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Combinational System for the Treatment of Textile Waste Water: A Future Perspective

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Abstract: In recent times, control of pollution has been a major concern. Textile dyes which are important organic compounds are also significant industrial pollutants. Textile dyes are commonly xenobiotic in nature and are not degraded easily by biological systems. Currently the treatment of textile waste water for remediation of recalcitrant dyes is based on either physical, chemical and biological treatment. Each process has its own advantages as well as disadvantages and therefore various combinations have been tried to achieve efficient, eco-friendly and economic treatment of textile waste water. The present review is an attempt to summarise the three treatments and the possible combination in use. We have also proposed alternatives comprising of adsorption, chemical oxidation and biodegradation process. The proposed combination system involves use of pre treated sugarcane bagasse for adsorption of dyes followed by treatment of dyes with Fenton reagent for chemical oxidation which can then be easily biodegraded with suitable micro organisms under aerobic conditions.

Key words: Bagasse based adsorption, Fenton treatment, biodegradation, combinational method, reactive black 5.

Introduction

Textile waste water effluent consists of mainly two components: (1) effluent from preparation process and (2) effluent from dyeing process. Majority of waste water is released during the preparation process depending upon type of product. Effluents released from dying process, consists of dyes, salts and surfactants (Koyuncu, 2002). The dyes used in textile industry are varieties of synthetic organic compounds, forms the major constituent of the textile waste water and thus are also major pollutant. Of all the dyes produced 50% are azo dyes. The reactive dyes form a critical part of the azo-dye group which forms the largest group of colorants used in the industry (Zollinger, 1991). Reactive dyes are typically azo-based chromophore with different types of reactive groups, differs from all classes of dye in their ability to form covalent bond with cotton (Eren and Acar, 2006). Reactive dyes constitute the class of most problematic dyes due to the highly xenobiotic nature (Willmott et al., 1998). Municipal waste water treatment systems are inefficient in treatment of reactive dyes due to their resistance towards aerobic and short term anaerobic treatment (Shaul et al., 1991). Some azo dyes are found to possess carcinogenic properties (Brown and De Vito, 1993). Under aerobic conditions only small amount of dye can be precipitated or adsorbed, while under anaerobic conditions azo dyes are cleaved by microorganisms, forming potentially carcinogenic aromatic amines (Chung and Cerniglia, 1992).

The three methods for the treatment of textile waste water for the removal of dyes have been broadly categorized on the basis of principle involved. The physical treatment involves the physical removal. The chemical method involves the chemical degradation of the dyes while the biological treatment involves the biodegradation of the dye.

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Physical Treatments

A variety of physical methods have been devised for the removal of reactive dyes like adsorption based processes, membrane filtration, ion exchange and irradiation.

Adsorption Based Methods

Adsorption based method for the removal of industrially important dyes is now widely used owing to its high dye removal efficiency and low cost (Iqbal et al., 2007). A number of adsorbents like activated carbon (Pereira et al., 2003) and non-conventional adsorbents (Mckay et al., 1986) like coal, fly ash (Khare et al., 1987; Singh and Rawat, 1994) silica, wood, clay material (Theng and Wells, 1995; Juang et al., 1997) agricultural wastes and cotton wastes have been used. The decolourization process is governed by two related mechanisms: adsorption and ion exchange (Slokar and Le Marechal, 1997). The notable physiochemical factors that influence the efficiency of dye decolouration are dye-adsorbent interaction, contact time, pH, and concentration of dye as well as adsorbent (Rachakornkij et al., 2000).

Powdered activated charcoal as adsorbent is widely used owing to its high surface area, micro porous structure and radiation stability (Iqbal and Ashiq, 2007). In a study the monolayer adsorption capacity of powdered activated charcoal was found to be far better than that of other non-conventional adsorbents (Eren and Acar, 2006). One of the major drawbacks in the use of activated charcoal is the high cost arising due to the need for regeneration of the adsorbent resulting in 10–15% loss in sorption power and thus adds up to the cost. Another drawback is the limited range of specific adsorption behaviour for a particular dye (Iqbal and Ashiq, 2007) and hence has emphasising need for cheaper alternatives (Guruswamy et al., 2002).

Agricultural and industrial waste provides a cheaper option and can be used in bulk amount for large scale processes thereby limiting the need for regeneration. The agricultural wastes includes wood chips, straw, rice and wheat husk (Liew et al., 2005), banana and orange peel (Guruswamy et al., 2002), coir pith (Namasivayam and Kavitha, 2002), Chitosan (Uzun, 2006), corn and barley husk (Robinson et al., 2002) and treated bagasse (Rachakornkij et al., 2000), while the industrial waste includes coal, liginite, flyash, sludge and red mud have been used as adsorbents (Crini, 2006). The agricultural waste can be used in two ways; (1) to derive activated carbon from these wastes (Rodriguez-Reinoso, 1997) and (2) to use them directly in their native form with or without a simple preliminary treatment (Crini, 2006). Various researchers have reported varying degree of success with the use of agricultural waste as adsorbents.

Natural materials like clay, siliceous material and zeolites have been used as potential adsorbents due to its low cost, abundance, high sorption and ion exchange capacity (Babu et al., 2007). Variation in pH greatly affects the adsorption efficiency (Ozdemir et al., 2004). Side reactions such as air binding and air fouling with particulate matter prevents siliceous materials to be used commercially (Crini, 2006). Recently zeolites are being used as alternative where sorptive applications are required, due to their cage like structure suitable for ion exchange; enabling investigation using a fixed bed reactor incorporated modified organo-zeolite for the removal of reactive dyes (Benkli et al., 2005). Chitosan, a linear polymer of acetylamino-D-glucose and peat, a porous organic material have been used for removal of reactive dyes (Allen et al., 1998, Uzun, 2006).

Membrane Filtration

Membrane technologies can be differentiated into ultrafiltration, nanofiltration and reverse osmosis. Ultrafiltration has been successfully applied in many industries except textile industry (Watters et al., 1991). Nanofiltration and reverse osmosis are two widely used processes for dye removal. Nanofiltration is a technically feasible process for treatment of the dye bath at high water recoveries (Tang and Chen, 2002). The gel layer consisting of rejected dye formed in nanofiltration technique serves as a resistance to the permeation of dyes due to complete rejection of high molecule weight dyes, especially for the low salt concentrations. Colour removal decreases with increase in salt concentration (Koyuncu, 2002). The drawbacks include high priced membrane and high cost of energy. Periodical regeneration of membrane is required due to susceptibility of membranes to clogging. The filter cake obtained holds problem of disposal (Soares et al., 2006).

Ion Exchange Methods

The general opinion that ion exchange cannot accommodate a wide range of dyes and dying conditions hence was not considered suitable for dye treatment has been contradicted. Quaternized cellulose, an anion exchanger is used for dye removal as it hydrolyses reactive dye bonds through columbic association or with additional interactions (Slokar and Le Marechal, 1997). Anion exchangers like strong basic S6328a and weak basic MP62 exhibit good sorption characteristics for reactive dyes. Factor influencing dye uptakes by both the resins were competition of inorganic anions sulphate, carbonate and phosphate (Karcher et al., 2002). Advantages of ion exchange process are regeneration of solvent as well as dye and no loss of adsorbent. The drawbacks include high cost and use of expensive solvent (Robinson et al., 2002).

Irradiation

Various radiations like ultraviolet, radio waves and ultrasound waves have been used for generation of free radicals which attack on the dye resulting in its degradation. The photo catalytic degradation of dyes using ultraviolet rays suggested that increase in pH, increases the reaction rate (Chu and Ma, 1998). Pulse radiolysis experiments performed for the removal of reactive black 5 showed the generation of short lived intermediates, hydroxyl radical and hydrogen ion intermediates which destabilizes the azo group and the aromatic ring structure favouring dye decolouration (Dajka et al., 2003). The reported disadvantage associated with the use of radiations for dye removal is the requirement of sufficient quantities of dissolved oxygen required for organic substances to be broken down effectively by radiation (Robinson et al., 2002).

Chemical Methods

Physical methods being non-destructive cannot be used for complete treatment of dye effluent as it requires further post-treatment of solid wastes that adds to the cost of the process while biological methods, because of high resistance of synthetic dyes to aerobic degradation of organic compounds show low efficiency (Sohrabi and Ghavam, 2008**)**. Chemical methods although have many drawbacks, are commonly used because of their simplicity and economic benefits. Chemical methods are mainly based on oxidative processes known as Advanced Oxidation Processes (AOP). Advanced oxidation processes include number of methodologies based on the generation of highly reactive and non-selective hydroxyl radicals that cause the destruction of organic pollutants of wastewater and waste. Some of them include the use of ozone (O_3), UV/H_2O_2, UV/TiO_2 and Fenton reagent (Sudarjanto et al., 2005). The main advantages of advanced oxidation method are high treatment efficiency, less reagents consumption due to fast reaction rates and degradation of resulting carcinogenic compounds (Colonna et al., 1999).

Ozonation

Chemical oxidation with ozone (O_3) plays many important roles in the treatment of textile wastewater containing reactive dyes such as in decolorization of dyes (Liakou et al.,1997), reduction of inert Chemical Oxygen Demand (COD) fractions (Karahan et al., 2002), toxicity removal (De-Moraes et al., 2000; Meric et al., 2005; Selcuk, 2005) and pre-oxidation that enhance the biodegradability (Ledakowicz et al., 2001; Arslan et al., 2002; Baban et al., 2003) and post treatment of textile industry wastewater so that the effluent is suitable for discharge in environmental waterways (Lim et al., 2004).

O_3^- targets the chromophore group of reactive dye and converts it into smaller compound resulting in colourless effluent (Liakou et al., 1997). In ozonation, the ozone decomposition generates molecular ozone and hydroxyl radicals, both of them act as non-selective oxidizing agent (Hoigne and Bader, 1983). Process preference is significant for overall COD and colour removal and reduction of soluble non-biodegradable COD fraction for the optimum use of the chemical oxidation (Orhon et al., 2002). Pre-ozonation is preferred for simpler compound while post-ozonation is more effective for the breakdown of refractory organic compounds. Pre-ozonation is more efficient in COD reduction but only 85% colour removal is possible while post-ozonation offers complete colour removal but not so efficient in COD reduction (Orhon et al., 2002). The major advantage of ozonation is that ozone being in gaseous state occupies very less volume of wastewater sludge (Robinson et al., 2002). But the drawback of this process is the requirement of continuous ozonation because of short-life of ozone that adds to the cost of the process (Xu and Lebrune, 1999).

Photochemical Methods

This method employs mineralization of organic compounds into CO_2 or H_2O using chemicals such as H_2O_2 (Yang et al., 1998; Peralto-Zamora et al., 1999) or semiconductor catalyst such as TiO_2 under the influence of UV (Kiriakidou et al., 1999; Lachheb et al., 2002; Sivalingam et al., 2003; Konstantinou and Albanis, 2004). TiO_2 is widely used catalyst owing to its high photochemical stability in a broad pH range, its low cost and its non-toxicity (Konstantinou et al., 2004; Kiriakidou et al., 1999; Zielinska et al., 2001). The rate of removal of dye is affected by pH, intensity of UV irradiation, dye concentration and structure of dye molecule (Slokar and Marechal, 1997). TiO_2 coated on paper fibre used for the degradation of reactive black 5 and reactive yellow 145 resulted in conversion of heteroatoms (carbon, nitrogen and sulphur) to simpler inorganic products such as CO_2, nitrate and sulphate (Aguedach et al., 2005).

In case of H_2O_2/UV, UV light activates the H_2O_2 forming highly active hydroxyl radical which plays an important role in the conversion of high molecular weight stable organic compound to easily degradable small molecules (Chun and Yizhong, 1999). This Advanced Oxidation Process (AOP) is commonly used because of its low cost, simplicity of operation and even the chemicals required such as H_2O_2 are easily available and quite stable, complete mineralization of the dye is not possible, as 60% of COD was still remaining after treatment requiring further treatment for complete mineralization (Sudarjanto et al., 2005). The main advantage of this process is that no sludge generation (Zhang et al., 1999) and foul odours are greatly reduced (Robinson et al., 2001).

Fenton Process

Fenton process is widely used for the elimination of reactive dyes due to the catalytic oxidation and coagulation properties of Fenton reagent (Liu et al., 2007). Ferrous salt in the Fenton's reagent catalyses the decomposition of H_2O_2, another component of Fenton's reagent, to form hydroxyl radicals (Venkatadri and Peters, 1993; Chen and Pignatello, 1997; Chou and Huang 1999; Yuranova et al., 2004) capable of H-abstraction and addition to C-C unsaturated bonds in organic substrates (Noh and Schwarz, 1990).

In photo Fenton process, UV light directly influences the formation of hydroxyl radicals (Feng et al., 2003; Muruganandham et al., 2004). Lucas et al. (2006) efficiently decolorized RB5 using Fenton and photo Fenton process, with 97.5% and 98.1% decolourization suggesting similarities between the two processes but application of UV lamp play significant role in dye mineralization thereby enhancing the efficiency of photo Fenton compared to Fenton process. Till date, several modifications have been made in conventional Fenton process like solar photocatalytic degradation using photo Fenton (Chacón et al., 2005); using a new composite Fe_2O_3/carbon in Fenton process (Dantas et al., 2006), substitution of ferrous catalyst with other transition metal oxides/salts, called pseudo-Fenton catalysts (Teel et al., 2001; Dongre et al., 2002), use of chelated iron complexes for increasing the operational pH range (Watts et al.,1999; Aplin et al., 2001), incremental addition of peroxide to maximize oxidation efficiency (Merli et al., 2002), in situ generation of Fe^{2+} catalysts by application of direct current between suitable electrodes thus avoiding the need for iron salt addition (Huang et al.,1999; Chiarenzelli et al., 1997) and in situ generation of hydrogen peroxide at suitable anodes and through cathodic reduction of molecular oxygen (Alvarez-Gallegos et al., 1998; Qiang et al., 2002). Fenton process is very efficient and has many advantages, like requires very less contact time but the production of sludge during coagulation limits the application of this process.

Electrochemical Method

Electrochemical method is the most eco-friendly, easily operated method for effective dye removal, also referred to as "Green Technology" (Esteves and Saliva, 2004). Most of the electrolytic cell used for reduction of reactive dyes contains mercury electrode (Zanoni et al., 2001). Ti/Pt as anode and stainless steel 304 as cathode, type of electrode have been used for the treatment of textile wastewater containing dyes. The major toxic constituents of textile waste water are organic pollutants which are converted to simpler compounds such as carbon dioxide and water by the strong oxidizing potential of the chemicals produced during passage of wastewater through electrolytic cell. This method can also be incorporated with natural resources such as solar energy making it economical as well as environment friendly. Variations in electrolyte concentration, current density, pH of the solution and the initial dye concentration affect dye degradation by electrochemical method (Priya and Palanivelu, 2007). This is a potential method for pollution control having very high efficiency for degradation of recalcitrant pollutants without any sludge production. The major advantage of this method is the consumption of chemicals is very less, making it a cost effective method (Priya and Palanivelu, 2007).

Cucurbituril

Cucurbituril, a hexameric macropolycyclic caged compound, which is self-assembled from an acid-catalysed condensation reaction of glycouril and formaldehyde (Freeman et al., 1981; Karcher et al., 1999). In presence of dyes, solubility of cucurbituril is drastically decreased in wastewater. Due to its solubility issues, it is covalently fixed on to a fixed support material to serve as a feasible alternative for treatment of reactive dyes (Karcher et al., 2001).

Biological Methods

The lack of implementation of the various physico–chemical decolourization techniques is largely due to high cost, low efficiency and inapplicability to a wide variety of dyes. Biodegradation is an environment-friendly and cost effective alternative. However, anaerobic bio-degradation of dye-stuffs by azoreductase activity of microbes leads to the formation of highly biotoxic aromatic amines by reductive fission and exposure of such anaerobically degraded products to oxygen may result in reverse colorization (Hai et al., 2003), whereas the aerobic treatments are ineffective for textile wastewater (Banat et al., 1996).

The various biological methods currently employed include fungi, bacteria, actinomycetes or algae, i.e., based on the type or micro organism used. The biological methods can be aerobic, anaerobic or sequential aerobic-anaerobic systems (Hai et al., 2003). These methods may utilize either single or mixed population of micro-organisms, free cells or immobilized cells or enzymes. Efficiency of microbial treatment depends on the survival, adaptability and activity of the selected micro-organism (Kim et al., 1995).

Fungal Methods

In fungal decolourization, fungal biomass, i.e., only dead cells, for the biosorption of the dye whereas live cells, for effective dye degradation from the cells are utilized. The fungal cell wall is the major site for sorption, especially the chitin/chitosan components (Fu and Viraraghavan, 2001).

Commonly used white rot fungi, i.e., *Coriolus versicolor, Phanerochaete chrysosporium* and *Trametes versicolor* possess a highly oxidative and non-specific ligninolytic enzyme system like lignin peroxidase, manganese-dependent peroxidase (MnP) and laccase, which degrade a wide variety of recalcitrant compounds, especially the aromatic polluted complex (Tien and Kirk, 1988; Chivukula and Renganathan, 1995; Borchert and Judy, 2001; Chagas and Durrant, 2001). This extracellular enzyme system enhances the tolerance to high concentration of pollutants thus offering significant advantages for decomposition of recalcitrant compounds by this group of fungi (Srikanlayanukul et al., 2006). *Geotrichum candidum* found in soil and water and which utilizes cheap energy sources like acetate, ethanol and acetone may be effectively utilized not only for biodegradation of dyes in waste water but also for soil bioremediation (Kim et al., 1995). However, the major limitations being the long growth cycle, moderate decolourization rate, the aging of fungal mycelium and contamination by bacteria under non-sterile conditions have impeded their application in wastewater treatment (Borchert and Judy, 2001).

Yeast has been successfully used to treat a variety of industrial effluents. Two such isolates, *Debaryomyces polymorphus* and *Candida tropicalis*, have been reported to produce MnP and effectively decolorize some reactive dyes through biodegradation (Yang et al., 2005).

Bacterial Methods

Biodegradation without addition of an extra carbon source has been found to be difficult as dyes are deficient in carbon content. Few micro-organisms are capable of utilizing dyes as their sole source of carbon, whereas most micro-organisms require a co-substrate like glucose or yeast extract (Sarnaik and Kanekar, 1999). Decolourization of azo dye by *Pseudomonas aeruginosa* has been found to be dependent on carbohydrate metabolism and decolorization of certain textile dyes like Orange II, AO8 and AR-88 by *Sphingomonas sp.* strain ICX has been observed only in the presence of carbohydrate (Moosvi et al., 2007).

Shewanella sp. has a potential for bioremediation of dye-polluted wastewaters of alkaline pH discharged from textile and other dyestuff industries (Khalid and Crowley, 2008). *Actinobacillus succinogens, Mycobacterium avium, Proteus mirabilis, Pseudomonas luteola, Pseudomonas sp.* have also shown promising azo dye degradation potential (Oranusi and Ogugbue, 2005).

Algal Methods

The various algal species have also been used like *Chlorella* and *Oscillatoria* which have been found to be capable of degrading dyes to aromatic amines and further metabolism to simpler organic compounds or carbon dioxide (Banat et al., 1996).

Immobilization Techniques

Immobilized microbial cells offer a wide range of advantages like long retention time of biomass in the system, protection from high concentration of recalcitrant organics toxic to free cells, high potential of degradation of toxic chemicals faster than conventional wastewater treatment systems and the ease of use in a continuous reactor and the capability for scale up (Srikanlayanukul et al., 2006). The most efficient decolorization in bioreactors has been achieved by using immobilized mycelia of the dye degrading fungi (Oranusi and Ogugbue, 2005).

Enzymatic Methods

Enzymatic treatment can be an attractive option for wastewater treatment because of several reasons owing to advantages like their biocompatibility and the ease and simplicity of the process control, reduction of water costs, energy savings and reduction in sludge volume. The enzymes like the various oxidoreductases and phenoloxidase laccases which degrade the various azo, disazo and anthraquinone based structures (Soares et al., 2006). Laccases are multi-copper phenol oxidases that decolorize azo dyes through a highly non-specific free radical mechanism forming phenolic compounds, thereby avoiding the formation of toxic aromatic amines. The process utilizes the immobilized enzyme so as to avoid coupling reactions of the reaction products with the undegraded dye (Zille et al., 2005). Peroxidases like Lignin Peroxidase (LP) and Horse Radish Peroxidase have been screened for their dye degrading ability as Lignin-degrading ability is related to it. LP breaks non-specifically the aromatic and substituted aromatic rings in the dye, while HRP requires other microbial peroxidases for their decolorisation (Kim et al., 1995).

Other Methods

Biological aerated filter (BAF) involves the growth of an organism on media that are held stationary during the normal operation and exposed to aeration. In recent years several BAF-based technologies have been developed to treat wastewater (Babu et al., 2007).

Many physical and chemical methods including adsorption, filtration, ion exchange, irradiation, chemical degradation, ozonation have been used for treatment of dye containing effluents (Robinson et al., 2002). Decolouration of textile dye effluent does not occur when treated aerobically by municipal sewerage systems (Willmott et al., 1998). Each of these processes is associated with various advantages as well as dis-advantages.

Hence a combinational system of physical, chemical and biological treatment can be devised in which the lacunae of one method can be minimised by use of another method.

Combinational Methods

Various combinations methods involving the use of various physical, chemical and biological methods have been tried to achieve a bettAmrita er efficiency in removal of dyes from textile waste water. They may involve combining two or more types of only physical or chemical or biological methods or may involve the use of a combination of a type of physical or chemical method with a type of biological method.

Combination of nanofilteration and reverse osmosis can be devised, both to solve the problem of low flux of reverse osmosis membrane and poor separations of nanofilteration membranes (Tak-Hyun et al., 2005). Ozone can be used in combination with UV and H_2O_2. UV removes the remaining toxic intermediate product present in solution after oxidation (Rein, 2001) while H_2O_2 enhance the production of hydroxyl radical and accelerates decomposition of ozone (Adel et al., 2004). The combination of three of them, i.e., O_3, H_2O_2, and UV shows most promising and efficient results because sequential ozonation and H_2O_2/UV treatment increase COD removal of textile wastewater efficiency (Azbar et al., 2004). Applicability of micro-organisms in the field decreases due to the presence of a mixture of dyes in the industrial effluent. Moreover, the cross-reactivity of dyes results in blockage of active sites of azoreductase enzymes, due to the presence of sulphonic groups (Moosvi et al., 2007). Thus instead of utilizing either an aerobic or an anaerobic process at a time, complete degradation and decolourisation of a mixture of azo dyes can be achieved by utilizing sequential aerobic/anaerobic processes (Isik and Sponza, 2008).

Some studies have also suggested the use of some of the agri-adsorbents containing dye in adsorbed form as a substrate for solid state fermentation for protein enrichment (Nigam et al., 2000). Ozonation can also be applied at two different stages, either before biological treatment referred to as pre-ozonation which enhances the ease of biological treatment or after biological treatment referred to as post-ozonation (Orhon et al., 2002). A newer approach for the applicability of both the advanced oxidation processes (AOPs), i.e., the chemical oxidation and the biological oxidation processes to wastewater treatment has been to apply the two methods of wastewater treatment as an integrated process instead of separately or consecutively. Such integrated solutions could lead to use of chemical oxidants more efficiently as well as cause reduction in the effect of toxic or inhibitory compounds in bioreactors, thus resulting in a more robust and stable biological treatment. Such a kind of abiotic-biotic process has become the subject of recent research aimed at obtaining a cost effective method for complete decolourisation of anthraquinone dyes (Ledakowicz et al., 2001).

Proposed Alternative

The combinational systems currently in use comprises physico–chemical, physico–biological, chemico–biological or combinations within the biological methods. None of these methods are completely efficient in degradation and complete removal of the dye. Hence a combination system comprising adsorption, chemical oxidation and biodegradation process can be devised for the remediation of azo dyes from textile waste water. This proposed combination system would involve the use of untreated sugarcane Bagasse for adsorption of azo dyes followed by chemical oxidation with Fenton reagent for reduction in COD thus increasing its suitability for biological treatment with appropriate micro organisms under aerobic conditions.

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