

# ADSORPTIVE REMOVAL OF DYES FROM AQUEOUS SOLUTION ONTO COST EFFECTIVE AND NON-CONVENTIONAL ADSORBENTS: A REVIEW

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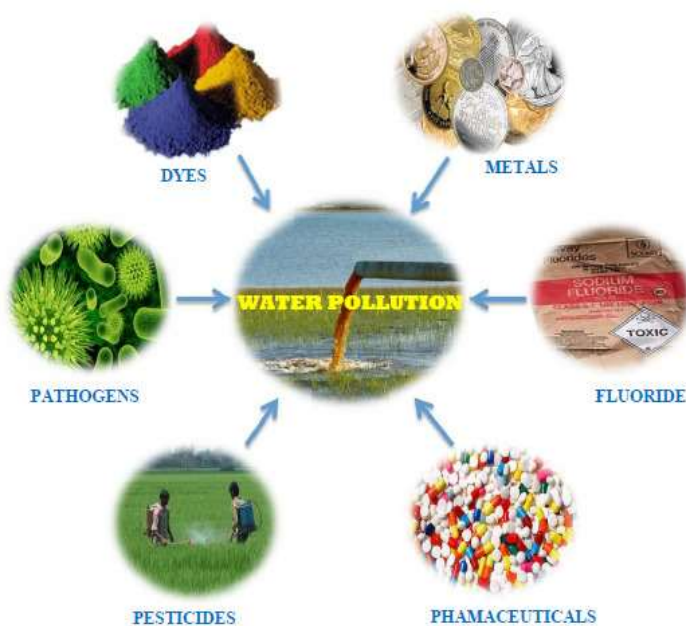
**Abstract:** A number of research activities have been carried out by many researchers to explore most suitable and efficient technique for the removal of dyes from industrial effluent. Various techniques namely coagulation, precipitation, filtration, reverse osmosis, ion exchange, adsorption and photocatalytic degradation have been used to remove organic and inorganic compounds from the aquatic environment. Among all the reported methods, the adsorption study has been found a most promising technique for the removal of these types of contaminants. A phenomena of accumulation of substances on the surface of solid by some physical or chemical process than into the bulk is known as adsorption. Over the last decades, adsorption has gained importance as a purification and separation technique on an industrial scale and become an attractive option for industrial water treatment. This review paper would be supportive to find the most capable technique for the removal of dye contaminants from industrial effluent taking into consideration the merits and demerits of each method.

**Keywords:** Water pollution, Dyes, Removal techniques, Adsorption, Adsorbents.

## I. INTRODUCTION

Water is an essential constituent of all animal and vegetable matter and forms about 75% of the matter of earth's crust. Water is used for many purposes including industrial and municipal purposes. Each industry has its own water requirements and sometimes adequate supply of water may be very suitable for one industry but the same may be dangerous for the other. It is, therefore, extremely important to take into account the uses of water for the work to be carried out, its suitability based on the results of chemical analysis and bacteriological examinations. The quality and quantity of available water are important in the location of a chemical plant. For this purpose surface water as well as ground water may be used, but the supply must be adequate and continuous throughout

the year. More than 50% of water supply used in chemical plants is utilized for cooling purpose. Water can be obtained from different sources therefore it has a large number of impurities. For example, water gets impurities from ground or soil with which it comes into contact. Water also gets contaminated with sewage and industrial wastes or effluents when these are allowed to flow into running water or through percolation through the ground. In all over India, an estimated 90% of waste-water is discharged directly into rivers and streams without treatment. The main cause of wastewater production is the manufacturing or chemical processes in industries. Industrial waste-water generally contains specific and readily identifiable chemical compounds. But water pollution is concentrated within a few sub sectors, mainly in the form of toxic wastes and organic pollutants. Out of this, a large portion can be traced to the processing of industrial chemicals and to the food product industries. The textile industry, a major consumer of water for several of its wet processing operations, is also a major producer of effluent waste-water containing organic surfactants, salts, acids, alkalis, solvents and dyes as some of its main constituents. Dyes, though present in only small amounts are highly detectable and thereby are capable of causing serious problems of an aesthetic nature in the receiving water bodies. Major sources of water pollution are showed in Scheme 1.



## II. Water pollution due to dyes

India's dye industries produce every type of dyes and pigments. India is the second largest exporter of dyestuffs and intermediates developing countries, after China. About 90,000 tones of dyestuff and pigments produced

frequently in India. Mostly the textile industries have largest consumption of dyestuffs, at nearly 80%. Wastewater generated from textile industries pose a threat to the environment because a large amount of chemical containing dyes are used for various industrial applications and a some amount of these wastes enter the environment via wastewater. The presence of even very low concentrations of dyes in effluent is highly visible and degradation products of these textile dyes are often carcinogenic [1]. Dye removal has ecological and economical importance. The interaction between polymer and dye leads to the formation of polymer–dye complex which exhibits many interesting and important practical features. Coulombic, hydrophobic and steric interactions are major factors governing the thermo chemical and dynamic aspects of complex formation. The interactions of the hydrogels with dyes are of principal interest. Taking into account the environmental requirements, the development of water-based coloured polymer materials is one of the modern targets for the chemical industry. The textile finishing industry has a specific water demand of about 100-500 L.Kg<sup>-1</sup> product [2,3]. Colour in textile effluents has become particularly identified with the dyeing of cotton products and the use of reactive dyes. Upto 30% of the used dyestuffs remain in the spent dye-bath after the dyeing process [4]. Out of many contaminants present in wastewater, such as acids, bases, toxic organic and inorganic dissolved solids and colours, colours are considered as the most undesirable and are mainly caused by dyes [5]. Dyes are synthetic aromatic water soluble dispersible organic colourants, having potential applications in various industries. The dyestuff usage has been increased day by day because of tremendous increase of industrialization and man's urge for colour [6]. Dyes pictorial value is high, less than 1 ppm of the dye produces obvious colouration [7]. Synthetic dyestuffs are used extensively in textile, paper, printing industries and dye houses. The effluents of these industries are extremely coloured and the discarding of these wastes into water bodies causes damage to the environment. Removal of colour from dye bearing wastewater is a complex problem because of difficulty in treating such wastewaters by conventional treatment method [8]. Dye industries and many other industries which used dyes and pigments generated wastewater, characteristically high in colour and organic content. Presently, it was estimated about large number of different commercial dyes and pigments exists and over huge tones are produced annually worldwide [9]. About 10–15% of the total dyes from various textile and other industries get discharged in water causing extensive pollution [10,11]. From an environmental point of view, the removal of synthetic dyes is of great concern, since some dyes and their degradation products may be carcinogens and toxic [12]. Dye pollutants from textile dye

industries are an important source of environment contamination [13]. It is estimated that some of the dyes are lost during processes and is released in wastewater. The release of this colored wastewater poses a major problem for the industry as well as a threat to the environment [14]. The treatment of highly coloured waste-water containing hazardous industrial chemical effluents is one of the growing needs of the present time [15, 16]. Colour in water body is not only aesthetically unpleasant but also interferes light penetration and reduces photosynthetic action. Many dyes or their metabolites have toxic as well as carcinogenic, mutagenic and teratogenic effects on aquatic life and humans [17, 18]. Many industries use dyes extensively in different operations such as textile, paper, plastic, leather tanning etc [19, 20]. All dyes used in textile industry are designed to resist fading upon exposure to sweat, light, water, many chemicals including oxidizing agents and microbial attack. During processing up to 15% of the used dyestuffs are lost in industrial effluents [21, 22]. Major classes of dyes used are azo, anthraquinone and triphenylmethane. In addition to their visual effect and adverse impact in terms of Chemical Oxygen Demand (COD), many synthetic dyes show their toxic, carcinogenic and genotoxic effects [23].

### III. Methods of dye removal

During the last 35 years India has become a major producer of dyes and pigments. A number of dyes are prepared to fulfill the needs of not only the textile industries but also of other industries like paper, rubber, plastics, paints, printing inks, art and craft, leather, food, drug and cosmetics [24]. In particular, printing and dyeing unit wastewaters contain several types of coloring agents, which are difficult to be treated by biological methods [25]. Dyes even in very low concentrations, can affect the aquatic life and the food web. Some dyes are carcinogenic and mutagenic in nature therefore some techniques are required to remove the dyes from wastewater. The treatment of highly coloured wastewater containing hazardous industrial chemical effluents is one of the growing needs of the present time [26][27]. Various chemical and physical methods like coagulation, flocculation, adsorption, photocatalytic oxidation, chemical oxidation and froth flotation processes have been used by a number of research workers for the removal of organics as well as inorganic from wastewaters. [28]. Recently, sophisticated instrumentation involving electrochemical, photochemical, chromatographic techniques, etc., has also been employed for this purpose [29,30]. Several scientists have also tried water treatment of dyes over low cost materials using the adsorption technique. Photo catalytic degradation is considered a favoured, promising, cleaner, and greener technology for the removal of toxic organic and inorganic pollutants from water and

wastewater [31]. Our laboratories are also contributing in this direction with adsorption and electrochemical methods for the removal of some toxic textile and food dyes [32-34]. Many industries like the textile industry used dyes to colour their products and thus produce wastewater containing organics with a strong color, where in the dyeing processes the percentage of dye lost wastewater is 50% of the dye because of the low levels of dye-fiber fixation [35]. Discharge of these dyes into effluents affects the people who may use these effluents for living purposes such as washing, bathing and drinking [36]. Therefore It is very important to verify the water quality, especially when even just 1.0mg/L of dye concentration in drinking water could impart a significant color, making it unfit for human consumption [37]. Further more dyes can affect aquatic plants because they reduce sunlight transmission through water. Also dyes may impart toxicity to aquatic life and may be mutagenic, carcinogenic and may causes severe damage to human beings, such as dysfunction of the kidneys ,reproductive system, liver ,brain and central nervous system [38–40]. The removal of color from waste effluents becomes environmentally important because even a small quantity of dye in water can be toxic and highly visible [41]. Since the removal of dyes from wastewater is considered an environmental challenge and government legislation requires textile wastewater to be treated, therefore the reisa constant need to have an effective process that can efficiently remove these dyes [42]

In view of the aforesaid problems, recently much attention has been focused on the development of more effective, lower-cost, robust methods for waste-water treatment, without further stressing the environment or endangering human health by the treatment itself [43]. Extensive studies have been undertaken in recent years with the aim of finding alternative and economically feasible technologies for water and waste-water treatment. Discharge of dyeing industry waste-water into natural water bodies is not desirable as the colour prevents reoxygenation in receiving water by cutting off penetration of sunlight. This upsets the biological activities in waterbodies. Most of the dyes used as colouring materials are toxic to aquatic organisms [44]. In addition, wastewaters from dyeing and textile industries easily produce toxic tri halo methanes when chlorinated [45]. Methods such as chemical coagulation [46], ozonization [47], membrane filtration [48], electrolysis [49], oxidation [50] and bio-degradation have been widely used for the removal of dyes from water and wastewater. Adsorption has become one of the most effective and comparatively low cost methods for the decolourization of textile wastewater[51-53]. Numerous approaches have been made by various researchers to develop cheaper and effective

adsorbents to remove dyes from a variety of starting materials from waste [54]. Adsorption is by far the most effective and non-destructive technique that is widely used for the removal of dyes from aqueous solutions. It is attractive as the adsorbed dyes can be recovered with suitable regenerating agents. To make the treatment process economic, several investigators have concentrated their work on low cost, adsorbent materials. Textile industries have shown a significant increase in the use of synthetic complex organic dyes as colouring materials [55]. Adsorption has been found to be more efficient to other techniques for water treatment in terms of simplicity of design, initial cost, use of operation and insensitivity to toxic substances [56]. Adsorption has been used extensively in industrial process for separation and purification. The removal of coloured and colourless organic pollutants from industrial wastewater is considered as an important application of adsorption processes [57]. The major advantages of an adsorption treatment for the control of water pollution are less investment in terms of initial development cost, simple design, easy operations, free from generation of toxic substances and easy and safe recovery of the adsorbent as well as adsorbate materials [58]. In the adsorption technique the major concern is the selection of adsorbent material. In recent years “adsorption” process became more popular as “biosorption” by the application of biomaterials as adsorbent for contaminated water treatment [59]. However this process has not widely employed in industrial scale for waste-water treatment. Also the application of magnetic adsorbent technology for separation of pollutants in water has received considerable attention in recent years. During the past decade, great efforts have been devoted to the preparation of variety of magnetic composites/materials for waste-water treatment. Magnetic adsorbents are an attractive solution for metallic and dye pollutants, particularly due to the simple magnetic separation process.

There are many structural varieties of dyes that fall into either the cationic, nonionic or anionic type. Anionic dyes are the direct, acid and reactive dyes [60]. Brightly coloured, Water soluble reactive and acid dyes are the most problematic, as they tend to pass through conventional treatment systems unaffected [61]. Municipal aerobic treatment systems, dependent on biological activity, were found to be inefficient in the removal of these dyes [62]. Nonionic dyes refer to disperse dyes because they do not ionise in an aqueous medium. Concern arises, as many dyes are made from known carcinogens such as benzidine and other aromatic compounds [63,64] demonstrated that azo- and nitro-compounds are reduced in sediments, and similarly Chung et al.[65] illustrated their reduction in the intestinal environment, resulting in the formation of toxic amines. Anthraquinone-based dyes

are most resistant to degradation due to their fused aromatic ring structure. The ability of some disperse dyes to bioaccumulate has also been demonstrated. [66]. This review illustrates the critical study of the most widely used methods of dye removal from dye-containing industrial effluents. These methods have been discussed under three categories: chemical, physical and biological. Currently the main methods of textile dye treatment are by physical and chemical means (Table 1) with research concentrating on cheaper effective alternatives.

<b>Advantages and disadvantages of the current methods of dye removal from industrial effluents</b>		
<b>Physical/chemical methods</b>	<b>Advantages</b>	<b>Disadvantages</b>
<b>Activated carbon</b>	Good removal of wide variety of dyes	High cost
<b>Cucurbituril</b>	Good sorption capacity for various dyes	Very expensive
<b>Electro kinetic coagulation</b>	Economically feasible	High sludge production
<b>Fentons reagent</b>	Effective decolourisation of both soluble and insoluble dyes	Concentrated sludge generation
<b>Irradiation</b>	Effective oxidation at lab scale	Requires a lot of dissolved O <sub>2</sub>
<b>NaOCl</b>	Initiates and accelerates azo-bond cleavage	Release of aromatic amines
<b>Ozonation</b>	Applied in gaseous state: no alteration of volume	Short half-life (15-20 min)
<b>Membrane filtration</b>	Removes all dye types	Sludge production
<b>Peat</b>	Good adsorbent due to cellular	Specific surface areas for



	structure	adsorption are lower than activated carbon
<b>Silica gel</b>	Effective for basic dye removal	Prevent commercial application

Adsorption methods employing solids absorbents are widely used to remove certain classes of chemical pollutants from wastewater. However, among all the sorbent materials proposed, activated carbon (AC) is the most popular material for the removal of pollutants from wastewater. AC is an amorphous carbon compound in which a high degree of porosity has been developed during manufacture. It is this porosity, which governs the way in which AC performs its purifying role, and the very large surface area provides many sites upon which the adsorption of impurity molecules can take place. The factors which favor the selection of agricultural adsorbents are its low-cost, widespread presence and organic composition which shows strong affinity for some selected dyes. Because be disposed of with out expensive regeneration. A wide variety of ACs has been prepared from agricultural byproducts.

<b>Dyes</b>	<b>Adsorbents</b>	<b>Equilibrium time</b>	<b>q<sub>e</sub> (mg/g)</b>	<b>References</b>
Malachite green	Neem bark	7 h	0.36	67
Malachite green	Mango bark	7 h	0.53	68
Malachite green	Pandanus leaves	40 min	9.737	69
Congo red	Tamarind shell	4h	10.48	70
Acid blue	Pitch pine saw dust	60 min	27.5	71
Methylene blue	Cherry saw dust	2 h	39	71
Rhodamine B	Banana bark	40 min	40.161	72
Methylene blue	Sunflower seed husk	4 h	45.25	73



Malachite green	Rice husk	40 min	63.85	74
Congo red	Neem leaf powder	5 h	72	75
Methylene blue	Hazlenut shell	60 min	76.9	71
Methylene blue	Rice husk	30 min	690	76

The main aim of the review of the past work is to give an idea for the systematic study of the utilization of low cost adsorbents for the removal of dyes from aqueous solution and from industrial effluents. Among various ways of treating industries effluents containing dyes, one can utilize the resources of inexpensive techniques. The summary of the published data with some of the latest important results with up to date literatures on the adsorption properties of some alternatives adsorbents used for the removal of the dyes. Photo catalytic and adsorption studies on the removal of dye Congo red from wastewater investigated by Rajeev Jain and Shalini Sikarwar [77]. The photocatalytic results of the study indicate that anatase titanium dioxide, as a catalyst is very efficient and effective to enhance the photocatalytic activity. Catalyst concentration and additives such as  $H_2O_2$  were used to obtain a high degradation rate of Congo red. Removal of Colour from Different Dye Wastewater by Using Ferric Oxide as an Adsorbent was reported by Kartik H. Gonawala & Mehali J. Mehta [78]. They are concluded that  $Fe_2O_3$  powder is used for removal of Color from textile dye wastewater by batch experiments. Adsorption Equilibrium is attained within 45 min. It obeyed Freundlich isotherm model as compared to Langmuir isotherm and Tempkin isotherm. The order of disperse blue 73 (Anthraquinone dye) adsorption was governed by pseudo second-order kinetics. Removal of Dyes from Wastewater Using Bottom Ash studied by V. K. Gupta. et. al [79] and they represent the bottom ash generated in a MSWI was used as a low-cost adsorbent for the removal of alizarin yellow, fast green, and methyl violet from wastewater. The adsorption of alizarin yellow and fast green has been found to be exothermic, whereas it is endothermic in the case of methyl violet. The results indicate that both the Freundlich and Langmuir models can be used to fit the data and estimate the model parameters.

Degradation of Congo Red Solution by Zinc Oxide/Silver Composite Preheated at Different Temperatures article reported by Oda. et al [80]. Congo red dye was degraded with high photo degradation efficiency by sun light. The reaction done without focusing sun radiant and the catalyst work properly. The photo oxidation of

methanol in the photo deposition making Ag ion converts to Ag<sub>2</sub>O system making a good doping on the ZnO surface.

Chaudhary et al investigated the use of chromium waste sludge for the adsorption of colour from dye effluent streams [81]. Adsorption studies reveals that chromium hydroxide precipitates can be used as an adsorbent for the removal of Methylene blue, Reactive blue, Congo red and disperse Orange dyes from aqueous system. It include three different mechanisms such as; attraction of negative surface charges on hydroxide at high pH for dye cations (Methylene blue), attraction of positive surface charges on the precipitate at low pH for dye anions (Reactive blue and Congo red) and dye particle entrapment for the neutral disperse orange.

#### IV. Conclusion

The presence of dyes in industrial effluents when exceed the permissible limit causes various disorders such as allergic dermatitis, skin irritation, cancer etc. the prominent effect of their presence is the visual coloration of the water. Adsorption process is the most widely used and effective method. This technique offers much potential in the treatment of dye-containing effluents. It has been concluded that removal of dyes with adsorption technique using low cost/no cost adsorbent materials like naturally occurring, agricultural and industrial waste materials, has been found to be more effective with better removal efficiency. By utilizing waste discharged residues as adsorbents thereby, would improve textile industry economically.

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