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Removal of COD and Color from Dye Waste Water using Combined processes Coagulation, Activated Sludge and Adsorption process

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Abstract

This technical note summarizes the results of Reactive Blue (H3RP) dye wastewater of treatment process aiming at the destruction of the wastewater's color by means of coagulation technique using ferrous sulfate and lime, Biological Treatment using Activated Sludge Process and Adsorption technique using Activated Carbon. All the experiments were run in a pilot plant. Treatment with lime and ferrous sulfate proved to be very effective in removing the color (70–90%) and part of the COD (35–40%); Activated Sludge process removing the color (10-20%) and part of the COD (25-30%) and Activated carbon removing the color (5-10%) part of the COD (15-20%) from the dye wastewater. Moreover, the results showed these combined processes are capable of achieving high COD removal.

Keywords- *dye wastewater; coagulation; lime; ferrous; activated sludge process; Reactive Blue; Adsorption; activated carbon; industrial wastewater; COD; Color.*

I. INTRODUCTION

Water, pre-requisite for life and key resource of humanity is in abundance on earth. The total water that exists on the Earth surface is present as a water of oceans, lakes, rivers and glaciers. The small cube corresponds roughly to 9000 km3 of drinkable water per year. It is estimated that: 1.2 billion people (a quarter of the world population) have no direct access to drinking water.1.4 billion people are without effective evacuation of waste water. More than 80 countries (> 40% of the world population) lacking tap water. (Aitali M.K, 2002)

Dyes have long been used in dyeing, paper and pulp, textiles, plastics, leather, cosmetics and food industries. Colour stuff discharged from these industries poses certain hazards and environmental problems. These coloured compounds are not only aesthetically displeasing but also inhibiting sunlight penetration into the stream and affecting aquatic ecosystem. Dyes usually have complex aromatic molecular structures which make them more stable and difficult to biodegrade. Furthermore, many dyes are toxic to some microorganisms and may cause direct destruction or inhibition of their catalytic capabilities.

Textile industry use dyes and pigments to colour their product. There are more than 100,000 commercially available dyes with over 7×105 tonnes of dyestuff are produced annually. Many types of dye are used in textile industries such as direct, reactive, acid and basic dyes. Most of these dyes represent acute problems to the ecological system as they considered toxic and have carcinogenic properties, which make the water inhibitory to aquatic life .Due to their chemical structure, dyes possess a high potential to resist fading on exposure to light and water. The main sources of wastewater generated by the textile industry originate from the washing and bleaching of natural fibers and from the dyeing and finishing steps. Given the great variety of fibers, dyes and process aids, these processes generate wastewater of great chemical complexity and diversity, which are not adequately treated in conventional wastewater treatment Plant.

Numerous studies have been conducted to assess the harm impacts of colorants on the ecosystem. It was found that colorants may cause problems in water in several ways: (i) dyes can have acute and/or chronic effects on exposed organisms with this depending on the dye concentration and on the exposure time; (ii) dyes are inherently highly visible, minor release of effluent may cause abnormal coloration of surface waters which captures the attention of both the public and the authorities; (iii) the ability of dyes to absorb/reflect sunlight entering the water, this has drastic effects on the growth of bacteria and upsets their biological activity; (iv) dyes have many different and complicated molecular structures and therefore, are difficult to treat and interfere with municipal waste treatment operations; (v) dyes in wastewater undergo chemical and biological changes, consume dissolved oxygen from the stream and destroy aquatic life; (vi) dyes have a tendency to sequester metal ions producing micro toxicity to fish and other organisms. (Bibek Dash, 2010)

The need for high quality drinking water is one of the most challenging problems of our times, but still only little knowledge exists on the impact of these compounds on ecosystems, animals and man. Reliable access to clean and affordable water is considered one of the most basic humanitarian goals, and remains a major global challenge for the 21st century. Worldwide, some 780 million people still lack access to improved drinking water sources. (WHO, 2012)

Dye manufacturing industry

Dye manufacturing Industry mainly covers the following process operations for manufacturing of product.

Manufacturing process generally adopted involves conversion of simple organic products like benzene, xylene, naphthalene, anthracene *etc.* into a vast number of complex chemical intermediate and dye through several steps of operation like

1. Chemical conversion
2. Sulphonation
3. Neutralization
4. Fusion
5. Chlorination
6. Nitration
7. Reduction
8. Amination
9. Acetylation
10. Hydrolysis
11. Corboxylation, etc.

Each process requires different operations like charging, reflux, distillation, filtration, washing, drying, and grinding, *etc.* in the manufacture of dyes. The process requires large number of chemical compounds but often in limited quantity. The raw material is fed into the reactor where reactions are carried out ordinarily at atmospheric pressure. Usually the reactions are exothermic for which adequate temperature control is maintained to avoid side reactions. Generally, batch process is followed for production of dyes. Temperature control is accomplished primarily by addition of ice to the reaction tank. When the reaction is complete, dye particles settle out from the mixture. The liquid from reactor is then sent to a plate and frame filter press where the dye particles are separated from the mother liquor, which is discharged as wastewater. The filter cake is first washed with compressed air while still in the process. The moist cake is discharged into shallow trays, which are placed in circulating dryer. The moisture is removed in temperature between 50 and 120oC. The dried dye is ground and mixed with diluents such as salt to improve the colour and strength as shown in Fig.1

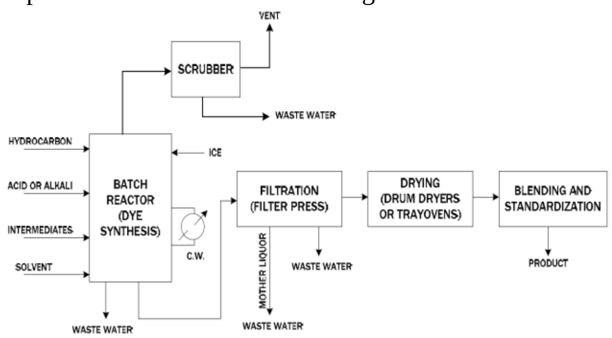


Figure 1: Dye Manufacturing Process

The process of wastewater is mainly the mother liquor left over after the product is isolated and separated by filter press. This wastewater is of smaller volume and highly concentrated in terms of pollutants. The vessel washings also contain similar type of pollutants but with lower concentration. It has been identified that the wastewater of the industries has the following characteristics: high levels of BOD and COD; high acidityhigh TDS; deep colour of different shades; high levels of chlorides and sulphates; presence of phenolic compounds; presence of heavy metals e.g., copper, cadmium, chromium, lead manganese, mercury, nickel and zinc; presence of oil and grease. (MoEF,2010)

Dye wastewater is generally characterized by high chemical oxygen demand (COD), biochemical oxygen demand (BOD), suspended solids (SS), conductivity and highly intense colours, which is very difficult to treat to a satisfactory degree (Koch et al. 2002). The discharge of strongly coloured wastewater from dyeing operations not only has adverse aesthetic effects, but such discharges can be carcinogenic, mutagenic and generally detrimental to our environment (Arslan et al. 2000; Papic´ et al. 2004). Among commercial textile dyes, disperse and reactive dyes are of significant environmental concern because of their widespread use in dyeing cotton and polyester (Kim et al. 2004). Nonionic disperse dyes have extremely low water solubility; therefore, this class of dyes can be removed effectively by the coagulation-flocculation method (Kuo 1992). Reactive dyes hydrolyze easily, resulting in high portions that are unfixed or are in a hydrolyzed form. Typically, around 20 to 40% of the initial dye load is wasted and present in the effluent, because of dye hydrolysis (Camp and Sturrock 1990; Armagan et al. 2003).

There are many processes available for wastewater treatment of dyes: chemical oxidation, foam flotation, electrolysis, biodegradation, adsorption, chemical coagulation and photocatalysis (McClung and Lemley, 1994; Lin and Lo, 1996; Bousher et al., 1997; Oakes and Gratton, 1998; Poulios and Aetopoulou, 1999; Papic et al., 2000; Lopez- Grimau and Gutierrez, 2006; Tahir and Rauf, 2006; Mohorcic et al., 2006; Chen and Zhu, 2006; Arami et al., 2006; Fu et al., 2007). A variety of physio-chemical methods have been studied for the removal of color from industrial effluents. These studies include the use of oxidizing agents (N. Ince and D. Gonenc, 1997), membrane filtration (Y. Xu and R. Lebrun, 1999; K. Majewska-Nowak, 1989), electro-chemical (Z. Ding, C. Min and W. Hui, 1987), and adsorption techniques (G. Annadurai, R. Juang and D. Lee, 2002). The advantages and disadvantages of each technique have been reviewed (T. Robinson, G. McMullan, R. Marchant and P.Nigam, 2001).

Coagulation-flocculation is a frequently used physico-chemical treatment method employed in textile wastewater treatment plants to decolourize textile effluent and reduce the total load of suspensions and organic pollutants. Complete decolourization of dye wastewater is possible using this process (Perkowski and Kos 2002; Papic´ et al. 2004). The main advantage of the coagulation-flocculation method is that the decolourization of the textile wastewater that can be achieved through removal of dye molecules from the dyebath effluents, and not by partial decomposition of dyes, which could produce potentially harmful and toxic aromatic compounds (Golob et al. 2005). The efficiency of the coagulation-flocculation method depends on the raw wastewater characteristics, pH and temperature of the solution, the type and dosage of coagulants, and the intensity and duration of mixing (Rossini et al. 1999; Radoiu et al. 2004). Many studies have investigated the treatment of effluents containing a single dye or a mixture of the same class of dyes, but the treatment of mixtures containing different classes of dyes has not been adequately addressed. The present study investigates the effectiveness of coagulation flocculation as a treatment method for a reactive dye waste water in terms of colour removal and COD reduction. The effects of solution pH and the type and dosage of coagulant on colour removal and COD reduction are studied.

Presently, wastewater from dye manufacturing industry is usually treated by combination process of biological treatment and coagulation treatment, before being fed to the biological treatment units, coagulation can reduce the wastewater loading and thus reduce the treatment cost. (YUAN Yu-li, WEN Yue-zhong, LI Xiao-ying, LUO Si-zhen, 2006).

Despite a wide range of wastewater treatment techniques available, there is no single process capable of adequate treatment for these effluents. Adsorption is an efficient method for the removal of dyes from wastewater and activated carbon is one of the most studied adsorptive materials (Walker GM, Weatherley LR. 2000.; Pelekani C, Snoeyink 2001.; Pereira MFR, Soares SF, Orfao JJM, Figueiredo JL., 2003; Singh KP, Mohan D, Sinha S, Tondon GS, Gosh D., 2003; Valdes H, Sanchez-Polo M, Rivera-Utrilla J, Zaror CA, 2002;). Biotreatment offers a cheaper and slants environmentally friendlier alternative for colour removal (Olukanni, O.D., A.A.Osuntoki and G.D. Gbenle, 2005). Bioremediation is a pollution control technology that uses biological systems transformation of various toxic chemicals to less harmful forms. This natural process, bioremediation, includes bioengineering the capabilities of intrinsic microorganisms, to clean up the environment is an effective alternative to conventional remediation methods (Vidali, M., 2009).

Wastewater sampling

The untreated waste water sample of Dye manufacturing industry was collect from the inlet of the effluent treatment plant of the industry located near Ahmedabad, Gujarat. The sampling bottle was cleaned and rinsed with distilled water, filled and seal air tightly. About 5.0 cm air space is left in the bottle to facilitate mixing by shaking. Sample was stored at 4 °C immediately after collection of the waste water.

Characterization of wastewater

PARAMETERS	RESULTS	TEST METHOD
pH	7.19	IS 3025(PART 11) 1983, (APHA 22nd Ed.,2012,4500-H^{+}B)
Colour	53333	APHA, 22nd Ed., 2012, 2120-C)
Biochemical oxygen Demand (3days,27 ^{0}C)	1578	IS 3025(PART 44) 1993
Chemical oxygen Demand (COD)	7117	IS 3025(PART 58) 2006, (APHA 22nd Ed.,2012,5220-B)
Total Dissolved Solids (TDS)	42227	IS 3025(PART 16) 1984, (APHA 22nd Ed.,2012,2540-C)
Total Suspended Solids (TSS)	886	IS 3025(PART 17) 1984, (APHA 22nd Ed.,2012,2540-D)

Table 1 Physical and chemical characteristic of wastewater

II. MATERIALS AND METHODS

Various methods and devices were used to both characterize and monitor the processes. Some of these methods and devices are briefly described here. The chemicals used in this study were manufactured by Merck Specialties Pvt. Ltd., Mumbai.Various devices were used like pH meter (Supplied by HANNA Instruments, Model-pH211 Microprocessor pH Meter), Beaker, COD apparatus and Magnetic Stirrer (Supplied by REMI-2L capacity).

Experimental Procedure

The procedure of Coagulation was as follows: the wastewater was put into beaker of 1.0L volume and then powdered Quick Lime (CaO) added and pH was adjusted at neutral by Ferrous Sulphate were added with continuous magnetic stirring. After 1hour reaction time, Add some polyelectrolyte and settle down the solids for 30minutes. the wastewater was neutralized pH-7. After sedimentation, the residual was removed.

Treated wastewater was further treated by Biological treatment (Activated Sludge process) for 1hr.

The treated waste water filtered by activated Carbon bed.

All experiments were carried out in batch mode. Several set of experiments were carried out to check the optimum range of results. All the Experiments were carried out in normal atmospheric temperature at 28°C.The Model was fabricated at Vikas engineering, Vatva, Ahmedabad. All the chemicals used for the measurement of parameters were obtained from MERCK.

III. EXPERIMENTAL SETUP

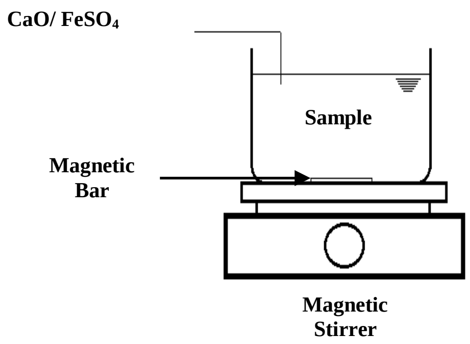
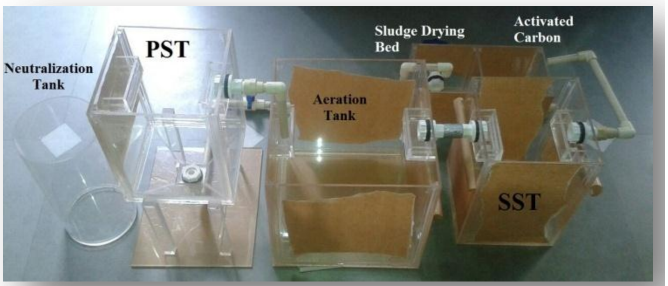


Figure 1 Experimental set-up



IV. RESULTS AND DISCUSSION

CHARACTERISTICS	VALUES Raw	VALUES Coagulation	VALUES ASP	VALUES AC
Chemical Oxygen Demand	7117 mg/l	2530 mg/l	1176 mg/l	712 mg/l
Colour	53333	15958	850	120

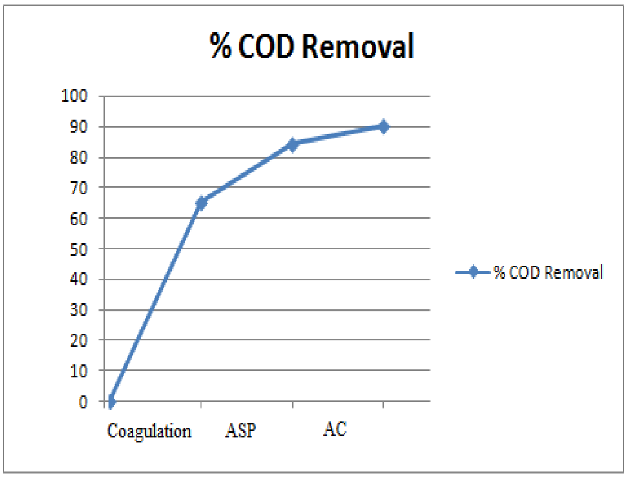


Figure 2 Effect of processes on COD Removal

II. CONCLUDING REMARKS

The Reactive Blue (H3RP) dye wastewater treatment process aiming at the destruction of the wastewater's color by means of combined processes of coagulation technique using ferrous sulfate and lime, Biological Treatment using Activated Sludge Process and Adsorption technique using Activated Carbon. Treatment with lime and ferrous sulfate proved to be very effective in removing the color (70–90%) and part of the COD (65–60%); Activated Sludge process removing the color (10-15%) and part of the COD (16-20%) and Activated carbon removing the color (5-10%) part of the COD (9-10%) from the dye wastewater. there was also significant reduction in colour. the colour removal on Pt-Co Scale. All the experiments were carried out according to APHA, Standard methods for the examination of water and wastewater, APHA, 22nd Ed., 2012.

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