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Research Article

Bio Nanotechnological Intervention: A Sustainable Alternative to Treat Dye Bearing Waste Waters

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ABSTRACT

Waste water treatment issues have been a growing problems these days. It has become stringently important to treat waste water prior its release into adjoining surface water bodies. In recent past, bio nanotechnological solutions have proved to be of paramount importance in circumventing the issues associated with dye bearing waste waters. Nanoparticles have a great potential to be used in waste water treatment. Its unique characteristic of having high surface area can be used efficiently for removing toxic metal ions, disease causing microbes, organic and inorganic solutes from water. Various classes of nanomaterials have been efficiently utilized for above cited facts including treatment of dye bearing waste water released from textile industries like metal-containing nanoparticles, carbonaceous nanomaterials, zeolites and dendrimers. The paper presents a comprehensive review of recent advances on different nanomaterial based mitigation strategies. Special emphasis has been given to green synthesis of nanoparticles aimed to address problems associated with textile effluents through nano bioremediation.

Introduction

The problem of environmental pollution has become a global threat. On one hand, industrialization is the key behind socio-economic development but lack of sustainable practices may lead to adverse effect on the natural resources. The problem of environmental pollution is on rise by virtue of different xenobiotic substances being released into water, soil and air. The problems associated with water pollution needs to be answered indiscriminately. Among the wide spectrum of water pollutants, the synthetic dyes cause an environmental menace extensively used in textile industries. Water is the most vital substance in our life. A reliable and accessibility to clean water is demand of a common man. Overpopulation, industrial filtration, dwindling water resources, pollution, lack of proper treatment technology has instigated a demand to develop an eco friendly, cost and time effective and viable culminating into Triple R (Recycle Reuse and Reduce) concept.

Rajasthan with it's cultural heritage and age old tradition has recently witnessed exponential growth in industrial sector especially in the ethnic hues of bandhej, lehria, originating from upcoming textile units. Due to the nature of various chemical processing of textiles, large volumes of waste water with numerous pollutants are being discharged. The effluents of textile industries are released into adjoining water bodies considerably altering the physicochemical nature. It has long being known that the textile dyeing and printing units situated at Pali discharge effluents in the river Bandi which adversely effects the quality of water [1]. The presence of dyes is omnipresent as it is evident in the form of coloured effluents. Pali city has been in limelight since decades. Very recently, on 22.02.2016, the team of environmentalists had conducted the visit to monitor the rampant condition. "The result portrays the most dismal picture wherein thousands of acres of once fertile land turned barren and the polluted groundwater reportedly wreaked havoc in terms of cancer, asthama and other diseases in the area. Unfortunately, while such cases abound, no health surveys have been conducted in the area while untreated hazardous effluents from almost 600 of these industries continue to find their way into the Bandi River, a seasonal river"[2].

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The existing treatment options fail to comply with standards prescribed by authorized agencies. Consequently, partially treated effluents are being drained into adjoining river Bandi. Focusing on the current scenario of water pollution extensively caused by textile units and proving detrimental to both biotic and abiotic factors of ecosystem, the dismal picture of Pali city severely under the catastrophic effect of synthetic textile dyes is evident in figure 1.

Pali : "The Textile Hub", known for Water Pollution

03.09.2012 'Bandi river has become a reservoir of polluted water'

Nov 5, 2012 All textile units in Pali ordered shut for 2 days

20.09.2012 In Pali, a river being killed

Flouting HC Order, Effluents Being Dumped In Bandi

TOXIC TROUBLES

'Rivers have become reservoirs of effluents' 03.11.2012

बंद होगी 550 औद्योगिक इकाइया 10.09.2013

'म्हाने भी तो जीवण दो' 25.08.2013

TIMES CITY

893 textile units in Sanganer served closure notices

Effluents from dyeing industry spoiling groundwater in Pali town 02.01.2014

Figure 1: Pali in limelight since decades for water pollution

Current treatment strategies adopted to mitigate problems associated with dye bearing waste waters in presented in table 1.

S.No	Treatment methodology	Treatment stage	Advantages	Limitations
	PHYSICO-CHEMICAL METHODS			
1	Precipitation, Coagulation, flocculation	Pre/main treatment	Short detention time and low capital costs. Relatively good removal efficiencies.	Agglomerates separation and treatment. Selected operating condition.
2	Electrokinetic Coagulation	Pre/main treatment	Economically feasible.	High sludge production.
3	Fenton process	Pre/main treatment	Effective for both soluble and insoluble coloured contaminants. No alternation in volume	Sludge generation; problem with sludge disposal. Prohibitively expensive.
4	Ozonation	Main treatment	Effective for azo dye removal. Applied in gaseous state: no alteration of volume.	Not suitable for dispersed dyes. Releases aromatic dyes. Short half-life of ozone (20 min).

5	Oxidation with NaOCl	Post treatment	Low temperature requirement. Initiates and accelerates azo bond cleavage.	Cost intensive process. Release of aromatic amines.
	ADSORPTION WITH SOLID ADSORBENTS			
6	Activated carbon Economically attractive.	Pre/post Treatment	Good removal efficiency of wide variety of dyes.	Very expensive; cost intensive regeneration Process.
7	Peat	Pre treatment	Effective adsorbent due to cellular structure. No activation required.	Surface area is lower than activated carbon.
8	Coal ashes	Pre treatment	Economically attractive. Good removal efficiency. Larger contact times and huge quantities are required.	Specific surface area of adsorption is lower than activated carbon.
9	Wood chips/ Wood sawdust	Pre treatment	Effective adsorbent due to cellular structure. Economically attractive. Good adsorption capacity for acid dyes.	Long retention times and huge quantities are required.
10	Silica gels	Pre treatment	Effective for basic dyes	Side reactions prevent commercial application
11	Irradiation	Post treatment	Effective oxidation at lab scale	Requires a lot of dissolved oxygen
12	Photochemical process	Post treatment	No sludge production	Formation of byproducts
13	Electrochemical oxidation	Pre treatment	No additional chemicals required and the end products are non-dangerous/hazardous.	Cost intensive process; mainly high cost of Electricity
14	Ion exchange	Main treatment	Regeneration with low loss of adsorbents	Specific application; not effective for all dyes
	BIOLOGICAL TREATMENT			
15	Aerobic process	Post treatment	Partial or complete decolourisation for all classes of dyes	Expensive treatment
16	Anaerobic process	Main treatment	Resistant to wide variety of complex coloured compounds. Bio gas produced is used for stream generation.	Longer acclimatization Phase
17	Single cell (Fungal, Algal & Bacterial)	Post treatment	Good removal efficiency for low volumes and concentrations. Very effective for specific colour removal.	Culture maintenance is cost intensive. Cannot cope up with large volumes of wastewater.
	EMERGING TECHNOLOGIES			
18	Other advanced oxidation process	Main treatment	Complete mineralization ensured. Growing number of commercial applications Effective pre-treatment methodology in integrated systems and enhances biodegradability.	Cost intensive process

19	Membrane filtration	Main treatment	Removes all dye types; recovery and reuse of chemicals and water.	High running cost. Concentrated sludge production. Dissolved solids are not separated in this process
20	Photocatalysis	Post treatment	Process carried out at ambient conditions. Inputs are no toxic and inexpensive. Complete mineralization with shorter detention times. Effective for small amount of coloured compounds.	Expensive Process
21	Sonication	Pre treatment	Simplicity in use. Very effective in integrated systems.	Relatively new method and awaiting full scale application.
22	EnzymaticTreatment	Post treatment	Effective for specifically selected compounds.	Enzyme isolation and purification is tedious.
23	Redox mediators	Pre/ supportiveTreatment	Easily available and enhances the process by increasing electron transfer efficiency	Concentration of redox mediator may give antagonistic effect. Also depends on biological activity of the system..
24	**Engineered wetland systems**	**Pre/post treatment**	**Cost effective technology and can be operated with huge volumes of wastewater**	**High initial installation cost. Requires expertise and managing during monsoon becomes difficult**

Need to envisage the plausible role of biological and bio nanotechnological treatment strategies lies in the fact that these options are eco friendly and minimize load of toxic pollution causing compounds.

Biodegradation of dyes: Applied aspect of bacterial diversity

Traditional wastewater treatment technologies are markedly ineffective for handling wastewater of synthetic textile dyes because of the chemical stability of the pollutants [3]. Additionally, the water recycling issue remains unaddressed [4]. Physico-chemical methods have long been used to treat textile wastewater influxed with synthetic dyes. The major disadvantage of physicochemical methods is primarily the high cost, low efficiency, limited versatility, need for specialized equipment, interference by other wastewater constituents, and the handling of the generated waste [5, 6]. Physical methods can effectively remove colour, but the dye molecules are not degraded, becoming concentrated and requiring proper disposal. With the chemical techniques, although the dyes are removed, accumulation of concentrated sludge creates a menace. A possibility of secondary pollution problem always arises because of the excessive amounts of chemicals involved [7]. Recently, other emerging techniques like advanced oxidation processes, which are based on the generation of very powerful oxidizing agents such as hydroxyl radicals- have been applied with success in pollutant degradation [8]. Although these methods are efficient for the treatment of waters contaminated with pollutants, they are very costly and commercially unattractive compounds [9-10]. These compounds may be biodegradable, persistent or recalcitrant [11] which may be cleaved into smaller compounds by viable microbes [12].

The high electrical energy demand and the consumption of chemical reagents are common problems. The development of efficient, economic and eco friendly technologies to decrease dye content in wastewater to acceptable levels at affordable cost is of utmost importance [13]. Biological methods are generally considered environmentally benign because they lead to complete mineralization of organic pollutants at effectively low cost [14]. They also dissipate BOD, COD and suspended solids. The main limitation relates, in some cases to the toxicity of some dyes and/or their degradation products to the organisms used in the process.

Significance of Nanobiotechnology in Treatment of Dye bearing waste waters

Nano biotechnology is defined as aspect of biotechnology that deals with synthesis, design and stability of various nanoparticles using biological tools [15-16]. It can merge with other technologies and modify, endorse or clarify an existing scientific concept making a platform technology [17]. The use of nanotechnology in future is expected to expand into numerous industrial applications and help decrease production costs by reducing energy consumption and attenuate pollution [18]. In current scenario, bioremediation through use of adapted microbes has gain attention in recent past which ultimately leads to bio mineralization of recalcitrant compounds The extent of pollution caused by different combinations of synthetic dyes used in textile industries is rendering the naturally attenuated micro flora insufficient to carry out the “clean up”. The main limitations are increase in prohibitive cost, carbon dioxide release due to bio mineralization and aggregation of biomass content at large [19] Further more recent applications of nanotechnology in bioremediation by utilising nano particles has been focal theme of research investigations at pilot scale [20] Combinatorial approach utilising bionanotechnology and bioprocessing for dye removal from textile effluents has been considered in recent times [21]. Nanotechnology facilitates the utilisation of different types of nanomaterials like metal containing nanoparticles, carbonaceous nanomaterials, zeolites and dendrimers [22-23]. As a nanocatalyst, nanoparticles have been promiscuously used in waste water treatment systems [24] owing to their high surface area, high catalytic efficiency, mass transfer effect, effective enzyme storage and high surface reaction activity [25]. The high surface absorbing, interacting and reacting capabilities of nanoparticles along with energy conversion and cost effectiveness is attributed to its small size (1- 100 nm) and high proportion of atoms at surface [26]. So far, amongst all conventional technologies available, nanoparticles have greatest advantage of treating water at any depths and location. Utilising nanoparticles as a supplement in biodegradation systems and their rates , microbial populations is significantly enhanced [27] Nanoparticles can be mixed with aqueous solutions to form a colloid and as a composite utilising soil for removal of Reactive Turquoise Blue from industrial effluent Nanosensors have emerged as pollution monitoring devices which can be engineered to interact with pollution of interest and decompose to less toxic species [28].

Synthesis of nanoparticles

In recent years, considerable efforts have been made in synthesizing Magnetic Nano Particles (MNPs) with atleast one dimension of size 1-100 nm possessing wide applications [21]. The most common ones to be explored are gold, silver, platinum and palladium. Classically, they have been synthesized by physical and chemical methods [29] like heating [30] irradiation [31] and flammable toxic solvents. These methods are not cost effective and pose an environmental threat in terms of toxicity they generate [32] This disadvantageous factor urged the need to explore green route of synthesizing eco friendly nano particles, the characteristics being high in yield, lost in cost, non-toxic [33] Synthesizing and stabilization of MNPs via green route depend upon factors such as green reducing agent, reaction medium and stabilizer [34]. (Biogenic synthesis of nanoparticles from plants is relatively unexplored [35]. Plants could be preferential source of green technology for nanoparticle synthesis as they are widely distributed, easily available, safe to handle and source of several metabolites [36-37] has demonstrated synthesis of silver nanoparticles with sea weed *Padina tetrastomatica* for dye degradation. Plant extracts of *Ocimum tenuiflorum* coupled with soil as a composite through bioreduction have been used in synthesizing silver nanoparticles for adsorption of toxic dyes from textile effluents. Zinc nanobeads prepared by plant extracts of seed of *Cuminum cyminum* for treatment of Alizarin Red containing waste water [38]. Microorganisms comprise of a huge and almost untapped reservoir of myriad forms of molecular and chemical diversity in nature, as they constitute the most diverse forms of life and are resourceful in terms of extrapolating some innovative applications for the mankind. The presence of microorganisms in extreme conditions of stress or contaminated environments facilitates their use in different biotechnological interventions as their enzymatic systems are coded by genes which could be exploited. Additionally, the use of such highly tolerant autochthonous strains in wastewater bioremediation is a focal point of research [39]. Exploring bioremediation aspects of micro-organisms, they have been appropriately termed as ecofriendly nanofactories. The role of environmental isolates (bacteria, fungi and algae) for synthesis of nanoparticles as potential tool of nano bioremediation has been substantiated in recent past [40]. Nanoparticles are synthesized when the micro-organism grabs the target ions from the environment and converts metal ions into elemental metal through metabolic pathways via precipitation [41, 42]. Intracellular or extracellular production of nanoparticles by microbial route depends upon growth temperature, synthesis time, extraction methods and production ratio of sample [43]. Bacteria have been correctly termed as biomanufacturers on account of extracellular synthesis of nanoparticles. Cell free extracts of psychrophilic bacteria Pseudomonas antartica, Pseudomonas proteolytica, Pseudomonas meridiana,Arthrobacter kerguelensis and Arthrobacter gangotriensis and mesophilic strains of Bacillus indicus and *Bacillus cecembensis* have been used to synthesize silver nanoparticles by inductive effect [44]. A combinatorial approach utilising cell free extract of 20 Bacillus subtilis and microwave radiation for nanoparticle synthesis has been successfully investigated [45].

Myconanotechnology is the interface of mycology and nanotechnology involving use of fungi in biosynthesis of nanoparticles [46-48]. Fungi require simple nutrients; possess high wall binding capacity, uptake metals intracellularly [49]. Dye degrading potential of silver nanoparticles synthesized by endophytic fungi *Garcinia xanthochyumus* and *Aravae lanata* has been cited [50]. [21] in CSIR-CLRI have developed eco-friendly technology based at nano bioremediation of dye bearing waste water. Intracellular protein obtained from was used for synthesis of silver nanoparticles on nano-silica surface. [51] had reported extracellular and intracellular synthesis of gold nanoparticles by Trichothecium sp. Microalgae have been known to synthesize metal nanoparticles by bioaccumulation of metals leading to their biotransformation. This micro system has been well established in remediation of metal bearing waste waters [52] Marine alagae *Sargassum wightii* and *Gracilaria corticator* have been reported to synthesize silver and gold nanoparticles. Bioremediation of waste water through a combinatorial approach using enzymes and nanoparticles has been referred to as Single Enzyme Nanoparticles (SEN). It is an armoured enzyme surrounded by a protective cage [53]. Laccases are versatile enzymes reported to have different applications. Laccase mediated synthesis of naoparicles for therapeutic purpose has been reported in recent times [17]. Laccases obtained from Trametes versicolor immobilized on iron nanoparticles has been used for decolourisation and degradation of textile dyes [54]. Different modes of immobilisation of laccases have been used like silica nanoparticles [55] nanotubes [56] magnetic particles coated with chitosan. Lignin peroxidises are a special set of enzymes possessed by fungi and bacteria which biomineralize recalcitrant dyes and other xenobiotics. This enzyme coupled with magnetic nanoparticles and been purified from *Pseudomonas aeruginosa* has been used for bioremediation of Reactive Blue azo dye compound containing waste water [57]

Polysaccharides are emerging as stabilizing and reducing agents for nanoparticle synthesis. They form the main component of bioflocculants. Plant and animal derived polysaccharides have been used in synthesis of metal nanoparticles. Bioflocculant derived from *Bacillus subtilis* MSBN17 has been explored to synthesize silver nanoparticle. This approach has been selectively used for minimizing bacterial load in sewage waste water [58].

Discussion

Environmental sustainability; addressing the problems associated with toxic water pollution caused intensively by xenobiotic textile dyes have been based primarily on physico-chemical methods. These methods in current practice are not cost effective. Current treatment methods employ biological methods aimed at bioremediation. As an advancement , methods based at an interface of nanotechnology and biotechnology have gained momentum in recent past. Synthesis of nanoparticles via green route have substituted nanoparticles synthesized via chemical route. These nanoparticles have found immense usage in combating toxicity related issues. Microbial synthesis of nanoparticles have been used in bioremediation of toxic textile effluents influxed with synthetic dyes. Moreover, an amalgagamation of microbial enzymes and nanoparticles have led to inception of Single Enzyme Nanoparticles (SEN) which have proved to be of immense potential in treating dye bearing waste waters. Future insights in domain of nano bioremediation includes searching for novel microbial counterparts capable of synthesizing nanoparticles which would address problems associated with recalcitrant dyes.

Conflict of interest: We declare that we have no conflict of interest.

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