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## A REVIEW ON EFFICACIOUS METHODS TO DECOLORIZE REACTIVE AZO DYE

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### Abstract:

This paper deals with the intensive review of reactive azo dye, Reactive Black 5. Various physicochemical methods namely photo catalysis, electrochemical, adsorption, hydrolysis and biological methods like microbial degradation, biosorption and bioaccumulation have been analyzed thoroughly along with the merits and demerits of each method. Among these various methods, biological treatment methods are found to be the best for decolorization of Reactive Black 5. With respect to dye biosorption, microbial biomass (bacteria, fungi, microalgae, etc), and outperformed macroscopic materials (seaweeds, crab shell, etc.) are used for decolorization process. The use of living organisms may not be an option for the continuous treatment of highly toxic organic/inorganic contaminants. Once the toxicant concentration becomes too high or the process operated for a long time, the amount of toxicant accumulated will reach saturation. Beyond this point, an organism's metabolism may be interrupted, resulting in death of the organism. This scenario is not existed in the case of dead biomass, which is flexible to environmental conditions and toxicant concentrations. Thus, owing to its favorable characteristics, biosorption has received much attention in recent years.

**Keywords:** Decolorization, Reactive Black 5, Azo dye, Biosorption, Bioaccumulation, Dead Biomass.

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## INTRODUCTION

Increasing population results in rapid industrialization and urbanization. Due to that, the world has been confronted with two major problems. One is depletion of fossil fuels and another one is polluting the environment. Manmade activities on water by domestic, agriculture, aquaculture, industrial, shipping, radioactive wastes; on air by industrial pollutants, mobile combustion, burning of fuels, ionization radiation, cosmic radiation, suspended particulate matter; and on land by domestic wastes, industrial waste, agricultural chemicals and fertilizers, acid rain, animal waste have negative influence over biotic and abiotic components of different natural eco-systems.

Though water, air and land are equally important, especially potable water is of great. Two third of the earth's surface is comprised of water. That too it is undeniably the most valuable natural resource existing on our planet. Industries are polluting the water resource is a common occurrence by emanating the effluents. Especially the potable water has become greatly polluted. Due to many instances, water lost its originality. The discharge of highly colored wastewater into the potable water sources, will convert soon this planet into a desert. Then, it is a serious environmental issue.

Dyes and dye pigments are the major sources for polluting the water resource. Dyeing process is a significant consumer of water and producer of huge contaminated aqueous waste streams (Barakat, 2010). In a textile industry, 200 to 500 L of water is needed to produce 1 kg of finished products (Marcucci *et al.*, 2002). Specifically, the dyeing of 1 Kg of cotton with reactive dye demands 70 to 150 L of water, 0.6–0.8 Kg NaCl and 30 to 60 g of dyestuffs (Colindres *et al.*, 2010).

Effluents emanating from textile, paper, wool, cotton, silk, paper printing and leather industries contain a large varieties of reactive dyes. These dyes are of great environmental anxiety due to their enormous discharge and toxic character (Zollinger, 1987; Crini, 2006; Vijayaraghavan & Yun, 2008; Chatterjee *et al.*, 2010). More than 80 000 tons of reactive dyes are produced and consumed each year, making it possible to quantify the total amount of pollution caused by their use (Maria Rivera *et al.*, 2011). Dyes usually have a synthetic origin and complex aromatic molecular structures, which possibly come from coal-tar based hydrocarbons such as benzene, naphthalene, anthracene, toluene and xylene.

To limit our scope, this review takes into consideration of Reactive Black 5, which is more difficult to remove. The reactive dyes are the largest class of water soluble synthetic dyes with the greatest variety of colors and structure and are generally

resistant to aerobic biodegradation processes (Erdal & Taskin, 2010).

## REACTIVE DYES

A dye is described as a colored substance with affinity to substrate applied. Dyes are soluble at some stage of the application process, whereas pigments in general retain basically their particulate or crystalline form during application. These are used to impart color to materials of which it becomes an integral part. Aromatic ring structure coupled with a side chain is usually required for resonance and in turn imparts color.

Based on the origin and complex molecular structure, dyes can be classified into three categories: (1) Anionic: acid, direct and reactive dyes; (2) Cationic: basic dyes; and (3) Non-ionic: disperse dyes (Gong *et al.*, 1993; Mishra & Tripathy, 1993; Fu & Viraraghavan, 2001; Greluk & Hubicki, 2010).

It has been estimated that over 10,000 different textile dyes and pigments were in common use (Easton, 1995; McMullan *et al.*, 2001). Also it is reported that there are over 100000 commercial dyes are available with a production of over  $7 \times 10^5$  metric tons per year (Zollinger, 1987; Fu & Viraraghavan, 2001).

Among the various classes of dyes, reactive dyes are one of the prominent and most widely used types of azo dyes and are too difficult to eliminate. They are extensively used in different industries, including rubber, textiles, cosmetics, paper, leather, pharmaceutical and food (Aksu & Donmez, 2005; Vijayaraghavan & Yun, 2008; Wang *et al.*, 2009). Because these dyes have favorable characteristics, such as wide color spectrum, bright color and color shades, high wet fastness profiles, ease of application, brilliant colors and minimum energy consumption (Lee & Pavlostathis, 2004; Aksu, 2005; Vijayaraghavan *et al.*, 2008).

The most common group reactive dyes are azo, anthraquinone, phthalocyanine (Axelsson *et al.*, 2006) and reactive group dyes (Lin & Peng, 1994; Sanghi *et al.*, 2006; Daneshvar *et al.*, 2007). Most of these dyes are toxic and carcinogenic (Acuner & Dilek, 2004). Disposal of these dyes into the environment causes serious damage, like they may significantly affect the photosynthetic activity of hydrophytes by reducing light penetration (Aksu *et al.*, 2007) and also they may be toxic to some aquatic organisms due to their breakdown products (Hao *et al.*, 2000; He *et al.*, 2007).

Once they are released, they not only produce toxic amines by reductive cleavage of azo linkages which causes severe effects on human beings through damaging the vital organs such as brain, liver, kidneys, central nervous and reproductive systems (Aksu, 2005; Iscen *et al.*, 2007) and light penetration (Brown & De Uito, 1993; Mahony *et al.*, 2002; Yesilada *et al.*, 2003; Forgacs *et al.*, 2004; Kalyani *et al.*, 2007) in aquatic

environment. Therefore, their removal causes a big environmental concern in industrialized countries and is subjected to many scientific researches.

It is estimated that 10–20% of reactive dyes remain in wastewater during the production and nearly 50% of reactive dyes are lost through hydrolysis during the dyeing process and their removal from effluent is difficult by conventional physical/chemical as well as biological treatment (Manu & Chaudhari, 2002; Li *et al.*, 2009; Greluk & Hubicki, 2010). Therefore, a large quantity of the dyes appears in wastewater (Heinfling *et al.*, 1997). These dyestuffs are designed to resist biodegradation.

Synthetic reactive dyes are considered as recalcitrant xenobiotic compounds, due to the presence of an N=N bond and groups such as aromatic rings that are not easily degraded. The discharge of these colored compounds into the environment causes considerable non-aesthetic pollution and serious health risks (Martínez & Brillas, 2009).

## REMOVAL METHODS

Many processes were employed to remove dye molecules from industry effluents and the treatment methods can be divided into the following categories:

### Physical methods

Physical methods such as Adsorption (Chatterjee *et al.*, 2009a; Chatterjee *et al.*, 2009b), Ion exchange (Labanda *et al.*, 2009) and Membrane filtration (Ahmad & Puasa, 2007) were employed in the removal of dyes. The main disadvantages of these physical methods were they simply transfer the dye molecules to another phase rather than destroying them and they were effective only when the effluent volume is small (Robinson *et al.*, 2001).

### By Adsorption

Adsorption is the transfer of solute dye molecule at the interface between two immiscible phases in contact with one another. The removal of colour from dye industrial effluents by the adsorption process using granular activated carbon has emerged as a practical and economical approach.

### By Ion Exchange

Removal of Anions and Cations from dye industry effluent can be carried out by Ion exchange method by passing the waste water through the beds of ion exchange resins where some undesirable cations or anions of waste water get exchanged for sodium or hydrogen ions of the resin.

Greluk & Hubicki (2010) recommended the adsorption/ion exchange as an alternative method for the removal of reactive dyes. Application of commercial anion exchange resins to water contaminated with a broad range of reactive dyes were studied by Karcher *et al.* (2001, 2002) and reported that anion exchangers possess excellent adsorption capacity (200–1200  $\mu\text{mol/g}$ ) as well as efficient regeneration property for their removal and recovery. The applicability of ion exchange resin containing acrylic matrix for removing other classes of dyes were well documented by Bayramoglu *et al.* (2009), Dulman *et al.* (2009), Wawrzkiwicz & Hubicki (2009) and Barsanescu *et al.* (2009). Thus Acrylic anion exchangers is more advantage than styrenics by exhibiting high efficiency of anion exchange capacities and polluting less.

### By Membrane filtration

Reverse osmosis (RO) and electro dialysis are the important examples of membrane filtration technology. Electrolyte is important in dyeing process for exhaustion of dye. The concentration of neutral electrolyte like NaCl in the dyeing bath is in the range of 25–30 g/L for deep tone, 41.5 g/L for light tone and extended to 50 g/L in some exceptional cases. The exhaustion stage in reactive dyeing on cotton also requires sufficient quantity of salt. The contribution of reverse osmosis in removing this high salt concentration is of great. This RO reject can be reused again in the process. For reactive dyeing on cotton, the presence of electrolytes in the waste water causes an increase in the hydrolyzed dye affinity making it difficult to extract. The total dissolved solids from waste water were removed by reverse osmosis. Though it is suitable for removing ions and larger species from dye bath effluents with high efficiency, it possesses some disadvantages like clogging of the membrane by dyes after long usage and high capital cost. In electro dialysis, the dissolved salts (ionic in nature) can also be removed by impressing an electrical potential across the water, resulting in the migration of cations and anions to respective electrodes via anionic and cationic permeable membranes. To avoid membrane fouling it is essential that turbidity, suspended solids, colloids and trace organics are to be removed prior to electro dialysis.

### Chemical methods

Chemical methods such as chemical oxidation (Osugi *et al.*, 2009), electrochemical degradation (Yi *et al.*, 2008), and ozonation (Moussavi & Mahmoudi, 2009) were employed in dye removal effectively.

The treatment of synthetic dye house effluent by ozonation and hydrogen peroxide in combination with Ultraviolet light was vast in literature. A variety of oxidizing agents were used to decolorize wastes by

oxidation techniques effectively. Among that sodium hypochlorite decolorizes dye bath efficiently. Even though it is a low cost technique, it forms absorbable toxic organic halides. Ozone on decomposition generates oxygen and free radicals. The later combines with coloring agents of effluent, resulting in the destruction of colors. The main disadvantage of this technique is that it requires an effective sludge producing pretreatment. Also, these chemical methods with high cost were rarely used in the actual treatment process and the disposal of sludge containing chemicals at the end of treatment requires further use of chemicals (Crini, 2006; Forgacs *et al.*, 2004).

### Advanced Oxidation Process (AOP)

Philippe *et al.* (1998); Slokar & Le Marechal (1998) were reported that the conventional water treatment technologies such as solvent extraction, activated carbon adsorption and chemical treatment process such as oxidation by ozone (O<sub>3</sub>) often produce hazardous by-products and generate large amount of solid wastes, which require costly disposal or regeneration method. Due to these reasons, Mahadwad *et al.* (2011) considerable attention had been focused on complete oxidation of organic compounds to harmless products such as CO<sub>2</sub> and H<sub>2</sub>O by the AOP. El-Dein *et al.* (2003) supported the AOP and reported that it provides a promising alternative method to treat the textile wastewater. The UV-driven AOPs use UV light with an oxidizer such as H<sub>2</sub>O<sub>2</sub> and/or ozone to generate hydroxyl radicals (OH<sup>•</sup>) that attack organic compounds non selectively with a high reaction rate. Based on the studies from Shu *et al.* (1994) and Galindo & Kalt (1998) it was observed that the decolorization of textile dyes using H<sub>2</sub>O<sub>2</sub>/UV had shown it to decolorize dilute aqueous solutions (20 mg/L) of azo dyes.

### Electrochemical Method

The requirement of chemicals and the temperature to carry the electro chemical reaction is less than those of other equivalent non-electrochemical treatment. It can also prevent the production of unwanted side products. But, if suspended or colloidal solids were high in concentration in the waste water, they slow down the electrochemical reaction. Therefore, those materials need to be sufficiently removed before electrochemical oxidation.

Ceron *et al.* (2004) reported that many of the commercially used dyes are resistant to biological and physico-chemical methods (Delee *et al.*, 1998; Vandevivere *et al.*, 1998; Anbia *et al.*, 2010). Also Ceron *et al.* (2004) suggested that coagulation (Vandevivere *et al.*, 1998), coagulation – electro oxidation (Xiong *et al.*, 2001), adsorption (Moraes *et al.*, 1999), electrolysis (Davila-Jimenez *et al.*, 2000),

photolysis (Ince, 1999) and ozonation are promising in terms of performance. But in terms of economic aspect, these methods have become most challenging problem.

Consequently, Gutierrez *et al.* (2001) discussed the interest in electrochemical methods to decolourise and degrade dye molecules. The electric current induces redox reactions resulting in the transformation and destruction of the organic compounds and almost complete oxidation to CO<sub>2</sub> and H<sub>2</sub>O.

At the same time Powell *et al.* (1994) reported that the small scale oxidizing methods using Fenton's reagent, which has lower costs in comparison with ozone process in dye liquor treatment. The oxidizing effect of the corona discharge is also known and it has been reported by Goheen *et al.* (1994) as an effective method to bleach organic dyes using a stainless steel electrode. Steel electrodes were used commonly in electrochemical technology to remove color by generating ferrous hydroxide and ferric oxyhydroxide. Yang *et al.* (2000) reported a new result for the color removal of dye from wastewater by applying electro generated hypochlorite ions and (Ru+ Pt)O<sub>x</sub> binary electrodes. Even if the removal of dyes from wastewater in an economic way by using electrochemical method, the low-cost electrode production remains a major concern. Zero Valent Iron (ZVI)

Chatterjee *et al.* (2010) discussed the development of new treatment strategies to degrade the dye molecules using Zero-Valent iron (ZVI) particles. These are inexpensive, environmental friendly strong reducing agents and Sun *et al.* (2006) reported that ZVI can donate two electrons to many environmental contaminants as  $\text{FeO} \rightarrow \text{Fe}^{2+} + 2\text{e}^{-}$ .

Chatterjee *et al.* (2010) also reported that due to its effective electron donating capacity, ZVI particles had been studied for the treatment of wastewater contaminated with chlorinated compounds, nitro aromatic compounds, nitrates, heavy metals, organochlorine pesticides, and dyes. Fan *et al.* (2009) reported that the reaction between FeO and H<sub>2</sub>O or H<sup>+</sup> can generate H atoms, which induce the cleavage of the azo bond (–N N–), thus damaging the chromophore group and conjugated system of azo dyes. Saxe *et al.* (2006) reported that ZVI particles convert azo dye into some products that were more susceptible to biological degradation process. Chang *et al.* (2006) discussed about the other advantages of using ZVI particles for the decolorization process include a low iron concentration remaining in the sludge, no requirement for further treatment of effluents and easy recycling of the spent iron powder by magnetism. Low-cost, is easy-to-obtain, and has good effectiveness and ability of degrading contaminants.

### Biological methods

Bioaccumulation and biosorption are the two main technologies in biological process for of dye bearing industrial effluents. They possess good potential to replace conventional methods for the treatment of dyes industry effluents (Volesky & Holan, 1995; Malik, 2004). Biological process can be carried out in situ at the contaminated site, these are usually environmentally benign i.e., no secondary pollution and they were cost effective. These are the principle advantages of biological technologies for the treatment of dye industry effluents. Hence in recent years, research attention has been focused greatly on biological methods for the treatment of effluents (Prasad & Freitas, 2003; Vijayaraghavan & Yun, 2008). The disadvantage of this degradation process is that it suffers from low degradation efficiency or even no degradation for some dyes (Stolz, 2001; Pearce *et al.*, 2003) and practical difficulty in continuous process. Vijayaraghavan & Yun (2008) clearly demonstrated the difference between bioaccumulation and biosorption in their review. Bioaccumulation is defined as the phenomenon of uptake of toxicants by living cells; whereas, biosorption can be defined as the passive uptake of toxicants by dead or inactive biological materials. The important advantage of biosorption than bioaccumulation process is the use of living organisms is not advisable for the continuous treatment of highly toxic effluents. This problem can be overcome by the use of dead biomass, which is flexible to environmental conditions and toxicant concentrations.

Erdal & Taski (2010) discussed about various treatment methods exist for the removal of color from industrial effluents, including physico-chemical and biological processes. Although a number of chemical, physical processes namely flocculation, chemical coagulation, precipitation, ozonation and adsorption were employed for the treatment of dye bearing wastewaters. Aravindhan *et al.* (2007) and Sarioglu *et al.* (2007) reported that they possess some inherent limitations such as high cost, formation of hazardous by-products and intensive energy requirements.

In addition to that Erdal & Taski (2010), Banat *et al.* (1996), Slokar & Marechal, (1998) reported that the physico-chemical processes were usually inefficient, costly and not adaptable to a wide range of dye wastewater. Erdal & Taski (2010), Fu & Viraraghavan (2001); Wang *et al.* (2009) and Aksu (2005) had suggested the increasing interest of biological processes, such as biodegradation, bioaccumulation and biosorption due to their cost effectiveness, ability to produce less sludge and environmental benignity.

Fungi and algae had been played important role in dye decolorization. Wang *et al.* (2009) reported that adsorption rather than degradation plays a major role during the decolorization process by fungi and algae.

#### **Anaerobic Treatment**

Karatas *et al.* (2010) reported the unsuitability of physicochemical decolorization methods regarding cost effectiveness, usage areas, interfere with other wastewater components, or cause wastes that require retreatment and also they suggested that the biologic treatment method especially anaerobic treatment in the case of azo dyes is an alternative to the physicochemical method which was relatively inexpensive and may be preferred for decolorization based on the investigation by Van der Zee *et al.* (2001); Van der Zee & Villaverde (2005); Carliell *et al.* (1995) supported the same i.e., in most cases, the dyes were easily reduced under anaerobic condition. The main disadvantage of azo dye reduction under anaerobic conditions were the production of aromatic amines, which usually do not degrade under these conditions (Mendez-Paz *et al.*, 2005; Razo-Flores *et al.*, 1996) and tend to accumulate at toxic levels (Carliell *et al.* 1995; Gottlieb *et al.*, 2003). Such amines, however, were reported to be readily bio-transformed under aerobic conditions (Tan *et al.* 2000; Ipýk & Sponza, 2004). The color and COD removal efficiencies were investigated by Sponza & Isýk (2002) using anaerobic - aerobic sequential processing for treatment of 100 mg/L of di-azo dye with glucose as the carbon source and reported the color removal efficiency as 96%. Supaka *et al.* (2004) obtained 78.2% color removal and 90% COD removal in a sequential anaerobic – aerobic system that was used to treat Remozal Black B dye. Isýk & Sponza (2004) reported 92.3 and 95.3% color and COD removal efficiencies, respectively, when using an upflow anaerobic sludge blanket -aerobic stirred tank reactor sequential system to treat Congo Red dye. Kapdan & Oztekin, (2006) investigated Remozal Rot dye and reported over 90% color removed and more than 85% COD removal efficiency in an anaerobic/aerobic SBR system. Khehra *et al.* (2006) reported 98% color removal and 95% COD removal efficiency in an anoxicaerobic sequential bioreactor system used to treat Acid Red 88 azo dye. Zaoyan *et al.* (1992) obtained 65% color and 74% COD removal efficiencies in textile wastewater contaminated with azo dyes using an anaerobic-aerobic rotating biodisc system.

#### **Enzymatic Treatments**

Roriz *et al.* (2009) mentioned that physical and chemical methods have high costs, low efficiency and cannot be used with a great variety of dyes and they suggested that the use of enzyme based methods are good alternative. Compared to the conventional methods, application to recalcitrant materials, operation at high and low contaminant concentrations over a wide pH, temperature and salinity range, biomass acclimatization was irrelevant and straight forward process control were the potential advantages of the

enzymatic treatments reported by Duran & Esposito (2000) and Roriz *et al.* (2009).

## REACTIVE BLACK 5 TREATMENT MECHANISMS

Surprisingly very few studies show the interest towards continuous operation for dye removal. That too the very low flow rate in micro level was used in their investigations. Though a high level of flow rate was desired to analyze, multidye treatment was essential to reach a sustainable solution to dye industry effluents since effluents emanating from the industry have the dye mixture (Vijayaraghavan *et al.*, 2008). Without intensive research in continuous treatment of effluents emanating from dye industries, the problem does not reach the sustainable end (Vijayaraghavan & Yun, 2008). The search for efficient, eco-friendly and cost effective continuous treatment for wastewater was very limited in literature. Serkan & Taskin, (2010), Karatas *et al.* (2010), Vijayaraghavan & Yun (2007), Vijayaraghavan *et al.* (2008), Vijayaraghavan & Yun (2008) and were discussed the continuous operation for dye industry waste water treatment. Vijayaraghavan & Yun (2008) reported that the industries need to develop on-site or in-plant facilities to their own effluents and minimize the contaminant concentrations to acceptable limits prior to their discharge. Also, Vijayaraghavan & Yun (2008) and Atkinson *et al.* (1998) suggested that, before selecting a wastewater treatment facility, a considerable amount of laboratory and engineering work must be completed prior to system design. Hence this review limits to a particular dye, i.e. Reactive Black 5 and an attempt is made to analyze the treatment of reactive black 5 in all circumstances through literature.

Fu & Viraraghavan (2001) reported in their review that the white rot fungi namely *Phanerochaete chrysosporium* was used in early 1980's to decolorize the lignin containing pulp and paper waste water. Thereafter *P.chrysosporium* had been examined for decolorization of pulp mill waste water and various dyes by many researchers (Glenn & Gold, 1983; Lankinen *et al.*, 1991; Cammarto & Sant Anna, 1992; Pasti-Grigsby *et al.*, 1992; Spadaro *et al.*, 1992; Ollikka *et al.*, 1993; Bilgic *et al.*, 1997; Young & Yu, 1997; Tatarko & Bumpus, 1998).

Among various dyes, Young & Yu (1997) reported that reactive black 5 showed 11.3 % removal after 9 days contact with *P. chrysosporium*. The initial dye concentration of reactive black 5 used in this investigation was 40–50 mg/L. The Biosorption is carried out by ligninase catalyzed.

At the same time, other than white rot fungi, namely *Rhizopus oryzae* investigated by Gallagher *et al.* (1997) and Polman & Breckenridge (1996) showed an adsorption of 99 mg/g of biomass for reactive black 5 dye waste while using this *Rhizopus oryzae* as a living fungal cell. Contradictorily the same *R. oryzae* was used as dead fungal cell adsorbent, Polman & Breckenridge (1996) reported 452 mg/g of dead biomass of *R. oryzae*.

Fu & Viraraghavan (2001) distinguish obviously about living cells and dead cells of biomass. Lignin modifying enzymes, laccase, manganase peroxidase (MnP) and lignin peroxidase (LiP) were produced in living cells to mineralize the dyes. Also, the relative contribution of laccase, MnP and LiP for the decolorization of dyes were different for different fungus. The mechanism for dead cells is biosorption, which involves physico-chemical interactions, such as adsorption, deposition and ion-exchange. An obvious comparison was reached by Fu & Viraraghavan (2001) for living and dead fungal biomass. In screening a number of bacteria, fungi and yeast for the binding capacity of reactive dyes, Polman & Breckenridge (1996) observed that among 28 microbial species 64% of the dead forms had a higher adsorption capacity for the reactive black 5 dye waste.

Operating conditions and nutrient supply were the two important constraints for the living cells though they had different decolorization mechanisms. Though the biosorptive capacity of dead cells may be greater than or equal to or less than those of living cells. Dead cells were easy to handle, simple for regeneration and can be utilized as obtained from industrial sources as a waste product. Therefore, Kapoor & Viraraghavan (1995) and Fu & Viraraghavan (2001) suggested that the dead cells were effective than living cells. Though the same was supported by the investigation of Polman & Breckenridge (1996) using *R.oryzae*, a contradictory was noticed by using *Xeromyces bisporus* for the biosorption of Reactive Black 5 Waste. **Table 1, Table 2, Table 3** represents the living cells, dead cells, Chemical methods for the treatment of reactive black 5, respectively.

**Table 1:** Earlier investigations on use of living cells for treatment of Reactive Black 5

Culture	% Removal (or) Dye uptake (mg/g)	Mechanism	Reference
<i>Candida rugosa</i>	31 mg of dye absorbed/g of biomass	Adsorption	Polman & Breckenridge (1996)
<i>Cryptococcus heveanensis</i>	60 mg of dye absorbed/g of biomass	Adsorption	Polman & Breckenridge (1996)
<i>Dekkera bruxellensis</i>	38 mg of dye absorbed/g of biomass	Adsorption	Polman & Breckenridge (1996)
<i>Endothiella aggregate</i>	44 mg of dye absorbed/g of biomass	Adsorption	Polman & Breckenridge (1996)
<i>Geotrichum fici</i>	7 mg of dye absorbed/g of biomass	Adsorption	Polman & Breckenridge (1996)
<i>Kluyveromyces waltii</i> (yeast)	60 mg of dye absorbed/g of biomass	Adsorption	Polman & Breckenridge (1996)
<i>Penicillium chrysosporium</i>	11.3%	Ligninase-catalyzed	Young & Yu (1997)
<i>Pichia carsonii</i> (yeast)	25 mg of dye absorbed/g of biomass	Adsorption	Polman & Breckenridge (1996)
<i>Rhizopus oryzae</i>	99 mg of dye absorbed/g of biomass	Adsorption	Polman & Breckenridge (1996)
<i>Trametes versicolor</i>	15.6%	Ligninase-catalyzed	Young & Yu (1997)
<i>Tremella fuciformis</i>	92 mg of dye absorbed/g of biomass	Adsorption	Polman & Breckenridge (1996)
<i>Xeromyces bispourus</i>	11 mg of dye absorbed/g of biomass	Adsorption	Polman & Breckenridge (1996)
<i>Penicillium chrysosporium</i>	21.0%		Ali Mazmanci & Ali Ünyayar, (2005)
<i>Penicillium florida</i>	40.0%		Ali Mazmanci & Ali Ünyayar, (2005)
<i>Penicillium eryngii</i>	9.6%		Ali Mazmanci & Ali Ünyayar (2005)
<i>Penicillium sapidus</i>	3.6%		Ali Mazmanci & Ali Ünyayar, (2005)
<i>Funalia trogii</i> ATCC 200800	99%		Ali Mazmanci & Ali Ünyayar (2005)
<i>Candida oleophila</i>	200 mg/g 100%	Biodegradation	Marco S. Lucas <i>et al</i> (2006)

**Table 2:** Earlier investigations for treatment of Reactive Black 5 by Dead Cells

Culture	% Removal (or) Dye uptake (mg/g)	Mechanism	Reference
<i>Cryptococcus</i>	76 mg /g	Biosorption	Polman & Breckenridge,



<i>heveanensi</i> (yeast)			(1996)
<i>Candida rugosa</i> (yeast)	31 mg /g	Biosorption	Polman & Breckenridge, (1996)
<i>Dekkera bruxellensis</i> (yeast)	36 mg /g	Biosorption	Polman & Breckenridge, (1996)
<i>Endothiella aggregate</i>	44 mg /g	Biosorption	Polman & Breckenridge, (1996)
<i>Geotrichum Fici</i>	45 mg /g	Biosorption	Polman & Breckenridge, (1996)
<i>Kluyveromyce waltii</i> (yeast)	72 mg /g	Biosorption	Polman & Breckenridge, (1996)
<i>Pichia carsonii</i> (yeast)	32 mg /g	Biosorption	Polman & Breckenridge, (1996)
<i>Rhizopus oryzae</i>	452 mg /g	Biosorption	Polman & Breckenridge, (1996)
<i>Treemella fuciformis</i>	79 mg /g	Biosorption	Polman & Breckenridge, (1996)
<i>Xeromyces bisporus</i>	11 mg /g	Biosorption	Polman & Breckenridge, (1996)
<i>Corynebacterium Glutamicum</i> ( raw)	111.8 (L)	Biosorption	Vijayaraghavan & Yun , (2007a)
<i>Corynebacterium glutamicum</i> (protonated)	165.2 (L)	Biosorption	Vijayaraghavan & Yun, (2007a)
<i>Corynebacterium glutamicum</i> (decarboxylated)	257.3 (L)	Biosorption	Vijayaraghavan & Yun, (2007a)
<i>Corynebacterium glutamicum</i> ( polysulfone-raw)	75.8 (L)	Biosorption	Vijayaraghavan & Yun, (2007a)
<i>Corynebacterium glutamicum</i> (polysulfone-protonated)	109.1 (L)	Biosorption	Vijayaraghavan & Yun, (2007a)
<i>Corynebacterium glutamicum</i> ( polysulfone-decarboxylated)	180.7 (L)	Biosorption	Vijayaraghavan & Yun, (2007a)
<i>Pleurotus sajor-caju</i> (purified laccase from a white rot fungus)	84.4%,	Biosorption	Kumarasamy murugesan <i>et al</i> .,(2007)
<i>Corynebacterium glutamicum</i> (free biomass)	352 mg/g	Biosorption	Vijayaraghavan <i>et al.</i> (2007)
<i>Corynebacterium glutamicum</i> (Alginate immobilized biomass)	282 mg/g	Biosorption	Vijayaraghavan <i>et al.</i> , (2007)
<i>Corynebacterium glutamicum</i> ( Polysulfone immobilized Biomass)	291 mg/g	Biosorption	Vijayaraghavan <i>et al</i> . (2007)
<i>Corynebacterium glutamicum</i>	419 (L)	Biosorption	Vijayaraghavan & Yun ,(2007b)
<i>Corynebacterium glutamicum</i> (Polysulfon	88.9 mg/g 61.8%	Biosorption	Vijayaraghavan & Yun, (2008)

e-immobilized)			
<i>Laminaria sp.</i> (Brown seaweed )	101.5 (L) , 41.9 mg/g 72.7%	Biosorption	Vijayaraghavan & Yun, (2008)
<i>Corynebacterium glutamicum</i> (Polysulfon e-Immobilized Esterified )	70.2 mg/g	Biosorption	Vijayaraghavan <i>et al.</i> ,(2008)
<i>Trametes Pubescens</i> (crude laccase )	60%	Decolorization	Margarida S. Roriz <i>et al.</i> (2009)
<i>Penicillium Restrictum</i>	142.04 mg/g	Biosorption	Cansu Filik Iscen <i>et al.</i> (2007)
<i>Rhodopseudomonas Palustris</i>	100%	Biodecolorization	Wang Xingzu <i>et al.</i> (2008)
Bacterial strain <i>Enterobacter sp. EC3</i>	92.56%	Biological decolorization	HuiWang <i>et al.</i> (2009)
<i>Penicillium Chrysogenum MT-6</i>	89%	Biosorption	Serkan Erdal & Mesut Taskin, (2010)

\*L dye uptake by Langmuir model

**Table 3:** Earlier investigations for treatment of Reactive Black 5 by chemical methods

<i>Method/chemical</i>	<i>% Removal (or) Dye uptake (mg/g)</i>	<i>Reference</i>
Photocatalytic degradation of reactive black-5 dye using TiO <sub>2</sub> impregnated ZSM-5. Batch Reactor	98%	Mahadwad <i>et al.</i> , (2011)
Electrochemical cell for the removal of Reactive Black 5. cubic and cylindrical cell configuration	100	Maria Rivera <i>et al.</i> , (2011)
Zero-Valent Iron modified with various surfactants		Chatterjee <i>et al.</i> (2010)
Acid acrylic resins Amberlite IRA-458 and Amberlite IRA-958	NR	Magdalena G & Zbigniew H, (2010)
Zero - Valent Iron		Chompuchan <i>et al.</i> (2009)
Fenton/UV-C and ferrioxalate/H <sub>2</sub> O <sub>2</sub> /solar light processes	90%	Lucas and Peres (2007)
Combined sonolysis and ozonation	84	Zhiqiao <i>et al.</i> (2007)
Solar assisted photocatalytic and photochemical Degradation		Muruganandham <i>et al.</i> (2006)
Diamond and metal alloys electrodes	95%	Ceron Rivera <i>et al.</i> (2004)
Hydrogen peroxide and UV radiation	90%	Mohey El-Dein <i>et al.</i> (2003)
Hydrogen peroxide and UV light	100 %	Mohey El-Dein <i>et al.</i> (2001)

Mohey El-Dein *et al.* (2001) reported that the kinetic parameters for the decolorization of Reactive Black 5 with H<sub>2</sub>O<sub>2</sub>/UV using batch experiments. The decolorization rate is first order with respect to dye concentration until 90% of the dye was decolorized. The dependence on H<sub>2</sub>O<sub>2</sub> concentration was shown to be first order for low concentrations and zero order for high concentrations. The reaction coefficient  $k_1$  was found to be a linear function of UV intensity,  $k_1 = k_{10} I_0$

with  $k_{10} = 10.334$  Einstein/L. Little mineralization of C.I. Reactive Black 5 (~20%) took place until 90% of the dye was decolorized. 100% decolorization corresponded to more or less 40–50% mineralization. The dye could be further mineralized (70–85%) with extended radiation time.

Mohey El-Dein *et al.* (2003) developed a kinetic model for the decolorization of the diazo dye Reactive black 5 by H<sub>2</sub>O<sub>2</sub>/UV.

Ceron Rivera *et al.* (2004) studied the treatment of Reactive black 5 by electrochemical method using diamond, aluminium, copper and iron - zinc alloy electrodes. The electrode potential range used in this investigation was  $-1.0$  to  $-2.5$  V. They found that 95% color removal and up to 65–67% COD removal were done with copper and iron electrodes.

Ali Mazmanci and Ali Unyayar, (2005) investigated the decolorization of Reactive Black 5 by immobilised *Funalia trogii*. Cultures of *F. trogii* immobilised on *Luffa cylindrica* sponge could effectively decolourise the dye. The effect of mycelial age was also studied and decolorization rate of a 3-day-old age culture was higher (8.22 mg dye/g dmw day) than those of 0- and 6-day-old cultures (6.86 and 7.80 mg dye/g dmw day). Macroscopic and microscopic examinations showed that dye was not biosorbed on the fungal mycelium. The growth of *F. trogii* was inhibited by all tested dye concentrations with compared to controls but this effect was minimised when the fungus was completely immobilised on the sponge. Using optimal mycelial age, cultures of *L. cylindrica* sponge were tested for their ability towards dye decolorization at different initial concentrations. The kinetic parameters of decolorization were calculated according to Lineweaver–Burk plots ( $K_m$  of 106.04 mg dye/L and  $V_{max}$  of 117.64 mg dye/L day).

Muruganandham *et al.* (2006) reported the photocatalytic oxidative degradation of Reactive Black 5 using  $TiO_2$ -P25 as photocatalyst and sunlight as irradiation source in slurry form. A complete degradation of  $3.85 \times 10^{-4}$  M dye solution under solar irradiation was observed in 3.5 h. The photochemical degradation using hydrogen peroxide resulted in the partial removal of the dye.

Vijayaraghavan & Yun (2007a) developed a biosorbent from *C. glutamicum* for the treatment of reactive black 5. Also, they suggested that bacteria possess high reactive dye biosorption capacity only in strong acidic conditions due to the nature of their binding sites also used a decarboxylated form of *C. glutamicum*, which can effectively biosorb reactive black 5 under moderate pH condition of 4. Even though the decarboxylation process may incur additional process cost, this step was necessary to make the process feasible. Also, it should be noted that *C. glutamicum* can be collected at free of cost from the amino acid fermentation industries. The problems of reusing the bacterial biomass for multiple cycles were solved by immobilizing the biomass in a polysulfone matrix. Both free and polysulfone immobilized decarboxylated *C. glutamicum* performed well at pH 4 for the biosorption of reactive black 5, with maximum uptakes of 257.3 and 180.7 mg/g dry beads, respectively, according to the Langmuir model. However, the reactive black 5 isotherms were well described by the Redlich-Peterson model with high

correlation coefficients compared to the Langmuir model. Kinetic experiments revealed the involvement of intraparticle diffusion resistance in the case of the immobilized beads. Desorption was possible only in the case of immobilized beads with 0.01 M NaOH as the elutant. Column experiments proved that immobilized beads can be efficient in the continuous biosorption of reactive black 5, with the decarboxylated biomass recorded at 78.6 mg/g dry beads. Although earlier breakthrough and delayed exhaustion times were observed with progressive cycles, the polysulfone immobilized decarboxylated biomass maintained high reactive black 5 uptake values of over 74.1 mg/g dry beads during all three cycles.

Marco S. Lucas *et al.* (2006) used *Candida oleophila* which efficiently decolorized the commercial textile diazo dye Reactive Black 5. Aerobic batch cultures of *C. oleophila* could completely decolorized up to 200 mg/L. Moreover, this performance was achieved in just 24 h of incubation at  $26^\circ\text{C}$  in the presence of as little as 5 g of glucose/L and without visible signs of dye adsorption to yeast cells. It was found that decolorization occurred during the exponential growth phase and neither laccase nor manganese-dependent peroxidase activities were detected in the culture medium.

Cansu Filik Iscen *et al.* (2007) studied the biosorption of Reactive Black 5 dye on dried *Penicillium restrictum* biomass with respect to pH, contact time, biosorbent dosage and dye concentrations. The effect of temperature on the biosorption efficiency was also carried out and the kinetic parameters were determined. Optimum initial pH, equilibrium time and biomass concentration for reactive black 5 were found that 1.0, 75 min and  $0.4 \text{ g dm}^{-3}$  at  $20^\circ\text{C}$ , respectively. The maximum biosorption capacities ( $q_{max}$ ) of reactive black 5 onto dried *P. restrictum* biomass were 98.33 and 112.50 mg/g biomass at 175 mg/L initial dye concentration at  $20^\circ\text{C}$  and  $50^\circ\text{C}$ , respectively, and it was 142.04 mg/g biomass at 200 mg/L initial dye concentration at  $35^\circ\text{C}$ . The results indicated that the biosorption process obeyed a pseudo-second-order kinetic model.

Zhiqiao He *et al.* (2007) investigated the decolorization of the azo dye C.I. Reactive Black 5 solution by a combination of sonolysis and ozonation. The results showed that the optimum pH for the reaction was 11.0. Increasing the initial concentration of reactive black 5 led to a decreasing decolorization rate. Under the experimental conditions, the decolorization rate increased with an increase in temperature. The decolorization of reactive black 5 followed pseudo-first-order reaction kinetics. Based on the decolorization rate constants obtained at different temperatures within the range 287–338 K and the Arrhenius equation, the apparent activation energy ( $E_a$ ) was calculated to be 11.2 kJ/mol. This indicated that the reaction had little

dependence on temperature. The color decay was considerably faster than the decrease in total organic carbon (TOC), which was attributed to the ease of chromophore destruction. Hence the efficiency of decolorization was 84% compared with 4% of TOC removal after 5 min reaction. Additionally, muconic acid, (2Z)-pent-2-enedioic acid and maleic acid were identified as main oxidation products by gas chromatography coupled with mass spectrometry (GC–MS) after 150 min of reaction.

Kumarasamy Murugesan *et al.* (2007) applied the response surface methodology (RSM) for the decolorization of the azo dye reactive black 5 using purified laccase from a white rot fungus *Pleurotus sajor-caju*. They observed that the presence of 1-hydroxybenzotriazole (HBT) was essential for decolorization of reactive black 5 by purified laccase from *P.sajor-caju*. Box Behnken design using RSM with four variables namely dye (25–100 mg/l), enzyme (0.5–2.5 U/ml), redox mediator concentrations (0.5–1.5 mM) and incubation time (24–48 h) were employed in this study to optimize significant correlation between the effects of these variables on the decolorization of reactive black 5. The optimum concentration of dye, enzyme, HBT, and time were found to be 62.5 mg/L, 2.5 U/ml, 1.5 mM and 36 h, respectively, for maximum decolourization of Reactive Black 5 (84.4%). A quadratic model is proposed for dye decolorization through this design. Increased decolorization was observed with increase in enzyme concentration at lower dye concentration. Interaction between HBT and dye concentrations was negligible. The optimization of HBT is independent of dye concentration.

Lucas & Peres (2007) studied the feasibility of employing different photooxidation systems like Fenton/UV-C and ferrioxalate/H<sub>2</sub>O<sub>2</sub>/solar light in the decolorization and mineralization of Reactive Black 5. Batch experiments were carried out to evaluate the influence of different processes on Reactive Black 5 decolorization in the first stage. During the second stage they investigated the optimal operational conditions of Fenton/UV-C and ferrioxalate/H<sub>2</sub>O<sub>2</sub>/solar light processes like pH, H<sub>2</sub>O<sub>2</sub> dosage, iron dosage, Reactive Black 5 concentration and source of light. The results indicated that reactive black 5 can be effectively decolorized using Fenton/UV-C and ferrioxalate/H<sub>2</sub>O<sub>2</sub>/solar light processes with a small difference between the two processes, 98.1% and 93.2%, after 30 min respectively. Although there was lesser difference in dye decolorization, significant increment in TOC removal was found with Fenton/UV-C process (46.4% TOC removal) related to ferrioxalate/H<sub>2</sub>O<sub>2</sub>/solar light process (29.6% TOC removal). This fact revealed that UV-C low-pressure mercury lamp although with its small effect on dye decolorization was particularly important in dye mineralization, when compared to solar light. However,

ferrioxalate/H<sub>2</sub>O<sub>2</sub>/solar light system showed large potential on photochemical treatment of textile wastewater with particular interest from the economical point of view.

Vijayaraghavan *et al.* (2007) used *Corynebacterium glutamicum*, a lysine fermentation industry waste, showed better removal of Reactive black 5. Due to practical difficulties in solid–liquid separation, the free biomass was immobilized in two polymer matrices: calcium alginate and polysulfone. Initially, the optimization of biomass loading in polymeric beads and bead dosage were examined. Of the different combinations examined, 4% (with bead dosage of 2 g per 40 ml) and 14% (with bead dosage of 1 g per 40 ml) in the case of alginate and polysulfone beads, respectively, were identified as the optimal conditions. According to the Langmuir model, at pH 1, the maximum reactive black 5 uptakes of 352, 282 and 291 mg/g were observed for free, alginate and polysulfone-immobilized biomass, respectively. According to the Weber - Morris model, intraparticle diffusion was found to be the potential rate limiting step for the immobilized beads. Regeneration experiments, with 0.01 M NaOH and Na<sub>2</sub>CO<sub>3</sub> as eluents, revealed that polysulfone beads exhibited invariable Reactive Black 5 uptake capacity and very high mechanical stability even at the end of twentieth cycle, confirming the technical feasibility of the biosorption process for industrial applications.

Vijayaraghavan & Yun (2007b) used *Corynebacterium glutamicum* as a biosorbent for the treatment of Reactive Black 5. The effect of pretreatment on the biosorption capacity of *C. glutamicum* towards Reactive Black 5 using several chemical agents such as HCl, H<sub>2</sub>SO<sub>4</sub>, HNO<sub>3</sub>, NaOH, Na<sub>2</sub>CO<sub>3</sub>, CaCl<sub>2</sub> and NaCl were reported. Among these reagents, 0.1M HNO<sub>3</sub> gave the maximum enhancement of the Reactive Black 5 uptake, exhibiting 195 mg/g at pH 1 with an initial Reactive Black 5 concentration of 500 mg/L. The solution pH and temperature were found to affect the biosorption capacity. The biosorption isotherms derived at different pH and temperatures revealed that a low pH (pH = 1) and high temperature (35°C) favored biosorption. The biosorption isotherm was well represented using three-parameter models (Redlich–Peterson and Sips) compared to two-parameter models (Langmuir and Freundlich models). As a result, high correlation coefficients and low average percentage error values were observed for three-parameter models. According to the Langmuir model, a maximum Reactive uptake of 419 mg/g was obtained at pH 1 and a temperature of 35°C, according to the Langmuir model. The kinetics of the biosorption process with different initial concentrations (500–2000 mg/L) was also monitored and the data were analyzed using pseudo-first and pseudo-second order models, with the latter describing the data well. This system indicated a spontaneous and endothermic process. The

use of a 0.1M NaOH solution successfully desorbed almost all the dye molecules from dye-loaded *C. glutamicum* biomass at different solid-to-liquid ratios examined.

Wang Xingzu *et al.* (2008) analyzed the strain of photosynthetic bacterium, *Rhodospseudomonas palustris* for the decolorizing Reactive Black 5 efficiently under anaerobic condition. By a series of batch tests, the suitable conditions for Reactive Black 5 decolorization were obtained, namely, pH < 10, light presence, glutamine or lactate as carbon source with concentration more than 500 mg/L when lactate is selected, NH<sub>4</sub>Cl as a nitrogen source with concentration more than 100 mg/L, NaCl concentration not exceeding 5%, and Reactive Black 5 concentration less than 700 mg/L. The results showed that partial aromatic amines produced with Reactive Black 5 reduction were further degraded during the extended period. Anaerobic partial mineralization of Reactive Black 5 was suggested and a possible degradation pathway was proposed.

Vijayaraghavan & Yun (2008a) employed Polysulfone-immobilized *Corynebacterium glutamicum* as a biosorbent, for the continuous removal of Reactive black 5 from aqueous solution, in an up-flow packed column. The biosorbent performance was evaluated with different bed heights (8–10 cm), flow rates (0.5–1 ml/min) and initial dye concentrations (50–100 mg/L). Favorable conditions for Reactive black 5 biosorption were observed with the highest bed height (10 cm), lowest flow rate (0.5 ml/min) and lowest initial dye concentration (50 mg/L); at which the Reactive Black 5 uptake and % removal, 88.9 mg/g and 61.8%, respectively, were recorded. Mathematical modeling of experimental data was performed, using a non-linear form of Thomas modified dose–response and Yoon–Nelson models, to simulate the breakthrough curves. Very favorable results were obtained with Thomas and Yoon–Nelson models, which described the experimental data well, with very high correlation coefficients. In an attempt to regenerate the exhausted biosorbent for possible reuse in multiple cycles, 0.1M NaOH was employed as elutant. Due to continuous usage of polysulfone-immobilized *C. glutamicum* in three sorption–desorption cycles, a decreased breakthrough time, increased exhaustion time, broadened mass transfer zone, flattened breakthrough curve and decreased Reactive Black 5 uptake were observed with progressive cycles. Linear regression of the breakthrough, uptake and critical bed length revealed that the sorption zone would reach top of the bed after 18 cycles, with the column bed completely exhausted after 35 cycles. The elutant, 0.1M NaOH, provided uniform elution efficiencies greater than 99.2% in all three cycles.

Vijayaraghavan & Yun (2008b) investigated the biosorption of Reactive Black 5 using the brown seaweed *Laminaria Sp.* in both batch and column modes

of operation. Protonation of the native *Laminaria* biomass with 0.1 M HCl, considerably improved its

Reactive Black 5 biosorption capacity. At various initial concentrations (50 - 200 mg/L), batch sorption equilibrium was reached within 3 h, followed by slow attainment of equilibrium and the kinetic data obtained were interpreted in terms of the pseudo-second order model. Biosorption isotherm experiments, under different pH and temperature conditions, revealed that decreasing the pH and increasing the temperature favored biosorption. According to the Langmuir model, the maximum Reactive Black 5 uptake of 101.5 mg/g was observed at pH 1 and temperature of 40°C. 0.01 M NaOH solution successfully eluted all dye from the Reactive Black 5 -loaded *Laminaria* biomass. The feasibility of the brown seaweed for the continuous removal of Reactive Black 5 from aqueous solution was examined in an up-flow packed column (1 cm ID and 12 cm height). With a bed height, flow rate and initial Reactive Black 5 concentration at 10 cm, 1 ml/min and 50 mg/L, respectively, the *Laminaria* biomass exhibited an RB5 uptake and removal efficiency of 41.9 mg/g and 72.7%, respectively. The column was successfully eluted using 0.01 M NaOH with an elution efficiency of 97.7%.

Vijayaraghavan *et al.* (2008) reported the ability of polysulfone-immobilized esterified *Corynebacterium glutamicum* for biosorption of Reactive Black 5 and Reactive Orange 16 from single- and dual-dye solutions were investigated. Single-dye biosorption isotherm experiments exposed that polysulfone-immobilized esterified *Corynebacterium glutamicum* performed well in the biosorption of Reactive Orange 16, with a higher experimental uptake of 248.1 mg/g, compared to 174.1 mg/g for Reactive Black 5. Conversely, the uptake of Reactive Orange 16 was suppressed almost 2.5 times in the presence of Reactive Black 5, whereas polysulfone-immobilized esterified *Corynebacterium glutamicum* maintained similar Reactive Black 5 uptakes in both single- and dual-dye systems. Several factors might be responsible for this effect, the most important being the number of sulfonate groups and the size of each reactive dye. The continuous biosorption of reactive dyes from single- and dual-dye solutions using an upflow packed column was successful with polysulfone-immobilized esterified *Corynebacterium glutamicum* being regenerated and reused for three cycles.

Hui Wang *et al.* (2009) studied the decolorization of the Reactive Black 5 by a bacterial strain *Enterobacter* sp. EC3. The optimal conditions for the decolorizing activity of *Enterobacter* sp. EC3 were anaerobic conditions with glucose supplementation, at pH 7.0, and 37°C. The maximum decolorization efficiency against Reactive Black 5 achieved in this study was 92.56%.

Roriz *et al.* (2009) studied the decolorization of the Reactive Black 5 by crude laccase from the white-rot fungus *Trametes pubescens* using response surface

methodology. The presence of the redox mediator 1-hydroxybenzotriazole greatly improved the decolorization levels of Reactive Black 5 by crude laccase from *T. Pubescens*. The optimum concentrations of 1-hydroxybenzotriazole, Reactive Black 5 and laccase were 1.17mM, 150 mg/L and 500 U/L, respectively, for a maximum decolorization of Reactive Black 5 (about 60% in 20 min).

Chompuchan *et al.* (2009) used the nanoscale zero valent iron (NZVI) to decolorize Reactive Black 5 and Reactive Red 198 in synthesized wastewater and investigated the effects of the iron particle size, iron dosage and solution pHs on the destruction of reactive black 5 and RR198. The removal kinetic rates ( $k_{obs}$ ) of RB5 ( $0.0109 \text{ min}^{-1}$ ) and RR198 ( $0.0111 \text{ min}^{-1}$ ) by 0.5% NZVI were many times higher than those of microscale zerovalent iron (ZVI) ( $0.0007 \text{ min}^{-1}$  and  $0.0008 \text{ min}^{-1}$ , respectively). The iron dosage increment exponentially increased the removal efficiencies of both Reactive Black 5 and RR198. Additionally, lowering pH from 9 to 5 increased the decolorization kinetic rates of both reactive black 5 and RR198 by NZVI. The destruction of azo bond (N=N) in the chromospheres of both reactive dyes led to decolorization of dye solutions.

Greluk & Hubicki (2010) used strongly basic acrylic anion exchangers namely Amberlite IRA-458 and Amberlite IRA-958 for the removal of Reactive Black 5. Adsorption experiments indicated that the amount of the dye adsorbed on both Amberlite IRA-458 and Amberlite IRA-958 were dependent on the initial dye concentration in the range of 50–500 mg/L. Modeling of kinetic results showed that the sorption process of the dye adsorption on both anion exchangers was best described by the pseudo second-order kinetic model in the investigated concentration domain. The effect of temperature on dye removal showed that the maximum capacity was obtained at 318 and 308 K for the dye adsorption on Amberlite IRA-458 and Amberlite IRA-958, respectively. The adsorption isotherm data were fitted well to the Langmuir isotherm and according to this model, Amberlite IRA-458 and Amberlite IRA-958 exhibited the highest monolayer sorption capacity of 1295.93 and 1723.964 mg/g.

Chatterjee *et al.* (2010) used Zero Valent Iron (ZVI) particles for the reductive degradation of Reactive Black 5 in aqueous solution. The sizes of the synthesized ZVI particles were in the microscale range, with an average diameter of  $13.57 \mu\text{m}$ . The efficiency of surfactant-treated ZVI particles for the decolorization of reactive black 5 solution was studied with three different surfactants namely Triton X-100, Cetyl Trimethyl Ammonium Bromide and Sodium Dodecyl Sulfate. The normalized residual concentration after decolorization of 500 mg/L Reactive Black 5 by ZVI for 3 h was 0.236, while ZVI particles treated with Triton X-100 (0.5 g/L), Cetyl Trimethyl Ammonium Bromide (CTAB) (1.0 g/L), and Sodium Dodecyl Sulfate (SDS)

(2.5 g/L) exhibited normalized residual concentration of 0.172, 0.154, and 0.393, respectively, after 3 h. The color removal efficiency was found to be increased with the decrease in initial pH of dye solution and ZVI exhibited good color removal efficiency at acidic pH. Decolorization kinetics by pseudo-first-order rate equation showed that removal rate was increased after treatment with Triton X-100 as well as CTAB, while that was reduced after SDS treatment.

Karatas *et al.* (2010) investigated the efficiency of the sequential anaerobic - aerobic system for decolorization of Reactive Black 5. The synthetic wastewater contained 150 mg/L dye and 3000 mg/L glucose-COD. An upflow anaerobic sludge blanket (USAB) (CSAR) reactor and continuously stirred aerobic reactors were used to remove color and COD. The methane gas production efficiencies were also investigated under the anaerobic conditions. The UASB - CSAR were operated at different organic loading rates (2.4–22.5 Kg COD/ $\text{m}^3 \cdot \text{day}$ ) and hydraulic retention times (3.2 - 30.1 h). The COD removal efficiencies decreased from 61 to 36.7% with increases in organic loadings from 2.4 to 22.5 Kg COD/ $\text{m}^3 \cdot \text{day}$  in the anaerobic UASB reactor. The color removal decreased from 99.8 to 90.7% when the hydraulic retention time decreased from 30.1 to 3.2 hours. The methane production efficiencies obtained were 75 and 38.3% at the organic loading rates of 2.4 and 22.5 Kg COD/ $\text{m}^3 \cdot \text{day}$  respectively. The effects of both sludge retention times and the food/mass (F/M) ratio on the COD removal efficiencies were investigated in the aerobic reactor. COD removal efficiencies of 62.2 and 86.3% were obtained at 2 and 19 days sludge retention time in the aerobic reactor. The COD removal efficiencies were found to be 86.3 and 62.2% at F/M ratios of 0.112 and 1.569 Kg COD/Kg day. The color and COD removal efficiencies obtained were 99.8% and 95% by using 150 mg/L of Reactive Black 5 dye concentration in the sequential anaerobic aerobic reactor.

Erdal & Taskin (2010) reported the decolorization of Reactive Black 5 by *Penicillium chrysogenum* MT-6. Dye uptake was strongly depended on mycelial morphology. Small uniform pellets with 2 mm size and nutrient-poor medium were found to be better for dye uptake. Optimal conditions for dye uptake were determined as initial pH of 5.0, shaking speed of 150 rpm, temperature of  $28^\circ\text{C}$ , spore concentration of 107/ml, 10 g/L sucrose and 1 g/L ammonium chloride. The maximum removal/uptake of dye by fungus was 89% (0.267 g removed-dye) with 3.83 g/L of biomass production at an initial dye concentration of 0.3 g/L in 100 h. The fungus was found to be a good bio-system for the decolorization of the medium containing Reactive Black-5.

Rivera *et al.* (2011) studied the decolorization of Reactive Black 5 by an electrochemical technology in both cubic and cylindrical cell configurations. Low

decolorization was detected in the treatment of pure solutions of Reactive Black 5, but a significant extent of decolorization was observed in the presence of Na<sub>2</sub>SO<sub>4</sub>. The extent of decolorization was largely dependent on the cell configuration and the best results were obtained when the cylindrical cell was employed. Nearly complete decolorization was achieved in 3 h for an effluent containing 70 mg/L Reactive Black 5 and 0.1 M Na<sub>2</sub>SO<sub>4</sub> and the TOC removal was approximately 95%. In the presence of the non-inert electrolyte NaCl, the complete decolorization was detected. However, due to the chloro-organic compounds formed in the electrochemical oxidation with NaCl, the TOC removal in the most optimal condition was approximately 93%.

Mahadwad *et al.* (2011) studied the photocatalytic degradation of Reactive Black 5 using supported TiO<sub>2</sub> photocatalyst based adsorbent as a semiconductor photocatalyst in a batch reactor. The synthesized photocatalyst composition was developed using TiO<sub>2</sub> as photoactive component and zeolite (ZSM-5) as the adsorbent. The optimum formulation of supported catalyst was found to be (TiO<sub>2</sub>: ZSM-5 = 0.15:1) which gave the highest efficiency with 98% degradation of 50 mg/L reactive black 5 solution in 90 min. The reduction in the chemical oxygen demand (COD, 88%) proves the mineralization of the Reactive Black 5 dye along with the colour removal. The supported TiO<sub>2</sub> was found to be stable for repeated use.

## CONCLUSION

This review makes a simple comparison among various physicochemical methods namely photo catalysis, electrochemical, adsorption, hydrolysis and biological methods such as biosorption and bioaccumulation and also discussed the merits and demerits of these methods involved in the decolorization of reactive black 5.

The main disadvantages of the physical methods such as adsorption, ion exchange and membrane filtration were that they simply transfer the dye molecules to another phase rather than destroying them and they are effective only when the effluent volume is small.

The main disadvantage of the chemical methods such as chemical oxidation, electrochemical degradation and ozonation were the requirements of an effective sludge producing pretreatment. Also, these chemical methods with high cost were rarely used in the actual treatment process and the disposal of sludge containing chemicals at the end of treatment requires further use of chemicals.

Conventional water treatment technologies such as solvent extraction, activated carbon adsorption and chemical treatment process such as oxidation by ozone (O<sub>3</sub>) often produce hazardous by-products and generate large amount of solid wastes, which require costly disposal or regeneration method.

The requirement of chemicals and the temperature to carry the electro chemical reaction was less than those of other equivalent non-electrochemical treatment. It can also prevent the production of unwanted side products. But if suspended or colloidal solids were high in concentration in the waste water, they slow down the electrochemical reaction. Therefore, those materials need to be sufficiently removed before electrochemical oxidation.

Compared to the conventional methods, application to recalcitrant materials, operation at high and low contaminant concentrations over a wide range of pH, temperature and salinity range, biomass acclimatization is irrelevant and straight forward process control are the potential advantages of the enzymatic treatments.

Biodegradation, Bioaccumulation and biosorption were the three main technologies used in biological dye removal process. They possess good potential to replace conventional methods for the treatment of dye bearing industry effluents. Biological processes can be carried out in situ at the contaminated site, these were usually environmentally benign i.e., no secondary pollution and they were cost effective. These were the principle advantages of biological technologies for the treatment of dye industry effluents. Hence in recent years, research attention has been focused greatly on biological methods for the treatment of effluents. The disadvantage of the degradation process is that it suffers from low degradation efficiency or even no degradation for some dyes and practical difficulty in continuous process. The important disadvantage bioaccumulation process is using living organism, which is not advisable for the continuous treatment of highly toxic effluents. This problem can be overcome in biosorption by the use of dead biomass, which is flexible to environmental conditions and toxicant concentrations.

By considering all the above said factors, as a researcher, our prime aim is to find out the environmental benign technique to remove hazardous materials from environment. In this concern, from the literature we conclude that, the biosorption is harmless and cost effective method to achieve this goal and also this technique will not produce any secondary pollutants. The natural materials like marine algae, waste materials from industry and agriculture waste are very much useful in the process of removing the pollutants as biosorbent. Thus we proposed that, the biosorption is an opt method to remove the toxicants.

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