investigations. Water samples were collected from Sujan Ganga of Bharatpur District. The dye solution of cresol red (1.0×10^{-5}M) was prepared in this canal water and it was analyzed again for these parameters. For the photocatalytic degradation, 500 mL of cresol red (1.0×10^{-5}M) was exposed to sunlight with 3 g of ZnO for 4 hours. Sunlight intensity was measured by a solarimeter. After four hours, ZnO was separated using A G-3 sintered glass crucible and remaining solution was considered as treated water. Again, all the quality parameters of treated water were determined.

RESULTS AND DISCUSSION

The results are reported in Table 1.

Table 1: Results of photocatalytic treatment

Parameters	Canal water	Polluted water	Treated water
pH	8.13	8.17	8.23
Alkalinity (mg/L)	400	340	320
Hardness (mg/L)	980	970	890
Calcium (mg/L)	300	303	230
Magnesium (mg/L)	680	670	660
Chloride (mg/L)	1100	1105	1105
Fluoride (mg/L)	1.2	1.2	1.2
Sulphate (mg/L)	433	429	633
Nitrate (mg/L)	457	459	390
DO (ppm)	3.2	3.2	3.1
BOD (ppm)	5	3.25	3.66
COD (mg/L)	24	24	13.2
Cond. (μmhos/cm)	4.1×10^3	4.1×10^3	4.2×10^3
TDS (mg/L)	2660	2720	2823
Turbidity (NTU)	3	7	8

The photocatalytic treatment of cresol red was carried out in sunlight. In the presence of sunlight, ZnO was found to affect the water quality parameters like pH, alkalinity, hardness, calcium, magnesium, sulphate and nitrate; however, other parameters remained almost unaffected.

Effect on pH

pH of water sample denotes the extent of its pollution by acidic and alkaline wastes[5]. All chemical and biological reactions are directly dependent upon the pH of the medium[6]. According to Swingle[7], pH between 6.5 to 9.0 is required for fishery and drinking purpose. pH of polluted water depends on the nature of dye present in the water sample as contaminant. Cresol red dye is basic in nature and hence, it increases the pH of water sample from 8.13 to 8.17. For the photocatalytic treatment, the pH of cresol red was set at 9.0 and the sample was kept for photocatalytic oxidation in presence of ZnO and sunlight. After treatment, the pH was 8.23. This result indicates that pH values of all water samples were found to be in alkaline range but within the ISI permissible limits.

Effect on alkalinity

The alkalinity of surface waters is primarily due to carbonate, bicarbonate, and hydroxide contents and it is often interpreted in terms of the concentrations of these constituents. Alkalinity may also include contributions from borates, phosphates, silicates, or other bases, if they are present. Alkalinity is used to determine the suitability of water for irrigation, industrial use, raw water characterization and water & wastewater monitoring. Alkalinity is also important as an indicator of a water body's ability to resist pH change with the addition of acid from an accidental spill or acid precipitation. These calcium and magnesium ions precipitate certain dyestuffs. It decreases the alkalinity of polluted water from 400 to 340 mg/L. After photocatalytic treatment of this sample, the alkalinity was found to decrease i.e. 320 mg/L. The standard desirable limit of alkalinity in potable water is 200 mg/L and the maximum permissible level is 600 mg/L (ISI, 1983). All these three samples can not be used for drinking purpose; however, these samples after photocatalytic treatment can be used for irrigation.

Effect on hardness

Hardness of water is due to carbonates, bicarbonates, sulphates of calcium and magnesium etc.[8] Hardness is defined as the sum of the calcium and magnesium concentrations**.** Like alkalinity, the hardness was also found to be slightly low in water contaminated by cresol red, as calcium and magnesium are principal cations responsible for hardness. In polluted water, hardness was reduced from 980 to 970 mg/L and after photocatalytic treatment, this hardness was further reduced to 890 mg/L. The maximum limits for hardness in drinking water according to ICMR, 1963 is 600 mg/L and therefore, all the water sample were not found suitable for drinking purpose. The water samples of this area were hard enough.

Effect on calcium

Calcium salts and calcium ions are among the most commonly occurring species in nature. Calcium is usually one of the most important contributors to hardness. Even though the human body requires approximately 0.7 to 2.0 g of calcium per day as a food element,[9] maximum permissible limits of calcium hardness is 200 mg/L (ICMR, 1963), in drinking water. Calcium contents were found almost same in canal water and polluted water that is around 300 mg/L and after photocatalytic treatment, the value of calcium falls from 300 to

230 mg/L. Thus, calcium hardness in all the water samples was found to be higher than the permissible limits. Excess amounts of calcium can lead to the formation of kidney or gall bladder stones.

Effect on magnesium

Magnesium enters in the drinking water system from natural geological sources. In canal water, the magnesium content was 680 mg/L, which was reduced in polluted water and treated water to 670 mg/L and 660 mg/L, respectively. Magnesium is also found to be higher in all the three water samples. Very high concentration of magnesium can cause nausea, muscular weakness and paralysis in human body, when it reaches up to level of about 400 mg/L.[10]

Effect on BOD

BOD value also indicates the degree of pollution.[11] BOD represents the biological oxidisable load present in water.[12] It shows an inverse relationship with DO and COD. Water sample with BOD level exceeding 8 ppm is considered to be polluted.[13] BOD was found to decrease from canal water (5.00 ppm) to polluted water (3.25 ppm) because dye prevents the biological activity of organisms and therefore, the value of BOD in polluted water was lower than canal water as well as treated water. BOD of the treated water was observed to be 3.66 ppm, which is higher than polluted water and lower than canal water. It is a good sign, which shows an improvement in the quality of water.

Effect on COD

COD indicates the level of water pollution by reductive pollutants. It is the main determinant used to assess organic pollution in aqueous systems and is one of the most important parameters in water monitoring[14,15]. COD was found almost constant in canal water and polluted water but after photocatalytic treatment, the COD was found to decrease from 24.0 to 13.2 mg/L, which is an appreciable change. The maximum permissible limit of COD is 10.0 mg/L for drinking water[16]. All water samples were found within the range of COD hazards; however, photocatalytic treated water sample was relatively safe.

Effect on sulphate

Sulphates are the salts containing sulphur. Sulphates are naturally occurring salts containing sulphur and oxygen. It is present in various mineral salts found in soil. Sulphate forms salts with a variety of elements including barium, calcium, magnesium, potassium and sodium. Sulphates have a detoxifying effect on the liver and stimulate the function of the gall bladder and the digestive function as well.[17] During photocatalytic treatment, sulphate formation takes place in the treated water sample. Sulphate was increased from 429 to 633 mg/L, which shows that the mineralization of dye has taken place. The permissible limit, according to ICMR, 1963, is 400 mg/L. The consumption of drinking water containing high amounts of magnesium or sodium sulphate may result in intestinal discomfort, diarrhea and consequently, dehydration. This laxative effect is often observed, when someone drinks water that containing sulphate greater than 500 mg/L.

Effect on nitrate

Nitrate occurs naturally in the soil. Nitrogen is essential to life. Most crop plants require large quantities of nitrogen to sustain high yields. Photocatalytic treatment was also found to be effective in reducing the nitrates.[18] In treated water, nitrate was decreased from 459 to 390 mg/L. The maximum permissible limit of nitrate is 50 mg/L (ICMR). High nitrate levels in water can cause methemoglobinemia or blue baby syndrome, headache, dizziness, weakness and difficulty in breathing. Nitrate forms nitrosamine in stomach, which causes gastric cancer.[19] Proper management of fertilizers, manures, and other nitrogen sources can minimize contamination of drinking water supplies.

Effect on TDS

"Dissolved solids" refer to any mineral, salts, metals, cations or anions dissolved in water. This includes anything present in water other than the pure water molecules and suspended solids. TDS is expressed in units of mg per unit volume of water (mg/L) and also referred as parts per million (ppm). TDS is directly related to the purity of water and the quality of water. The maximum permissible limit of TDS is 1500 mg/L (ICMR). High TDS results in undesirable taste, which could be salty, bitter, or metallic. It could also cause gastrointestinal irritation.[20] 2660 mg/L TDS was found in canal water, which further increased in polluted water and treated water to 2720 mg/L and 2820 mg/L due to particles of dye and semiconductors.

Effect on conductivity

Conductivity is a measurement of the ability of an aqueous solution to carry an electrical current. Conductivity is a measure of the purity of water or the concentration of ionized chemicals in water. However, conductivity is only a quantitative measurement. It responds to all ionic contents and cannot distinguish particular conductive materials in the presence of others. Only ionizable materials will contribute to conductivity. Conductivity was found to be increased in treated water. Slight decrease in pH and increase in conductivity also confirms the mineralization of dye into CO_2 and inorganic ions.[21]

CONCLUSION

Photocatalytic treatment increased the biodegradability of dye containing polluted water. It helps to reduce pH, alkalinity, hardness, calcium, nitrate and COD. It also increases the BOD, conductivity, TDS, turbidity and sulphate. Increases BOD shows the reduction in toxicity. Higher conductivity is a result of ion formation after degradation of pollutants. Sulphate formation occurred because of degradation of dye. TDS and turbidity increased after photocatalytic treatment due to addition of ZnO, which can be further separated by coagulation- flocculation and.[22]

Thus, the potocatalytic treatment will provide us with a more effective method for recycling textile dye house wastewater. Dye containing coloured water is of almost no use, but after treatment, this water can be used for washing, cooling, irrigation and cleaning purposes. The photocatalytic bleaching seems to be quite promising technique and it can provide a low cost method to solve pollution problems of water and for treatment of waster water from printing, textile and dyeing industries.[23]

ACKNOWLEDGEMENT

The authors wish to thank Head, Department of Chemistry, M. L. Sukhadia Unversity, Udaipur and M. S. J. College, Bharatpur, for providing laboratory facilities.

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Revised : 24.02.2011 *Accepted : 26.02.2011*