Material Science Research India Vol. **7**(1), 167-172 (2010)

Effect of slurry from stone cutting industry in the treatment of dye wastewater

SARU GUPTA, P.S. VERMA and P.P. BAKRE*

Department of Chemistry, IGC For HEEPS*, University of Rajasthan, Jaipur (India).

(Received: December 01, 2009; Accepted: January 03, 2010)

ABSTRACT

The effectiveness of the use of slurry generated in stone cutting industry in the electrochemical treatment and reuse of the dye wastewater collected from various dyeing units of Sanganer area was studied using stainless steel electrodes and current density of 3mA/cm^2. It was observed to have a high pH, TDS, TSS, BOD, COD and high concentration of heavy metals. A substantial reduction in TDS, BOD, COD and heavy metals in the treated wastewater as compared to the original dye wastewater sample was observed. The efficacy of the treatment was tested by observing the survival rate of *Gambusia affinis* in the treated wastewater.

Key words: Slurry, electrochemical treatment, parameters, dye wastewater, *Gambusia affinis.*

INTRODUCTION

The textile industry which not only caters to the needs of the common people but also adds to the economy of the country, has recently acquired attention of the environmentalists due to the water consumption and wastewater generation. The wastewater discharged is characterized by a high pH, TDS, BOD, COD and heavy metals. The wastewater is discharged into the nearby water bodies which leads to various diseases in aquatic species and other organisms coming in contact. The water of these water bodies is used for irrigating the nearby fields as a result of which the hazardous components are also introduced at various trophic levels through the food chain. Thus, the discharged dye wastewater seriously endangers the environment. The heavy metals, typically, Fe, Cu, Zn, Cr etc., even at low concentrations are very harmful to human and aquatic life. The use of premetalised dyes and heavy metal afterwashes, which are used to increase the light fastness of the finished product, leads to the introduction of heavy metals in the wastewater generated in textile industry.

Rajasthan is famous for its marble deposits. There are around 4000 marble mines and about 1100 marble cutters in medium sector spread over the 16 districts of Rajasthan. Marble slurry is generated as a by-product during cutting of marble. The waste is approximately in the range of 20% of the total marble handled. The amount of marble slurry generated in Rajasthan every year is very substantial being in the range of 5-6 million tonnes.

While marble blocks are cut by gang saws, water is used as a coolant. The blade thickness of the saws is about 5 mm and normally the blocks are cut in 20mm thick sheets. Therefore, out of every 25mm thickness of marble block, 5mm are converted into powder while cutting. This powder flows along with the water as marble slurry. Thus, nearly 20 % of the total weight of the marble processed results into marble slurry. The marble slurry has nearly 35%-45% water content. The total waste generation from mining to finished product is about 50 % of mineral mined.

The marble cutting industries are dumping the marble slurry in any nearby pit or vacant spaces, near their unit, although notified areas have been marked for dumping. This leads to serious environmental and dust pollution and occupation of vast area of land especially after the slurry dries up. This also contaminates the underground water reserves. When dumped on land, it adversely affects the productivity of land due to decreased porosity, water absorption, water percolation etc. Slurry dumped areas can not support any vegetation and remain degraded. When dried, the fine particles become air borne and cause severe air pollution. Apart from occupational health problems, it also affects machinery and instruments installed in industrial areas. During rainy season, the slurry is carried away to rivers, drains, roads, and water bodies affecting quality of water, reducing storage capacities and damaging aquatic life. Due to long term deposition on land the finer particles block flow regime of aquifers thus seriously affecting underground water availability. The heaps of slurry remain scattered all round the industrial estate are an eye sore and spoil aesthetics of entire region. Subsequently tourism and industrial potential of the state is adversely affected.

Khan *et. al* (1995) have studied the effects of industrial effluents on physico-chemical characteristics of the Amanishah Nallah, near Sanganer. Nanda *et. al* (2000) exposed the air breathing fish to paper mill effluent to study the toxicity level. The 96 hr LC30 values was found to be 6.09%, 80.35%, and 81.28% in *Anabas testudineus*, *Channa punctatus* and *Clarius batrachus* respectively. Singh (2000) studied the cytotoxic effect of synthetic blue dye used by green grocer for colouring the green vegetables to make them more green and attractive. The blue dye decreased the percentage of seed germination, seedling growth and survival of seedlings with the increase in concentration and duration of treatment in *Vicia fobia L*. It also showed catatonic effect on mitotic division. The effect of trivalent and hexavalent Chromium was investigated on carbohydrate metabolism of a freshwater field crab *Barytelphusa guerini* (Sridevi and Reddy, 2000). In a sublethal long term exposure of 30-60 and 90 days, the depletion of glycogen and glucose levels reflected in the activity of glycogenphosphorylases ‘a’ and ‘ab’. The magnitude of responses were found more in the hexavalent form than in the trivalent form.

The removal of dyes in an economic fashion still remains an important problem and a number of studies have been done for the same. Panizza and Cerisola (2004) have studied the electrochemical oxidation of synthetic tannery wastewater using Ti/PbO_2 and Ti/RuO_2 as anodes under different experimental conditions.

Chen *et. al* (2005) have studied the reduction in TSS, COD and turbidity using electrochemical oxidation and membrane filtration. Ghalwa and Latif (2005) investigated the electrochemical degradation of Acid Green dye in aqueous wastewater dyestuff solutions using a lead oxide coated Ti electrode. The optimum operating conditions for the dye and modified electrode were determined, where good results for complete removal of the dye and COD were achieved. Panizza *et. al* (2005) considered electrochemical oxidation as an effective method for colour removal; there was little or no consumption of chemicals, no sludge production and degradation of recalcitrant pollutants could be achieved, including polyaromatic organic compounds like anthraquinone based compounds.

Vaghela *et. al* (2005) have studied the reduction in COD and removal of color by the electrochemical treatment of azo dye effluent.

Asilian, H. *et. al* (2006) removed acrylic water base colour from synthetic wastewater using coagulation with $FeSO_4$, alum, lime and polyelectrolyte. The obtained results showed that treatment with alum and $FeSO_4$ alone prove to be very effective in removing colour (>99%) and part of COD (60-70%) from aqueous solution. Fongstatikul *et. al* (2006) explored the effectiveness of an electrochemical process to treat a sulphur dye wastewater using fine steel electrode plates. Results indicated that COD, TSS removal efficiency improved with a decrease in initial pH and increase in electrical charge.

In the present investigations, various parameters like TDS, TSS, BOD, COD, and concentration of some heavy metals have been determined in the dye effluent and then the electrochemical treatment of the dye effluent is performed using suitable electrodes and current conditions in the presence of slurry generated from stone cutting.

The present study is focused on the optimization of the electrochemical decolourisation and detoxification of the textile effluents containing reactive dyes with the aim of making this method feasible –technically and economically, at industrial scale.

MATERIAL AND METHODS

The dye wastewater samples were collected from various dyeing industries nearby Jaipur. The samples were analysed for various parameters like pH, TDS, BOD (27^{0}C, 3d), COD, and heavy metals. AAS technique was employed for the determination of concentration of heavy metals. The same samples were now treated electrochemically. Rectangular plates of stainless steel (SS316) were used as cathode as well as anode. Electrodes of area 4cm X 2.5 cm were immersed in the dye effluent and the electrodes were separated by a distance of 3-4 cm respectively. A Remi (2LH model) hot plate cum magnetic stirrer was used throughout the electrolysis process. A glass beaker of 1000ml capacity was used as electrolysis vessel. Electrolysis was carried out for 45 minutes. The current density was 3mA/cm^2 throughout the electrolysis and 2gm NaCl was added to the one litre of the wastewater effluent. The electrolytic solution was stirred with the help of magnetic stirrer. The dye begins to precipitate and forms a loose sludge which is initially formed at the top of the mother liquor and eventually settles down at the bottom of the reaction vessel. After electrolysis the experimental electrolytic solution is filtered. The filtrate obtained was colorless and was tested for TDS, TSS, pH, BOD (27^{0}C, 3d), COD, and concentration of heavy metals.

In the second phase of the study, 250 ml slurry generated from stone cutting industry was added to one litre of dye wastewater effluent and electrochemical treatment was done using stainless steel 316 electrodes at a current density of 3mA/cm^2. Electrolysis was carried for 45 minutes. A Remi (2LH model) hot plate cum magnetic stirrer was used throughout the electrolysis process. After electrolysis the experimental electrolytic solution is filtered. The various parameters like pH, TDS, TSS, BOD, COD and heavy metal concentration were analysed again for the filtrate.

In the third phase of the study, ten *Gambusia affinis* were introduced in the dye wastewater effluent, electrochemically treated sample and stone slurry treated sample .These water samples were 100%, 75%, 50%, 25% concentrated samples .

RESULTS AND DISCUSSION

The various parameters were analysed for the dye wastewater (OS), electrochemically treated wastewater (ET) and stone slurry treated sample (ST). The results are listed in table 1.

The results show that the highly alkaline conditions of the OS have reduced and the pH of ET became 6.69, which is within the safe limits for ground waters. The TDS, TSS have reduced to a very large extent in ET by 98.4% and 99.56% respectively as compared to OS. BOD and COD have also reduced drastically to 0.65 mg/l and 32mg/l respectively in ET from 296 mg/l and 150 mg/l respectively in OS.

Analysis by AAS for heavy metals shows that Cu has decreased by 26.96% after electrochemical treatment. Fe and Zn are found to be totally removed from ET sample. The dark brown colour of OS was rendered colourless in ET.

The results show that the highly alkaline conditions of the OS have reduced and the pH of ST sample became 7.89, which is within the safe limits for ground waters. The TDS, TSS have reduced to a very large extent in ST sample. BOD and COD have also reduced drastically to 20 mg/l and 10mg/l respectively from 296 mg/l and 150 mg/l respectively in OS.

Analysis by AAS for heavy metals shows that Cu has decreased from 0.089ppm in OS to 0.015ppm in ST. Fe and Zn are found to be totally removed from ST. The dark brown colour of OS was rendered colourless in ST.

The ST sample when compared with ET sample shows that the conditions of pH are better in ST. The TDS, TSS show a decrease in ST. The BOD has shown an increase in ST but the increase is well within the safe limits. COD has shown a decrease in ST to 10mg/l from 32mg/l in ET. Cu has shown a further decrease in ST. Fe and Zn is totally absent in both the samples. Both ET and ST are colourless.

Table 1.

S. No.	Parameters	OS	ET	ST
1	pH	10.46	6.69	7.89
2	TDS(g/l)	5.216	0.0834	0.0765
3	TSS(g/l)	3.234	0.014	0.003
4	BOD(mg/l)	296	0.65	20
5	COD(mg/l)	150	32	10
6	Cu(ppm)	0.089	0.024	0.015
7	Fe(ppm)	0.6751	Nil	Nil
8	Zn(ppm)	3.614	Nil	Nil
9	Colour	Dark Brown	colourless	colourless

Area : Beyond Sanganer; OS: Dye wastewater sample
ET: Electrochemically treated sample of Dye Effluent; ST: Stone Slurry Treated Sample

Table 2.

%Concentrated Sample	Time (hrs.)	No. of *G. affinis* survived		
		OS	ET	ST
100	24	0	10	10
	48	0	10	10
	72	0	10	10
	96	0	10	10
75	24	0	10	10
	48	0	10	10
	72	0	10	10
	96	0	10	10
50	24	0	10	10
	48	0	10	10
	72	0	10	10
	96	0	10	10
25	24	3	10	10
	48	1	10	10
	72	0	10	10
	96	0	10	10

OS: Original sample of dye effluent
ET: Electrochemically treated sample of dye effluent
ST: Stone Slurry Treated Sample

In the third phase of the study, 10 *Gambusia affinis* were introduced in the OS, ET and ST, which each time were 100%, 75%, 50%, 25% concentrated samples. The results are reported in Table 2.

It was observed that no fish could survive for more than 1.5 hours in 100%, 75%, 50% concentrated OS samples. However 30% of the fish survived for 24 hours in 25% OS concentrated sample and 10% of the fish only could survive for the next 24 hours. No fish was observed to survive after 48 hrs.

In the electrochemically treated effluent, 100% fish could survive in all concentrations of the sample. So, the effectiveness of the electrochemically treated sample can be well established.

To test the efficacy of water treated using slurry from stone industry, ten *G. affinis* were introduced in the ST sample.It was observed that all the animals survived for 96 hours and beyond in all concentrations of the sample ST.

CONCLUSION

The electrochemically treated sample showed a decrease in pH, TDS, BOD, COD, heavy metal concentration. The dark brown coloured sample was rendered colourless. Thus, the electrochemically treated water is better than the effluent sample. Further the treatment with the slurry of stone cutting industry also showed a further decrease in TDS, TSS, COD, and Cu as compared to the electrochemically treated dye wastewater sample. Fe and Zn are totally removed after the electrochemical treatment. The survival rate of *Gambusia affinis* was found to be 100% at all concentrations in the stone slurry treated dye wastewater sample. This clearly establishes the role of stone slurry in the treatment of dye wastewater.

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