Removal of Reactive Blue 19 from Wastewaters by Physicochemical and Biological Processes-A Review

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Summary: The developments for the removal of reactive blue 19 dye (RB 19) by various physicochemical methods such as sonolysis, photocatalysis, electrochemical, ozonolysis, adsorption, hydrolysis and biological methods like microbial degradation, biosorption, chemical and biological reductive decolorization has been presented. It was found that none of the individual physical and chemical technique can be used in wastewater treatment with good economics and high energy efficiency. For example, the application of adsorption method is restricted as adsorbent materials requires frequent regenerations; ozonolysis and photocatalysis processes can efficiently decolorize and degrade the dye but these face operational difficulties are not cost effective. Similarly the performance of biological treatment processes is required to enhance by developing efficient strains of bacteria, fungi. The comparison of physiochemical and biological treatment of RB 19 dye suggested that biological treatment of RB 19 dye is comparatively cost-effective process. However, the integrated approach can be used to decolorize and degrade the dye by combining both physicochemical and biological processes.

Introduction

A variety of chemically different dyes are used for various industrial applications such as textile dyeing, paper printing, leather, shoe polish, plastics, food coloring *etc* [1]. A significant amount of these dyes enter the environment as wastewater [2]. There are more than 100,000 kinds of dyes commercially available and over 7 x 10^5 tones of dyestuff are produced annually [3]. These dyes are resistant to light, water and oxidizing agents and are therefore difficult to degrade once released into aquatic systems. The presence of very low concentrations of dyes in effluent can be highly visible and undesirable [4] on aesthetic grounds. Their presence disturbs aquatic communities present in ecosystem by obstructing light penetration and oxygen transfer into water bodies [5].

Dyes are synthetic in nature and have complex aromatic molecular structures which make them stable and difficult to biodegrade. Dyes are usually classified into three categories: anionic, cationic and non-ionic dyes. Further these categories cover variety of dye types *i.e.* anionic (direct, acid and reactive dyes) cationic (basic dyes) and non-ionic (disperse dyes) [6, 7]. In anionic and non-ionic dyes, the chromophores are mostly azo or anthraquinone groups. The reductive cleavage of azo linkages is responsible for the formation of toxic amines in the effluent. Anthraquinone-based dyes are persistent due to their fused aromatic structures and thus remain colored for a longer time in the wastewater. Reactive dyes are typically azo-based chromophores combined with different types of reactive groups *e.g.*, vinyl sulfone, chlorotriazine, trichloropyrimidine, difluoro-chloropyrimidine *etc*. They are used extensively in textile industries regarding favorable characteristics of bright color, water-fast, simple application techniques with low energy consumption [8-13] These water-soluble reactive dyes are the most problematic and considered an objectionable type of pollutants because they are toxic [14,15] generally due to oral ingestion, inhalation, skin and eye irritation, skin sensitization. They are also carcinogenic [16].

Reactive Blue 19 Dye

Reactive Blue 19 dye is an anthraquinone-based vinylsulphone dye. It is used in dyeing of cellulosic fibres. In different studies RB-19 was selected as a model compound because of its low fixation efficiency (75-80%) on cellulose due to the competition between the formation of reactive vinyl sulfone and formation of 2-hydroxyethylsulfone (Fig. 1). The 2-hydroxyethylsulfone does not fix on the cellulose fiber [17, 18]. Without adequate treatment, the dye may be stable and remained in the environment for a longer time, *e.g.* the half-life of RB-19 is about 46 years at pH 7 and 25 °C [17]. Due to chemical stability and low biodegradability of RB-

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19, a wide range of methods has been developed for their removal from waters and wastewaters to decrease their impact on the environment.

Treatment Methodologies

In this article various physicochemical methods and biological methods for the treatment of RB 19 are described. The physicochemical methods *i.e.*, sonolysis, photocatalysis, electrochemical, ozonation, adsorption, hydrolysis and biological methods *i.e.*, microbial degradation, biosorption, chemical and biological reductive decolorization for RB-19 removal from wastewater have been reviewed. The objective of this review is to compile the techniques for the removal of RB-19 from the wastewaters.

Physicochemical Methods

Sonolysis

Sonolysis is the use of ultrasonic waves for the degradation and decolorization of dyes. This attracts the attention as a new harmless treatment process. It is one of the numbers of intensification technologies that have undergone serious and extensive development over the past 10-15 years [19]. The mechanism proposed for the sonochemical processes is usually based on the formation of short-lived radical species generated in violent cavitation events. Cavitation is a micro-bubbles formation phenomenon (Fig. 2), in which the growth and collapse of microbubbles occur in extremely small interval of time *i.e.* in microseconds releasing large amount of energy [20]. The release of extreme temperature and pressure during the bubble collision causes the breakup of gas molecules that are trapped in these bubbles into localized high concentrations of oxidizing radical species. These radical species can effectively degrade the pollutants in water after their migration, by recombining or reacting with gaseous molecules within the cavity or in the surrounding liquid [21, 22]. The combination of the chemical and physical effects of cavitation allows the application of ultrasound in water and effluent treatment.

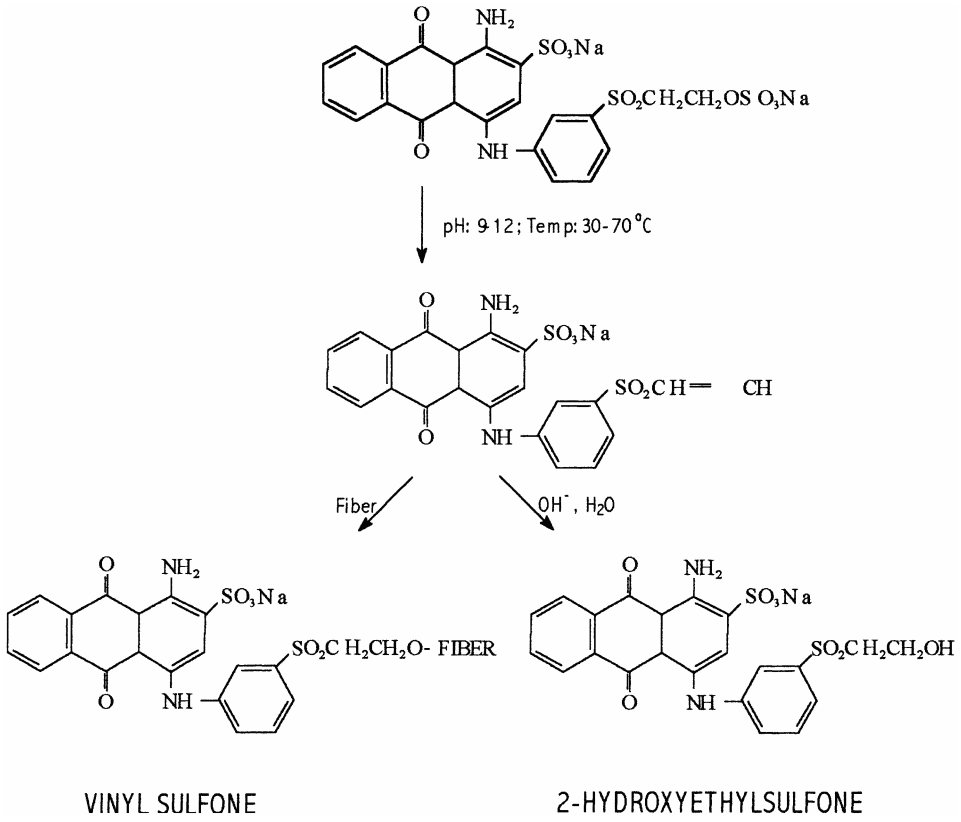

Fig. 1: Competition between formation of reactive and hydrolyzed forms of RB-19 [17].

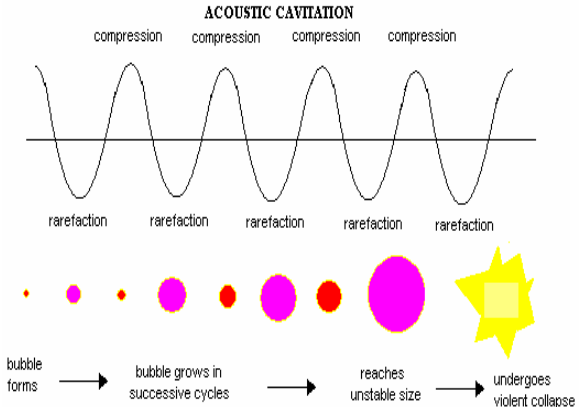

Fig. 2: Generation of an acoustic bubble

The studies on the degradation of RB-19 using ultrasound, activated carbon and combined ultrasound/activated carbon confirmed that decolorization of dye using combined ultrasound/activated carbon was greater than the individual methods and the use of ultrasonic irradiation was found to be useful for decolorization of RB-19 by adsorption from aqueous solution [23]. The combined ultrasonic irradiation with H_2O_2 yielded significant acceleration in color degradation and enhancement in chemical oxygen demand (COD) reduction [24]. The degradation of anthraquinone dyes using ultrasound, ozonation and ultrasound-enhanced ozonation reported the enhanced decolorization rates under conditions of constant ultrasonic radiation and continuous gas application. The increase in ultrasonic power was resulted to an increase in the mass-transfer coefficient [25]. Recently the combine use of ultrasound and electrochemical process for the enhanced degradation of RB-19 was investigated and found the combined process very effective in terms of chemical cost and energy consumption [26].

Photocatalysis

Photocatalytic oxidation process has been proposed as an alternative or supplement method for the removal and degradation of organic pollutants [27]. These processes usually utilize photocatalysts under UV irradiation. The oxidizing species either free holes or hydroxyl radicals are generated under these conditions (Fig. 3). The advantages of photocatalytic process are: (a) complete oxidation of organic compounds (b) without production of polycyclic product and (c) high efficiency towards oxidation of pollutant in ppm range [28].

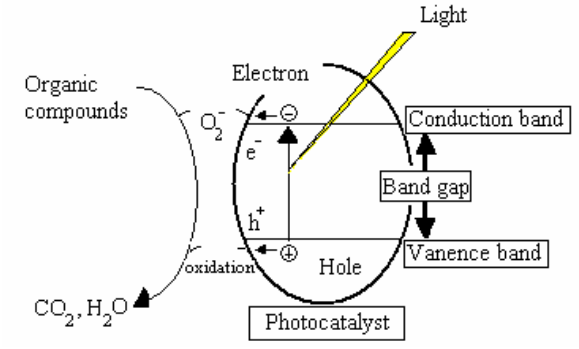

Fig. 3: Mechanism taking place on the surface of semiconductor.

Different photocatalysts have been investigated for the photodegradation of RB-19 *i.e.* $La^{3+}/S/TiO_2$ [29], UV/H_2O_2 [30], UV-A/$K_2S_2O_8$, UV-C/ $K_2S_2O_8$ [31], TiO_2 and ZnO [32]. The $La^{3+}/S/TiO_2$ photocatalyst showed strongest absorption for visible light (λ > 400 nm) and highest activities for degradation of RB-19 in solution. UV/H_2O_2 resulted in high color removal. Among photochemical oxidation processes (UV-A/$K_2S_2O_8$, UV-C/$K_2S_2O_8$) and chemical oxidation processes (dark/$K_2S_2O_8$), UV-C/$K_2S_2O_8$ showed much improved efficiency. The photocatalytic decoloration of RB-19 in aqueous suspension of TiO_2 and ZnO reported that ZnO has greater degradation activity than TiO_2. The degradation of reactive dyes (yellow 2, orange 16, red 2 and anthraquinone reactive blue 19) can best be obtained by the use of photo-assisted catalytic activity [33]. Recently Fe(III)/H_2O_2/solar UV process was employed to treat RB 19. The complete decolorization and 90 % TOC removal with 50 mg L^{-1} dye concentration with 2677 mg L^{-1} H_2O_2 and 0.5 mM Fe (III) at 10 L h^{-1} flow rate was obtained after 8 h of exposure to the solar irradiation [34].

Electrochemical

Electrochemical process is most popular procedure for the removal of organic compounds. The process uses different electrodes and hydroxyl radicals are produced in solution by electrolysis, which chemically reacts with pollutants. Organic compounds oxidation takes place indirectly through the generation of short lived species in solution. The electrochemical oxidation of organic compounds in the solution usually follows two steps using the traditional anodes;

1. Anodic electrolysis of water resulted the formation of hydroxyl radicals (OH) that are

adsorbed on to the active sites of the electrode M [35].

$$H_2O + M \rightarrow M^{-} \cdot OH + H^{+} + e^{-} \quad (1)$$

2. The oxidation of organic pollutant R by the adsorbed hydroxyl radicals that resulted the formation of RO which is the oxidized organic product. The oxidized product can be further oxidized by successive hydroxyl radicals that are continuously formed by the anodic discharge of water. The main side reaction in this process is the formation of oxygen, which is again used in process reactions [35].

$$R + M^{-} \cdot OH \rightarrow M + RO + H^{+} + e^{-} \quad (2)$$
$$H_2O + MOH \rightarrow M + O_2 + 3H^{+} + 3e^{-} \quad (3)$$

Electrochemical oxidation is an emerging technology and effective means for the treatment of synthetic and actual textile effluents [36]. Electrochemical methods such as electrocoagulation and electrooxidation have been widely used for treating reactive dyes and several applications have been recently reviewed [37]. Electrooxidation over graphite anodes, TiO_2, Pt, IrO_2, several Ti-based alloys and more recently, boron-doped diamond electrodes in the presence of a supporting electrolyte typically NaCl has been used for the decontamination of various reactive dyes [38].

A number of current studies reported the use of electrooxidation to treat model solutions containing RB-19. The electrochemical performance of doped with Fe and F (together or separately) or pure Ti–Pt/b-PbO_2 electrodes for the oxidation of simulated wastewaters containing the RB-19 were conducted. The Fe, F-doped PbO_2 electrodes were proved to be effective for the mineralization of the RB-19 [38, 39]. The photo-electrochemical oxidations of organic pollutants have been reported to improve the degradation efficiency of dyes [40]. The electrochemically assisted photocatalytic degradation of RB-19 on a dimensional stable anode (DSA), Ti/Ru$0._3$ Ti$0._7O_2$ electrode was studied and found decolorization percentages higher than 95% and TOC removal of about 52% during a period of 120 min. The electro-oxidation of RB-19 solutions at pH 11.0 in a quartz three-electrode cell equipped with this anode, only achieving 35% decolorization efficiency and 9.6% TOC removal after 2 h of electrolysis [41]. The applicability of electro-chemical-assisted photo degradation process for the treatment of RB-19 using TiO_2/Ti photoanode was also investigated and found that the method is more suitable when applied at the final stages of wastewater treatment where effluents have undergone pre-treatment [42].

Ozonation

Ozonation is one of the most efficient methods for eliminating color and textile dyes [43]. The main advantage of ozonation is its direct application, in its gaseous state with out generating large quantities of residues which need further disposal. It is found that the ozone is a strong oxidant and is able to form the nonselective, more powerful oxidant *i.e.*, hydroxyl radical [44]. Thus it can effectively break down the complex aromatic rings of dyestuffs, resulting in the degradation and decolorization of the dye compounds [45]. Ozone reacts more effectively with reactive dyes than with other types, such as acid, disperse and sulfur dyes. The literature review showed that most of the ozonation studies have been focused on azo dyes [46] and very less information is available on anthraquinone reactive dyes [47]. RB-19 representative reactive anthraquinone dye was investigated with a semi-batch [48] and cylindrical batch reactor [49] by ozonation. In former the degradation and decolorization of RB-19 efficiencies were about 83 and 97% after 10 min and in later the COD and TOC were 55 and 17% with complete color removal respectively [48, 49]. Similarly Hsu *et al.* studied the decolorization of RB-19 solution in a new gas-inducing reactor under continuous process [50].

Beside the individual ozonation process a number of combined techniques have been used for the removal of RB-19. Ozonation and ultrasonic irradiation (O_3/US) combination is another attractive process for the treatment of wastewater; it has been keenly explored over the past several years. The mineralization of RB-19 in aqueous solution by coupling ozonation with sonolysis was investigated, ultrasonic irradiation showed insignificant results when used alone, but O_3/US treatment showed higher mineralization rate compared with ozonation alone [51]. The efficiency of the ozone-enhanced electrocoagulation (EC) process for the decolorization of RB-19 using iron electrodes in water was examined, more than 96% of color removal and 80% total organic carbon (TOC) removal were achieved. By applying a simultaneous ozonation process, efficiency of the EC process was found to be also improved [52]. A comparative study of RB-19 using enzymatic, photochemical and ozonation processes was conducted. Each process

showed specific attributes; at a very less reaction time the ozonation process leads to complete decolorization; however, effective mineralization of the dye was not observed [53].

Adsorption

Adsorption process has been found to be a well-known method of treating textile effluents. It is also used in a variety of separation and purification purposes in industrial processes. The adsorption method was also found to be very effective in terms of cost and ease of operation for color removal. Decolorization by adsorption is influenced by some chemical and physical factors like adsorbent surface area, dye-adsorbent interactions, particle size, time, pH and temperature [54].

A number of adsorbents have been used for the removal of RB-19 from wastewaters. andrzejewska *et al.* studied the effect of aminosilane-modified silica for the removal of RB-19. The application of aminosilane- modified silica proved to be very efficient as it can remove more than 90% of dye from solutions [55]. The modification of the rutile titanium dioxide surface using 3-aminopropyltriethoxysilane and *N*-2-(aminoethyl)-3-aminopropyltri- methoxysilane in various solvents (toluene, methanol, methanol and acetone water mixture) were studied and found the higher efficiency of adsorption of RB-19 [55]. The adsorption of RB-19 onto cross-linked chitosan/oil palm ash composite beads showed the much higher uptake of dye in acidic solutions than those in alkaline and neutral conditions and maximum adsorption observed at pH 6. The cross-linked chitosan/oil palm ash composite beads (low-cost adsorbent) were found to be an excellent adsorbent for reactive RB-19 removal [56]. The use of modified bentonite (clay minerals) with a cationic surfactant (dodecyltrimethyl-ammonium (DTMA) bromide) as an adsorbent was carried out successfully by Ozcan *et al.* to remove RB-19 by adsorption from aqueous solutions. The study suggested that in acidic solutions the high adsorption capacity of DTMA-bentonite is due to the strong electrostatic interactions between its adsorption site and dye anion [57]. Further study was conducted by modifying bentonite with 1,6-diamino hexane (DAH) as a modifying agent. The characterization of modified bentonite (DAH-bentonite) was accomplished by using FTIR, TGA, BET and elemental analysis techniques. The results indicated that DAH-modified bentonite in acidic pH was also suitable adsorbent for the adsorption of RB-19 [58].

Hydrolysis

Hydrolysis is one of the principal detoxification mechanisms for organic compounds. At high temperature and pressure, pure liquid water becomes surprisingly effective medium and acts simultaneously as a convenient solvent, catalyst and reagent for reactions that are typically catalyzed by acid, bases or in the presence of organic solvents. By using this process very facile and selective transformations are accessible by reactions in pure hot water without the need to use the potentially toxic environmentally destructive materials such as co solvents or added catalysts.

The hydrolysis process was an unexplored alternative especially for the treatment of textile reactive RB-19. It converts RB-19 dye in simple and non toxic end products. The process was very effective in decreasing the chemicals cost, as a number of other treatment techniques used extensive chemicals for the degradation of organic compounds [59].

Biological Treatment Methods

It is the most common and well-known process used for the treatment of dye wastewater. Large number of species has been studied for decolouration and mineralization of various dyes. The methodology offers considerable advantages like being relatively inexpensive, having low running costs and non toxic end products after complete mineralization [60].

Microbial Degradation

The use of microorganisms is an effective method for the bio-degradation of dyes and is considered one of the most cost-effective alternatives when compared with other chemical and physical processes. Bacteria and fungi are the two microorganism groups that have been most widely studied for their ability to treat dye wastewaters. A number of species has been used (Table-1) for the degradation and decoloration of RB-19 [61]. Recently different yeasts types for their dye uptake capacities have been studied. They are widely used in a variety of large-scale industrial fermentation processes. The waste biomass from these processes is a potential source of cheap adsorbent material. Aksu *et al.* showed the performance of yeasts to remove RB-19 as a low-cost adsorbent [62, 63].

Fungal strains capable of decolourizing different varieties of dyes have been studied and white rot fungi has also been employed for the decoloration of a number of textile dyes. Hence,

Trametes Versicolo [64, 65] *Trametes modesta*, *Tramete hirsut*, *Sclerotium Rolfsii*, *Trametes villosa* [66, 67][*Ganoderma sp. Irpex lacteus*, *Rigidoporus sp*. *Phanerochaete magnoliae*, [68, 69, 75] *Pleurotus Pulmonarius* [70] *Pycnoporus cinnabarinus* [71] was able to decolorize the RB-19. The immobilization of *P. chrysosporium* on the biostructural matrix of loofa sponge as a dye biosorbent system for the removal of RB-19 from aqueous solution was investigated and found that loofa sponge immobilized fungal biomass (LSIFB) can be used as a useful biosorbent for the efficient removal of RB-19 [72].

A biofilm hydrolytic-aerobic combined treatment process based on mixed culture was used to degrade RB-19. The results showed that the majority of color and chemical oxygen demand (COD) were removed in the hydrolytic stage and in the subsequent aerobic process, respectively. The experimental results showed that the combined biofilm hydrolytic-aerobic process was an efficient and a stable process for the treatment of RB-19 containing wastewater with 93 batches for more than 3 months. In the presence of 2,000 mg L^{-1} of glucose, color and COD removal efficiencies of RB-19 could be up to 94.5 and 99. 4 %, respectively, by the aerobic treatment for 2 h and hydrolytic treatment for 10 h [73]. Kokol *et al.* demonstrated the production of ligninolytic enzymes laccase and Mn-Peroxidase by liquid cultures of the white-rot fungus *Ischnoderma resinosum* for decoloration of Remazol Brilliant Blue R. It was found that Mn-peroxidase decolorized the RB-19 while Laccase remained inactive. But the addition of the redox mediators; hydroxyl-benzotriazole (HBT) and violuric acid (VA) with laccase decolorized the dye more efficiently [74]. In recent study the decolorization of RB-19 was investigated by *Ganoderma* fungus using statistical optimization tools and response surface methology (RSM). At optimized conditions *i.e.*, temperature of 27 $^{\circ}$C, glycerol concentration of 19.14 mg L^{-1} and pH = 6.3, 94.89% color removal was achieved [75] as compared to other results reported in literature [76, 77].

Biosorption

The term biosorption indicated several metabolism-independent processes (chemical and physical adsorption, complexation, ion exchange, electrostatic interaction, chelation and microprecipi-tation) taking place in the cell wall rather than oxidation though aerobic or anaerobic metabolism. Both living and dead (dried, heat killed, acid and/or otherwise chemically treated) biomass can be used to eliminate harmful organic compounds. Textile dyes differ to a great extent in their chemical structures and hence their interactions with microorganisms depend on the chemical structure of a particular dye, characteristics of the dye solution or wastewater, the specific chemistry of the microbial biomass and environmental conditions (temperature, ionic strength, pH, existence of competing organic or inorganic ligands in solution) [78-81]. A large variety of microorganisms including fungi, bacteria and yeasts were used for the biosorption of numerous dyes due to their special surface properties. Few studies have been also conducted in recent years on biosorption of RB-19.

Table-1: List of organisms decolorizing the RB-19 [61].

Dye	Organisms	Reference
	Eukaryota Yeasts—Ascomycota	
	Candida lipolytica	**[63]**
	Candida tropicalis	**[62]**
	Kluyveromyces Marxianus	**[63]**
	Saccharomyces Cerevisiae	**[63]**
	Schizosaccharomyces pombe	**[63]**
	Filamentous- Fungi – Basidiomycota	
	Ganoderma sp.	**[69, 75]**
	Irpex lacteus	**[68, 69]**
	Phanerochaete magnoliae	**[69]**
Reactive Blue 19 dye		
	Pleurotus Pulmonarius	**[70]**
	Pycnoporus cinnabarinus	**[71]**
	Rigidoporus sp.	**[69]**
	Sclerotium Rolfsii	**[67]**
	Trametes hirsuta	**[67]**
	Trametes modesta	**[69]**
	Trametes versicolo	**[66,67]**
	Trametes villosa	**[66]**
	White Rot – Basidiomycete	
	Phanerochaete chrysosporium	**[72]**
	Ischnoderma resinosum	**[74]**

Depending on the species of microorganism and the RB-19 used different binding capacities have been observed in Table-2 [82-85]. Mahony *et al.*

showed the ability of oven-dried *R. arrhizus* biomass for the biosorption of RB-19 in a batch system from aqueous solutions. The results showed that pH 2.0 was found suitable for the maximum biosorption of dye by oven-dried *R. arrhizus* biomass from aqueous solutions. The change in uptake capacity of the *Rhizopus* biomass at different pH conditions in terms of its effective isoelectric point was further explained. The biomass have a net positive charge at pH values below the isoelectric point (<4.0). It is anticipated that imadazoles or amines (nitrogen-containing functional groups) in the biomass were also be protonated at lower pH values. These charged sites become available for electrostatic binding of anionic reactive dyes. It was also concluded that the RB-19 uptake by oven-dried *R. arrhizus* was improved by increasing dye concentration [82].

Table-2: Biosorption of RB-19 by different organisms [83].

Dye	Biosorbent	Biosorption capacity (mg of dye/ g of biomass)	Reference
Reactive Blue 19 dye	*Botrytis cinerea*	42 (13.0)	[83]
	Candida rugosa	8 (8)	[83]
	Cryptococcuss heveanensis	23 (22)	[83]
	Dekkera bruxellensis	19 (36)	[83]
	Geotrichum fici	17 (60)	[83]
	Kluyveromyces waltii	14 (20)	[83]
	Pichia carsonii	5 (3)	[83]
	Rhizopus arrhizus	90	[82]
	Saccharomyces cerevisiae	69 (52)	[82]
	Tremella fuciformis	35 (41)	[83]
	Xeromyces bisporus	60 (0)	[83]
	Funalia trogii	10.7	[85]
	Penicillium oxalicum	160	[86]

Values in parentheses represent percent removal

Polman and Breckenridge investigated 30 species of yeast, bacteria and filamentous fungi to eliminate RB-19 from simulated plant waste effluents. They used both live and dead forms of each of the species and found that among the 21 microbial species capable of binding RB-19 waste, 71% were more efficient dye binders in the dead form than in the live form. They suggested that this may be as a result of an increase in the surface area for adsorption due to cell rupture upon death [83, 84]. Chulhwan *et al.* investigated two methods for RB-19 decolorization by cultivation of fungi in either a liquid or on a solid phase via repeated-batch cultivation. The results illustrated that *Funalia trogii* when cultivated on a solid phase; it showed the greatest efficiency for decolorizing the dye rather than liquid-phase. Also the *F. trogii* ATCC decolorization mechanisms involved a complicated interaction of biosorption and enzyme activity [85]. The mycelium of *P. oxalicum* rapidly adsorbed the RB-19 with high adsorption capacities. Almost up to 60% of dye removal was achieved in 10 min and 91% in 80 min. The maximum adsorption capacities were found up to 160 mg g^{-1} at 20 $^{\circ}$C [86].

Chemical and Biological Reductive Decolorization

The reductive decolorization of dyes is a combination of chemical and biological mechanism under anaerobic condition. Under anaerobic conditions using either pure cultures or granular sludge, poor reductive decolorizations with different dyes were reported. Also anthraquinone dyes are shown to be nonbiodegradable [87, 88]. Some dyes are also proved to be noxious to the anaerobic microorganisms and in some cases it leads to permanent loss of methanogenic activity even at very low concentrations. For example the inhibitory concentration of RB-19 (55 mg L^{-1}) at 30 $^{\circ}$C, exert 50 % reduction in methanogenic activity [87, 89]. The decolorization of RB-19 using anaerobic granular sludge under mesophilic conditions is presented in Table-3 [90-92].

Table-3: Decolorization of RB-19 by anaerobic granular sludge under mesophilic conditions [88].

Dye	Decolorization (%)	Reference
Reactive Blue 19 dye	70	[90]
	99	[90]
	90	[92]
	>84	[93]

Andre *et al.* reported that the RB-19 was mainly toxic due to the acetate-utilizing methanogens, while acidogens were not affected by the dye toxicity [87]. High and moderate decolorization was also found for the anthraquinone dyes after a long incubation under anaerobic conditions with different carbon sources, even with the inhibition of the methanogenic activity [93]. Microbial reductive decolorization of RB-19 using a methanogenic culture fed with a peptone/dextrin mixture at initial concentrations ranging from 50-300 mg L^{-1} was attained with the color removal of 90-95%. Based on cumulative methane production, hydrogen concentration data and volatile fatty acids (VFAs), RB-19 inhibited both the methanogenic and acidogenic populations in the mixed cultures, although the highest inhibitory effect was on the methanogens. Thus, it was found that RB-19 was very much toxic to the methanogenic culture [94].

Conclusions and Future Recommendations

Different treatment methods have been employed and studied for the destruction of RB-19 containing wastewater. However, further research is needed to justify the decoloration and degradation efficiency for large variety of dye compounds and industrial effluents. In physicochemical methods, adsorption is an effective treatment technique applied for the purification of wastewaters but their application is restricted by the need to regenerate the adsorbent materials. Ozonation provides fast decoloration and degradation of dyes but the process is not completely accepted due to its expensive nature and operational problems and the disadvantage of photocatalysis is the excessive cost of artificial UV light. Hydrolysis process alone is not sufficient; a combination of techniques like physico-chemical, biological, enzymatic, *etc*. is required to enhance the degradation efficiency of process. Application of combined techniques for the decoloration and degradation of reactive dyes containing wastewaters can be expected in near future. The combination of ultrasound and electrochemistry may constitute an interesting technique for wastewater treatment because of its different beneficial effects *i.e.* enhanced mass transport, altered adsorption phenomena and surface effects, diminishing of electrode fouling, manipulation of reaction mechanism, production of altered product distributions, increased yields and current efficiencies, increased limiting current in analytical applications and lessened cell power requirements. It can be said here that application of sonoelectrochemistry for degradation of reactive compounds and in general for wastewater treatment looks to be very promising for those streams which are readily degradable by electrochemistry. Ultrasound will definitely enhance the effects induced by electrochemistry. Indeed, more studies are required in terms of application of sonoelectrochemistry for wastewater treatment to draw better conclusions.

In biological methods the bacterial, fungal and yeast strains are shown to be the main microorganism types capable of removing RB-19 from wastewater. Alive and dead microorganisms as biological adsorbents has attracted attention during recent years because of fastness, low cost, easy availability and operating conditions, high efficiency in detoxifying very dilute or concentrated effluents and no nutrient requirements and thus has been proposed to clean a variety of industrial organic compounds. Biosorption studies of organics are very limited and only sorption of selected toxic organics onto a few types of bacterial, fungal and yeast biomass have been reported. There is a need to study with other organic pollutants and to develop new strains which can be provided easily as waste and/or abundant biomass or can grow in simple, inexpensive medium and have high production rate and possess high biosorption capacity. In order to get better remediation of colored compounds from the textile effluents, a combination of aerobic and anaerobic treatment is suggested to give encouraging results. An advantage of such system is the complete mineralization which is often achieved due to the synergistic action of different organisms. Also, the reduction of the azo and anthraquinone bond can be achieved under the reducing conditions in anaerobic bioreactors and the resulting colorless aromatic amines may be mineralized under aerobic conditions, thereby making the combined anaerobic-aerobic azo dye treatment system attractive. Thus an anaerobic decolourization followed by aerobic post treatment is generally recommended for treating dye wastewaters.

The comparison of physiochemical and biological treatment of RB 19 dye suggested that bio-degradation of dyes is the efficient and cost-effective processes.

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