



Plant Archives

Journal homepage: <http://www.plantarchives.org>
doi link : <https://doi.org/10.51470/PLANTARCHIVES.2021.v21.S1.207>

BIOSORPTION: THE REMOVAL OF TOXIC DYES FROM INDUSTRIAL EFFLUENT USING PHYTOBIOMASS- A REVIEW

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ABSTRACT

At present, the increasing use of natural and synthetic dyes persists as a major environmental problem. Wastewater containing dyes, releasing on a large scale from various industries entered excessively into food web resulting in mutagenesis, allergenic and carcinogenic effects and serious health problems in living systems. Various technologies have been examined to date for the removal of inorganic and organic contaminants from wastewater. Among those, biosorption is the highly effective method because, it is employed as eco-friendly, cost-effective and sustainable biosorbents. Charcoal, chitin, peat, fungal biomass, microbial biomass, wood bark and other agricultural wastes are commonly used bio-adsorbents. Use of plant based biosorbents is seminal, over the other conventional adsorbents used. The plant based bio-adsorbents are highly used for the removal of dyes, remediation of toxic industrial effluents, removal of fertilizers and/or pesticides and atmospheric pollutants etc. This review is making a focus on the efficiency of the various types of plant based biosorbents, their uses, and mechanism of action with certain optimization. Various parameters to find out the efficiency of bioadsorbents and physicochemical conditions to remove the dyes from waste water bodies are described in this review.

Keywords: Plant biomass, Toxic dyes, Food web, Mutagenesis, Carcinogenic, Biosorption.

Introduction

Water pollution is the release of unwanted substances or compounds into the water bodies due to anthropogenic activities, in huge quantities that damage human health and the resources. It results from the release of undesirable amounts of harmful substances directly or indirectly. The natural disasters/incidences such as volcanoes, water blooms, storms and earthquakes also cause major detrimental effects in water quality and the water ecosystem (Lokhande *et al.*, 2011). Industrial effluents of various industries like textile, distillery, paint, finishing, natural and synthetic dyes, paper and pulp industries and oil mills etc. are the major contributors of water pollution. Industrial effluents, containing different types of inorganic and organic contaminants and discharged through the aquatic route either in water soluble or insoluble forms. It is believed that one third of the total water pollution comes in the form of discharge of industrial effluent (Bulgariu *et al.*, 2014).

Synthetic dyes are used more than that of natural dyes and are highly toxic, allergenic and carcinogenic. The content of these dyes reacts with metal ions to form substances which are highly toxic to aquatic flora and fauna and leads to the existence of several diseases (Karthikeyan and Chiranjeevi 1987). Dyes possess the complex structures which make them plenary with physico-chemical, thermal and optical stability. Due to these properties, they become resistant to many chemicals, microbial enzymes, oxidizing

agents and heat. Therefore the treatment of dyes in textile waste waters possesses several problems. These are biologically non-degradable and therefore difficult to decolorize once commingled into the aquatic system (McKay, 1982). To solve the ecological, sociological, techno-economical, biological, and industrial problems, the toxic dyes must be removed efficiently from the discharged wastewater. Presently, the used conventional methods such as membrane-filtration processes, flocculation, coagulation method, decolourisation, chemical precipitation, chemical oxidation, electrolytic process for the removal of dyes from waste water are highly effective for the mitigation of pollutants and toxicity (Wiesmann, 2007).

Because of the dyes are highly stable and complex organic molecules and, thus, are difficult to degrade by means of oxidizing agents, light, heat, and microbial attacks therefore these treatment methods are not so economical, so there is a need to produce low-cost adsorbents for the removal of dyes from polluted sites (Horning 1978; Tunay *et al.*, 1996; Forgacs *et al.* 2004; Singh and Arora 2011). The capacities of certain biomass are comparable with the commercial synthetic cation exchange. Besides this a large number of microorganisms and agricultural wastes have been investigated for decolouration of various dyes. The suitable enzyme systems of micro-organisms for the decomposition of dyes have largely been investigated by many workers. Biosorption of dyes by adsorption on to economical and

efficient solid support has also found to be advantageous (Hameed *et al.*, 2009). The dyes adsorption on to activated carbon is proved to be the most efficient method for treatment of dye contaminated waters, but it is not an economically viable method due to the cost of commercial activated carbon. A low cost technology for the removal of toxic dyes from wastewaters has received the attention to biosorption, based on binding capacities of various biological materials like algae, fungi, bacteria, waste plant materials and agricultural wastes. Biosorption is a steady process for the sequestration of metal or dye by the living or dead biomass (Volesky, 1999). An adsorbent can be appraised as low cost if it require less processing, abundant in nature or is a by-product of some process and obtained as waste materials either from another industries or from agricultural activities. From the last two and half decades, extensive research has been carried out to develop low cost adsorbent materials that could be an alternative to the activated carbon (Kousha *et al.*, 2012).

Biosorbents are attractive since naturally occurring or growing biomass adsorbents or spent biomass (spent brewery grains, tendu leaves, rice husk etc.) can be effectively used as adsorbent. In past few years this technique has been widely accepted for waste-water treatment due to its competence in the removal of colour. Cellulose is a plant based most abundant natural polymer with good properties such as low cost, biodegradability, eco-friendly, and high stability to most organic solvents. The cellulose-based bio-adsorbent can be used as a desirable adsorbent for environmental remediation (Zhou *et al.*, 2013; Bayramoglu *et al.*, 2012; Zhou *et al.*, 2014; Bonenfant *et al.*, 2010; Chen *et al.*, 2014). The cellulose molecules present in plants cell wall have high density of hydroxyl groups, and can be modified with specific functional groups, such as carboxyl, amino, sulfo group, and cyclodextrin, to remove specific pollutants.

Agricultural waste as biosorbent

Every year, more than 400 million tonnes of agricultural wastes is produced in India (Raghuvanshi *et al.*, 2004). Many of the plant biomass which generated every year, as low cost adsorbents require small-scale processing and are abundant in nature or is a by-product or waste material from another industry have been tested such as tea waste, sugarcane leaves, rice husk, cotton waste, teak wood bark (McKay *et al.*, 1986), maize cob, bagasse pith (Nassar *et al.*, 1991), coir pith (Namasivayam *et al.*, 1994), orange peel (Namasivayam *et al.*, 1996), banana pith (Namasivayam *et al.*, 1998), plum kernels (Juang *et al.*, 2000), wheat straw, apple pomace (Robinson *et al.*, 2002), cassava peel (Sivaraj *et al.*, 2001), saw dust (Garg *et al.*, 2003), pineapple stem (Garg *et al.*, 2003), castor seed shell (Oladoja *et al.*, 2008), *Nymphaea rubra* (Renganathan *et al.*, 2009), Pistachio hull (Moussavi and Khosravi, 2011), *Tectona grandis* leaf litter (Oyelude *et al.*, 2018), *Thespesia populnea* (Bhargavi *et al.*, 2018) and *Eichhornia crassipes* etc.

At the latest, several carbons derived from various crop wastes, such as wheat straw, rice straw, sugarcane leaves, carrot grass leaves, rice husk, and peanut shell, among others, were developed (Liu *et al.*, 2012; Mashhadi *et al.*, 2016; Vadivelan and Kumar, 2005; Huff *et al.*, 2014), and their maximum adsorption capacities for methylene blue were very good. One of the crop wastesis ginger straw, wasted in large quantities as a by-product of ginger farming and it is

easily available to reuse for various purposes. Zhang *et al.* (2019), suggested that the waste of ginger (*Zingiber officinale*) straw produced porous carbon (ginger straw waste porous carbon), which is a good adsorbent for removal of methylene blue dye from wastewater. The dispersal of pore size unfolded that the pore sizes of ginger straw waste derived porous carbon, were mainly located at micropore and mesopore regions. Just due to its pore structure, surface area and the presence of functional groups, it is greatly attractive as agriculture based adsorbent for the removal of methylene blue dye. The obtained material showed high adsorption efficiency toward methylene blue dye in context of high adsorption capacity, high adsorption rate, and good retreatment.

However, low adsorption efficiencies were reported with the developed adsorbents. Therefore, there is a crucial need to develop and practice large number of economical and locally available adsorbents that would bring deduction in dye waste water treatment capital costs (Sivaraj *et al.*, 2001). Dye adsorption is a consequence of two mechanisms *viz.* adsorption and ion exchange, and it is influenced by several aspects such as contact time, adsorbent interaction, adsorbent's surface area, particle size, dye concentration, agitation, contact time, temperature and pH.

a. Effect of particle size and surface area:

It has been investigated that the adsorbents with reduced particle dimension have a greater potential of adsorption process with augmented surface area. Therefore, major dye can be eliminated by small particles than the large particles of adsorbents. The adsorption augments the particle size reduces, because the circumference increases with decreased particle size and *vice-versa*. The suitable particle sized adsorbent can be used directly without any pre-treatment.

b. Effect of contact time and agitation:

Contact time is also an important factor which influences variously the adsorption efficiency of the biosorbent. The effect of agitation time on the biosorption of dyes from aqueous solution using various bio-sorbents was studied at different initial dyes concentrations and constant agitation speed and various temperatures (Peige *et al.*, 2017). Optimum contact time is determined by shaking of biosorbent with different dye solutions with a specific pH, constant temperature. The contact time has been studied by many researchers in a wide range from 1 to 10 minutes and up to 120 minutes until finally the equilibrium reached. It has been shown by many researchers that the percentage biosorption of dyes increase with increase in contact time with analysing the condition that maximum absorption occurs in the first 10 to 30 minutes while only an additional part of removal occurred in the rest (Swamyet *et al.*, 2017).

c. Effect of biosorbent dosage:

The dosage of biosorbent is another important factor because it determines the capacity of a biosorbent to adsorb the dyes. The removal of dyes increases with an increase in biosorbent dosage. As the adsorbent dosage increase, the percentage absorption increases. This is because of the availability of more binding sites for complexation of dye ions. Beyond optimum dosage, the adsorption diminish due to saturation of the adsorption sites and dye molecules in the

solution (Mittal and Kurup, 2006; Ravindra *et al.*, 2014; Mahadevaswamy and Padmawathy, 2016).

d. Effect of initial dyes concentration:

The initial dye concentration is also a factor which needs to be taken into the consideration of biosorption as it also influences the biosorption efficiency of the biosorbent. In the present study, it is trying to explain that the adsorption of dye is carried out at different initial dye concentrations ranging from 5 mg to 300 ppm for 15-120 minutes contact time at pH 1-7. It is very interesting to observe that the percentage of adsorption decreases as dye concentration increases. This is because the adsorption sites are not enough to absorb the dye molecules at higher concentration (Elith *et al.*, 2006). With a decrease in the concentration of dyes, the percentage of adsorption is found to be increased. From these observations we can get an idea that the availability of dye molecules to interact with the biosorbent should be in the optimum range. This indicates that the initial concentration of dye can alter the dye removal efficiency through a combination of factors such as the availability of specific surface functional groups and the ability of surface functional groups to bind dye molecules. Initial dye concentration of solution could be helpful to provide a key driving force to get the better of the massive transfer resistance of dye between the both aqueous and solid phases.

e. Effect of initial pH concentration:

The pH of the dye solution also plays a main role in the complete process of the biosorption and mainly on the adsorption capacity of the biosorbents. Moreover, the extent of ionization of the material present in the solution and the dissociation or segregation of functional groups exposing on the active sites of the adsorbent also affects the adsorption (Akar *et al.*, 2013). The pH of the solution affects both the chemistry of the aqueous solution and the binding sites present on the surface of adsorbents. The effect of the pH in turn can also influenced or fluctuate depending on charge and adsorbent surface area. If the adsorbent surface is negatively charged, at low pH, the large number of hydrogen (H^+) ions present counteracts the negatively charged surface of the adsorbent, hence reducing hindrance to the diffusion, and a better adsorption is gained. If the surface of the adsorbent possessing positive charge, the hydrogen ions (H^+) may

compete productively with the cations present in dye solution, resulting in a decrease in the amount of adsorbed dye.

f. Effect of temperature:

Depending on the types of adsorbent used, temperature can affect the adsorption capacity of adsorbent. The temperature effects of adsorption efficiency have been investigated on various temperatures ranging from 5°C to 45°C. Temperature can change adsorption equilibrium depending on the exothermic and endothermic nature of a process (Abbas *et al.*, 2013). The increasing biosorption rate with increasing temperature indicates that the adsorption process is endothermic. It has also been found that the adsorption rate remain constant with increasing temperature. It may be because the temperature has not much effect on adsorption efficiency. Therefore a room temperature *i.e.* 25±2°C, has been shown very good (Peige *et al.*, 2017).

Different plant biomass as effective biosorbent

The accession of pollutants on the cell surface or in the aqueous solution through the biological materials is defined as biosorption. In biosorption process, the contaminants cling on the cell surface of biosorbents and/or accumulate in cells (Kumar *et al.*, 2015). Cell surface has a negative charge in the presence of carbonyl, amino, hydroxy, amide, amine and the phosphate group and it can adsorb a significant amount of dye molecules (*i.e.* cations). It has been accentuated that the rate of dye adsorption is usually controlled by either the liquid phase large-scale transport rate or the intra-particle mass transport rate (Vimonses *et al.*, 2009). Although the mechanism of intra-particle proliferation actively involves in action of adsorption process but still is not the only rate-controlling step. Some other mechanisms like ion-exchange or ion-complication also play a major role in controlling the rate of dye adsorption (Poots *et al.*, 1978; Vimonses *et al.*, 2009). The findings of earlier investigation focused on the percentage removal of various chemical dyes using different plant biomass was summarized (Table 1). The findings reflected that the natural plant resources can be employed for the removal of several hazardous chemical dyes of industrial effluents from the natural habitat, agricultural land and environment.

Table 1 : The percentage removal of toxic dyes using different plant biomass as adsorbent.

Adsorbent	Dye	Biosorption (%)	Contact time (Min)	Particle size (µm)	pH	Initial conc.of dyes (mg/L)	Biosorbent dosage (gm/L)	Temp (°C)	Reference
Spent brewery grains	Acid yellow 17	94	40	-	2	150	0.5	29.85	Jaikumar and Ramamurthi, 2009
<i>Eichhornia crassipes</i> leaves	Amaranth red	86.19	48	2000-4000	2	50	1.0	25±1	Guerrero-Coronilla <i>et al.</i> , 2014
<i>Sorghum</i> sp. malted mash	Basic Fuchsin	92	30	2000	7	25	8	25±1	Oyelude <i>et al.</i> , 2015
<i>Aloe vera</i> leaves	Congo red	91	100	300-500	2-12	100-500	0.5	24.85	Omidi <i>et al.</i> , 2017
<i>Bauhinia purourea</i> leaves	Congo red	84	40	81-162.3	6.2	20-100	0.1	29.85	Kalpna <i>et al.</i> , 2016

<i>Posidonia oceanica</i>	Crystal violet	98.05	60		7	50	0.1	25	Mohamed and Gierak, 2020
<i>Rhizophora mucronata</i> stem bark	Crystal violet	99.80	60	70 -300	7	100	0.25	25	Oloo <i>et al.</i> , 2020
<i>Saccharum officinarum</i> stalk	Crystal violet	70	90	1000-2000	9	50	3	25	El-Sayed <i>et al.</i> , 2011
<i>Psidium guajava</i> leaves	Malachite green	92.70	75	75	1	20	0.1	29.85	Chaudhary, 2015
<i>Tamarindus indica</i> fruit shell	Malachite green	99.46	60	< 177	5	10-200	30	29.85	Saha <i>et al.</i> , 2010
<i>Carica papaya</i> peel	Methylene blue	90	35	-	8	40	30	35	Teja <i>et al.</i> , 2013
<i>Cyanthilium cinereum</i>	Methylene blue	98.15	50	Rnadam	7	15	0,05	-	Silva <i>et al.</i> , 2019
<i>Parthenium hysterophorus</i> flower	Methylene blue	88	30	-	6	5-10	0.005	30	Swamy <i>et al.</i> , 2017
<i>Paspalum maritimum</i>	Methylene blue	95.88	50	Rnadam	7	15	0.05	-	Silva <i>et al.</i> , 2019
<i>Populus</i> sp. sawdust	Methylene blue	98	120	-	6	10-100	4	25	Natalija <i>et al.</i> , 2018
<i>Posidoniaoceanica</i>	Methylene blue	99.40	60	-	7	50	0.1	25	Mohamed and Gierak, 2020
<i>Typha</i> sp. stem	Methylene blue	98.69	120	-	10	50-300	0.3	25±1	Sanchez-Orozco <i>et al.</i> , 2018
<i>Saccharum officinarum</i> bagasse	Reactive red 120	94.62	15	125-250	1	5	0.1	25±2	Ahmead <i>et al.</i> , 2018
Treated jute	Safranin	>90	60	-	6	50	20	25	Manna <i>et al.</i> , 2016

Conclusions

The present study has made an explanation of a variety of agriculture based low-cost biosorbents (*i.e.* phytomass) for the removal of dyes from polluted industrial effluents. For the decolourization of dyes, the use of economically available activated carbon, chemical filtration and other conventional methods can be replaced by the utilization of inexpensive, effective, and readily available naturally occurring or agricultural by-products as adsorbents. These non-conventional low-cost adsorbents are inexpensive, easily available, eco-friendly and effective biomaterials which alters the other conventional methods of decolourization of dye from industrial effluents or sewages. The phytomass possess a high adsorption capacity and shows impact, a very good adsorbent for the removal of toxic dyes from industrial effluents as investigated from their aqueous solution under optimized environmental conditions of adsorbent dosage, pH of the solution, particle size of the plant based adsorbent, contact time, agitation and initial dye concentration. There is no doubt that these agricultural low-cost adsorbents offers an

advantage over other adsorbents as these are easily available, renewable and are being wasted in large amount by many agricultural activities. Further research should be undertaken to investigate the possibility of adsorption capacity improvement by different modification techniques, as well as the dye removal from contaminated wastewater samples.

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