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A COMPARATIVE PHYSICO-CHEMICAL ANALYSIS OF JANUS GREEN B CONTAMINATED WATER AND TREATED WATER BY AMMONIUM PHOSPHOMOLYBDATE

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ABSTRACT

Present study is focused on comparative assessment of physico-chemical quality parameters of Janus Green B contaminated water and photocatalytically degraded water using ammonium phosphomolybdate semiconductor under constant conditions. In this study, we used pond water collected from Keoladev National Park, Bharatpur as reference water. Janus Green B is a basic azodye extensively used in Histology. Various quality parameters such as pH, Alkalinity, Hardness, COD, BOD, DO, Conductivity, Salinity, TDS, Concentration of Ca^{2+}, Mg^{2+}, Cl^-, F^-, NO_3^-, SO_4^{2-} and Turbidity were criteria of comparison.

Key words: Janus Green B, Ammonium phosphomolybdate (APM), Quality parameter.

INTRODUCTION

Water pollution is a major global problem. Contamination of water bodies by point and non point sources has become the leading cause of deaths and diseases world wide. Water is said to be polluted when it is unable to support a human use or constituent biotic communities. Contamination of surface water is more severe in Rajasthan due to low rain fall and scarce water sources. Water bodies are the life line of flora and fauna of Keoladev National Park, Bharatpur (KNP). Hence appropriate monitoring of lakes of this world heritage is immensely needed. WHO, CPCB, IS have declared safelimits of water for drinking, irrigation and wild life[1,2].

Several attempts have been made for treatment of polluted water using adsorption, coagulation, sedimentation, filtration, membrane technology, chlorination and semiconductor

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mediated photocatalytical degradation (PCD). Photocatalytical degradation is a preferred option for treatment of polluted water.

A lot of studies are reported on semiconductor mediated PCD of different dyes under different values of pH, amount of particular semiconductor, dye concentration and hence optimum condition chosen for optimum photo degradation. TiO_2 has been extensively used as semiconductor for many dyes in suspended, colloidal form[3], nanopartical[4-5], aqueous form[6], adsorbed[7], supported and powdered form.[8] Except TiO_2, many semiconductors such as ZnO[9-13], Fe_2O_3[14-15], MnO_2[16-17], CdS[18-19], WO_3[9], NiO and CuO[20] etc. have been studied for PCD of many systems. Ammonium phosphomolybdate (APM) has been reported as catalyst by Bansal et al.[21] on Rhodamine 6-G, Sachdeva et al.[22,23] on fast green and Azure B, Sharma et al.[24-25] on Erichrome Black T and Safrinine O. It is good semiconductor for PCD due to its optical properties, high refractive index, chemical stability, low cost, ready availability, greater efficiency, selectivity and convenient way of treating several undesirable chemicals. Sharma et al.[26] investigated photocatalytical activity of APM for PCD of Janus Green B.

Janus Green B is a basic azo and cationic dye. Its molecular formula is $C_{30}H_{31}ClN_6$ and molar mass is 511.06 g/mol. It acts as an indicator and changes colour according to the amount of oxygen present. If oxygen is present, the indicator is oxidised to blue colour and if oxygen is absent the indicator is reduced to pink colour.

A comparative study of photocatalytic activity of different semiconductors on same dye[13,20] or comparison of different dyes PCD using same catalyst[14,16] has been oftenly performed. But there is negligible attention paid towards modification in water quality after treatment. PCD of dyes can generate even more toxic intermediates and adverse effects on water quality. Bharadwaj et al.[27] analyzed bioassay and comparative study of quality parameters of untreated (Giemsa dye containing water) and treated water by TiO_2.

The focus of present study is to analyze the changes taking place in quality parameters of polluted water and photocatalytically treated water. Janus Green B containing water is degraded under sunlight by APM under constant condition. Comparison of quality parameters of pond water, polluted water (dye containing water) and treated water based on certain parameter like pH, Alkalinity, Hardness, COD, BOD, DO, Conductivity, Salinity, TDS, Concentration of Ca^{2+}, Mg^{2+}, Cl^-, F^-, NO_3^-, SO_4^{2-} and Turbidity were made.

Pond water was collected from Keoladev National Park, Bharatpur in Rajasthan.

EXPERIMENTAL

Chemicals

Janus Green-B from Loba chemia, Ammonium phosphomolybdate (APM) from Himedia, Sodium Fluoride, Zirconium Nitrate, Sodium Arsenite, Sodium Azide, Sodium Iodide, Hypo ($Na_2S_2O_3$), Erichrome Black-T and Methyl Orange were purchased from Qualigens. Murexide, Ferrous Ammonium Sulphate from Fisher Scientific. $AgNO_3$, AgCl, Silver Sulphate, Mercuric Sulphate, EDTA, $K_2Cr_2O_7$, Magnesium Sulphate, HCl, NaOH were purchased from CDH.

Apparatus

Spectrophotometer 106 (Systronics), Water Analyzer 371, Digital pH Meter 335, PC Based Double Beam Spectrophotometer 2202 and Citizen Balance.

Method

Water samples were collected from the ponds of KNP. The entire physico-chemical quality parameters of this water sample were taken for comparative reference.

A 100 mL stock solution (1 x 10^{-3} M) of Janus Green B dye was prepared in KNP water samples. 8.4 mL of this stock solution was diluted to 1000 mL using water samples to prepare 8.4 x 10^{-6} M dye solution which is considered as polluted water. This water was further divided into two equal parts. Dye solution 8.4 x 10^{-6} m was safely placed in borax glass beaker and exposed to sunlight for 4 hrs with 2 g APM at 10.5 pH in control condition for optimum PCD. After 4 hrs this treated water was centrifuged to sediment the APM using a G-3 sintered glass crucible. The remaining solution was considered as treated water.

Photocatalytically treated and untreated water samples were analyzed for pH using Digital pH Meter 335. Turbidity, TDS, Conductivity, Salinity were estimated using Water Analyzer 371. Alkalinity, Hardness, Concentration of Ca^{+2}, Mg^{+2}, F^-, Cl^-, NO_3^-, SO_4^{-2}, DO, BOD, COD were estimated as per method assessment of water, sewage and industrial effluents[28].

RESULTS AND DISCUSSION

For maximum photocatalytic degradation, all optimum conditions like pH, amount of semiconductor, concentration of dye solution were used according to Sharma et al.[26] In presence of sunlight and semiconductor, Ammonium phosphomolybdate photocatalytic treatment affected the quality parameters.

The results obtained are recorded in Table 1.

Table 1: Comparative analysis of quality parameters

Parameter	KNP Water	Polluted water	Treated water	IS
pH	7.81	7.83	6.5	6.5-8.5
Alkalinity (mg/L)	72	68	112	200
Hardness (mg/L)	370	250	270	100
Calcium (mg/L)	170	150	140	75-200
Magnesium (mg/L)	200	100	130	30-100
Chloride (mg/L)	310	329	290	250
Fluoride (mg/L)	1.2	1.2	1.2	1-1.5
Sulphate (mg/L)	45.6	67.8	138.9	200
Nitrate (mg/L)	2.215	3.326	13.29	45
DO (ppm)	6.4	6.0	4	5
BOD (ppm)	4.4	1.8	1.8	6
COD (ppm)	12.8	23.04	8.96	10
Conductivity (μS/cm)	9.04×10^2	8.39×10^2	12.9×10^2	1000
TDS (ppm)	445	492	750	500-2000
Turbidity (NTU)	1.4	3.8	1.83	5
Salinity (ppm)	530	500	760	-

Effect on pH

The pH of pond water is affected by its age and the chemicals discharged by communities and industries. In earlier stage all lakes and ponds are alkaline in nature and become more acidic with time due to build up organic material whose decay is the cause of formation of weak carbonic acid. According to Swingle[29], pH between 6.5-2.5 is required for fishery and drinking. pH of KNP water and dye contaminated water was found almost similar i.e, 7.81 and 7.83, respectively. For photocatalytic treatment, pH of polluted water set at 10.5 with APM. After the treatment, pH reduced to 6.5. This result shows that pH values of KNP water and dye contaminated water is in alkaline range, whereas pH of treated water is in acidic range but all three samples are in the standard range of drinking water.

Effect on alkalinity

The alkalinity of natural and treated water is normally due to the presence of bicarbonate, carbonate and hydroxide compounds of Ca, Mg, Na and K. It also includes borate, phosphate and silicate. In coloured water, anions also increase alkalinity. The determination of alkalinity provides an idea of salts present. In this study alkalinity decreased from 72 mg/L to 68 mg/L for polluted water. It shows that Ca^{2+} and Mg^{2+} ions precipitated with certains dye content. After photocatalytic treatment of samples, it increased to 112 mg/L, indicating that some ionic reaction might have taken place in treatment.

Effect on hardness

Hardness in water is due to the natural accumulation of salts from contact with soil and geological formation of it may occur from direct pollution by industrial effluents. Permanent hardness of water is due to salts of Calcium and Magnesium sulphate. Hardness of Janus Green B contaminated water reduced from 370 mg/L to 250 mg/L, which was slightly higher (270 mg/L) in treated water. All these values are in the limit of IS 1992, which is 300 mg/L extended upto 600 mg/L.

Effect on calcium

Calcium is an important parameter of water hardness. It is essential for normal plant growth, however its excess amount is undesirable for washing and bathing. In KNP pond water, calcium was noted to be 170 mg/L, which was reduced in polluted water and treated water to 150 mg/L and 140 mg/L, respectively.

Effect on magnesium

Magnesium is desirable nutrient for human, however high concentration causes unpleasant taste to water. Dye particles reacted with Mg^{+2} ions, hence Mg concentration reduced in polluted water from 200 mg/L to 100 mg/L. After photocatalytic treatment it raised to 130 mg/L. Mg was found to be slightly higher than permissible limit of IS 1992 in all three water samples.

Effect on chloride

If daily water consumption is 2 Liters and then average daily intake of chloride from drinking water would be approximately 20 mg per person[30]. The sample water is not so much alkaline and hence, chloride was found in limits. Chloride was noted to be 310 mg/L, which increased to 329 mg/L in polluted water, due to the presence of chlorine in dye. In treated water itreduced to 290 mg/L.

Effect on sulphate

Sulphates are discharged into water from mines, smelters and from craft pulp, paper mills, textile mills and tanneries. Sodium, Potassium and Magnesium sulphates are highly soluble in water whereas Calcium and Barium sulphates are less soluble. High amount of sulphate imparts a bitter taste to water. Magnesium sulphate causes laxative effects to children particularly in hot climate like Rajasthan.Sulphate concentration in reference water was found 45.6 mg/L, which increased in dye contaminated water to 67.8 mg/L. After PCD it again raised to 138.9 mg/L. Hardness value is greater than alkalinity, this supports high value of sulphate in treated water. But all these water samples were in the desired limit (WHO).

Effect on nitrate

Elemental nitrogen is present as nitrate in soil naturally through Nitrogen cycle. In aquatic environment it reaches by fertilized farm soil, animal wastes, washing and industrial effluent. Nitrates stimulate growth of planktons and water weeds which is food for fish, hence fish population may increase. However excess weed growth is the cause of death of aquatic animals due to lack of O_2. In KNP water concentration of NO_3^- is 2.215 mg/L, which raised in polluted water to 3.3225 mg/L. After treatment it increased to 13.29 mg/L. But all three water samples were in the range of IS 1992. Since NO_3^- concentration is high in treated water but in the desired range, so it is more useful for aquatic biota and irrigation.

Effect on DO

DO analysis measures the amount of gaseous oxygen dissolved in an aqueous solution. It is an index of physical and biological activity occurring in water. The minimum standard value of DO is 5 ppm[31]. Generally high level of DO indicates better quality of water. In present finding, DO value of KNP water was found to be 6.4 ppm. A depletion in DO after treatment to 4 ppmwas due to the time consumed in the treatment.

Effect on BOD

BOD values show the amount of oxidizable organic matter present[32]. Higher the value of BOD, greater the aerobic biological organisms in water to break down organic material by use of DO. BOD of KNP sample was reduced in polluted water to 1.8 ppm due to prevention of biological activity by dye particle. Photo catalytic treatment had no effect on BOD. This may be because of rise in temperature and different chemical processes.

Effect on COD

COD is the amount of O_2 (mg/L or ppm) consumed under specific condition in the oxidation of organic and oxidisable inorganic matter.[33] It is the main determinant used to assess organic pollution in aqueous system and is one of the most important parameters in water monitoring.COD values were increased from KNP water to polluted water. After treatment COD value fell to8.96 mg/L, which showed that content of oxidisable organic matter decreased. COD values of KNP waterwere reported at 12.8 ppm which raised in polluted water to 23.04 ppm. After treatment it reduced to 8.96 ppm which is in desired limit of COD according to WHO guidelines. Reference water and polluted water samples were in the range of COD hazards, whereas treated water were safe to use.

Effect on conductivity

Conductivity is a measure of level of ion concentration of a solution. It is an index of the salt load in wastewater or the purity of potable water[34], However it is only a quantitative measurement. It responds to all ionic contents and cannot distinguish particular conductive materials in the presence of others. It is an important quality parameter due to estimation of dissolved solid which may affect the taste of water and suitability for various uses. Conductivity was found to be slightly reduced in polluted water from 9.04 x 10^2 µS/cm to 8.39 x 10^2 µS/cm. PCD increased it to 12.9 x 10^2 µS/cm in treated water. Slightly decrease in pH and rise in conductivity confirms the mineralization of dye contaminated water samples into CO_2 and inorganic ions[35].

Effect on TDS

Total dissolved solid is the weight of all solid that are dissolved in a given volume of water. TDS is expressed in unit of mg/L or parts per million (ppm). WHO standard permissible limit is 500 mg/L. High TDS results in an undesirable taste which could be salty, bitter or metallic. It also causes gastrointestinal irritation[36]. TDS of KNP water was 445 mg/L, which further increased in dye contaminated water and treated water to 492 mg/L and 750 mg/L, respectively, this may be due to particles of dye and semiconductor.

Effect on turbidity

Turbidity is a measure of the degree to which the water loses its transparency due to the presence of suspended particles. Turbidity was reported at 1.4 NTU which increased in polluted water to 3.8 NTU due to presence of dye molecule. After PCD it dropped to 1.83 NTU, which showed that water regained its transparency.

CONCLUSION

Photocatalytic treatment was found effective to reduce many quality parameters like pH, Calcium, Chloride, COD, Turbidity and DO. However some parameters like Alkalinity, Hardness, Magnesium, Nitrate, Sulphate, Conductivity and TDS increased showing that dye molecules were completely mineralized along with colour removal. Conductivity, salinity and TDS values indicate that treated water is more useful for irrigation than wild life and fisheries according to CPCB standards (IS: 2296-1982). But DO, nitrate, pH, COD, turbidity together support itsuse for irrigation as well as for wild life and aquatic biota. Most of the quality parameters of treated water are in the range of WHO and BIS desired limit for drinking water, irrigation and wild life.

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