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Review Article

REVIEW ON ADSORPTION-DESORPTION STUDIES ON DYE SEQUESTRATION

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ABSTRACT

This review article provides extensive literature information about dyes, its classification and toxicity, various treatment methods, and dye adsorption characteristics by various adsorbents. One of the objectives of this review article is to study the potentially effective adsorbents in the removal of dyes. Therefore, an extensive list of various adsorbents such as natural materials, waste materials from industry, agricultural by-products, and biomass based activated carbon in the removal of various dyes has been compiled here. Dye bearing waste treatment by adsorption using low cost alternative adsorbent is a demanding area as it has double benefits i.e. water treatment and waste management. Once adsorption process is over adsorbent is to be discarded as waste. Generation of waste adsorbent is a serious environmental problem. Adsorbents can be regenerated and put to reuse in the same process line. Thus the recovery of adsorbate and subsequent regeneration and reuse of adsorbent are important attributes of this process from economy and environmental point of view. In the current review, the summery of research carried out for recovery and regeneration of adsorbent was presented. It was found that various methods like chemical, electrochemical and thermal methods were used effectively for regeneration of adsorbents. Conclusions have been drawn from the literature reviewed.

INTRODUCTION

Modern civilization relies to a significant extent on textile, paper, plastics, leather, cosmetics and dyeing industries. It has been reported that in a particular dyeing process 10-15% of dyestuff is generally lost directly to the effluent. The discharged dyestuff causes potential danger to bioaccumulation. Therefore, design of an effluent treatment plant that can effectively clean industrial effluents without leaving any fragments of dye species and generating secondary wastes during its operation has been one of the prime challenges to the scientific community.

Dye wastewater discharged from textile and dyestuff industries are one of the most significant sources of pollutants in the environment. Reactive dyes are extensively used in textile industries because of their exclusive properties which include bright color and low energy consumption. It is estimated that around 40% of consumed reactive dyes are discharged into the wastewater of dyeing operations. Reactive dyes are soluble in water, so removing them by flocculation and biodegradation is very difficult. The presence of dye in water can cause many problems including high biochemical oxygen demand (BOD), chemical oxygen demand (COD) and an increase in suspended solids; thus, effective treatment methods such as flocculation, membrane separation processes, oxidation, electrolysis and adsorption are needed to remove them from wastewaters. Among the mentioned methods, adsorption by adsorbent is one of the most effective methods for removing dye molecules. A successful sorbent material should have a high affinity and capacity for adsorbate molecules as well as regeneration potential. Also, it should be applicable for the majority of reactive dyes and economically affordable. Activated carbon (AC) is an appropriate adsorbent for dye adsorption because of its large surface area, appropriate porosity and hydrophobic properties. Dyes are basically chemical compounds that can connect themselves to surfaces or fabrics to impart color. The majority of dyes is complex organic molecules and is required to be resistant to many things such as the action of detergents. Synthetic dyes are widely used in many fields of advanced technology, e.g., in various kinds of the textile [1], paper [2], leather tanning [3], food processing, plastics, cosmetics, rubber, printing and dye manufacturing industries [4–6]. Synthetic dyes are also employed in ground water tracing [7], for the determination of specific surface area of activated sludge [8], sewage [9] and wastewater treatment [10], etc. Their discharges into hydrosphere possess a significant source of pollution due to their recalcitrance nature. This will give undesirable colour to the water body which will reduce

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sunlight penetration and resist photochemical and biological attacks to aquatic life (Table 1).

Table 1 Classification of Dyes

Group	Application
Acid	Wool, silk, paper, synthetic fibers, leather
Azoic	Printing Inks and Pigments
Basic	Silk, wool, cotton
Direct	Cotton, cellulosic and blended fibers
Disperse dyes	Synthetic fibers
Reactive	Cellulosic fiber and fabric
Mineral and pigments dyes	Cotton, cellulosic, blended fabric, paper
Sulphur	Cotton, cellulosic fiber
Vat dyes	Cotton, cellulosic and blended fiber

With respect to the number and production volumes, azo dyes are the largest group of colorants, constituting 60-70% of all organic dyes produced in the world. They have a wide range of applications in the textile, pharmaceutical and cosmetic industries and are also used in food, paper, leather and paints. The organized sector dominates, with 65% share of the total market, while the unorganized sector controls the remaining 35% of the market. Exports of dyes are also expected to increase by 6.4% due to the shift of production bases from developed countries to India on account of stringent pollution control measures being adopted in those countries. At present, India contributes about 6% of the share in the global market.

Toxicity effects of dyes

Basic dyes have high intensity of colours and are greatly visible even in very little concentration. The complex dyes are generally chromium based, which is carcinogenic. Dyes may affect the photosynthetic activity in aquatic life due to decreased light penetration and may also be toxic to some aquatic life due to the presence of metals, aromatics, etc. Furthermore, dyes are also carcinogenic, mutagenic, or tetragenic in various microbiological, fish species. Additionally it can also cause severe damage to human beings such as dysfunction of the kidney, reproductive system, liver, brain and central nervous system. Azo dyes are toxic because of the presence of toxic amines in the effluent. Similarly anthrax quinone based dyes are most resistant to degradation and remains colour for a large time in effluents. Reactive dyes are water soluble and 5–10% of the dyes go in the dye bath giving highly coloured effluent causing serious troubles in the environment. Additionally, reactive dyes that are chemically stable and having little biodegradability are likely to pass through conventional treatment plants untreated, so their elimination is of great importance. Due to their toxic effects, dyes have generated much concern regarding its use. It has been informed to cause mutagenesis, chromosomal fractures, carcinogenesis, and respiratory toxicity. Therefore focuses on specific methods and technologies to remove dyes from different kinds of wastewater streams are desired.

Adsorption

Adsorption techniques employing solid sorbents are widely used to remove certain classes of chemical pollutants from waters, especially those that are practically unaffected by conventional biological wastewater treatments.

Why we prefer biosorption?

Till date, research in the area of biosorption suggests it to be an ideal alternative for decontamination of metal/dye containing effluents. Biosorbents are attractive since naturally occurring biomass/adsorbents or spent biomass can be effectively used. Biosorption is a rapid phenomenon of passive metal/dye sequestration by the non-growing biomass/adsorbents. Results are convincing and binding capacities of certain biomass/adsorbents are comparable with the commercial synthetic cation exchange resins.

The biosorption process involves a solid phase (sorbent or biosorbent; adsorbent; biological material) and a liquid phase (solvent, normally water) containing a dissolved species to be sorbed (adsorbate, metal/dyes). Due to the higher affinity of the adsorbent for the adsorbate species, the latter is attracted and bound there by different mechanisms. The process continues till equilibrium is established between the amount of solid-bound adsorbate species and its portion remaining in the solution. The degree of adsorbent affinity for the adsorbate determines its distribution between the solid and liquid phases. Biosorption has advantages compared with conventional techniques. Some of these are listed below:

Cheap: the cost of the biosorbent is low since they often are made from abundant or waste material.

Dye selective: the dye sorbing performance depends on various factors such as type of biomass, mixture in the solution, type of biomass preparation and physico-chemical treatment.

Regenerative: biosorbents can be reused, after the metal is recycled.

No sludge generation: no secondary problems with sludge occur with biosorption, as is the case with many other techniques, for example, precipitation.

Competitive performance: biosorption is capable of a performance comparable to the most similar technique, ion exchange treatment. Ion exchange is, as mentioned above, rather costly, making the low cost of biosorption a major factor.

Biosorbents intended for bioremediation environmental applications are waste biomass of crops, algae, fungi, bacteria, etc., which are the naturally abundant. Numerous chemical groups have been suggested to contribute to biosorption. Biosorption by microorganisms have various disadvantages, and hence many low cost adsorbents (industrial/agricultural waste products/by products) are increasingly used as biosorbents (Table 2).

Table 2 Various low cost adsorbents in removal of Dyes

Adsorbents	Dye	Adsorption capacities (mg/g)	References
Neem Bark	Malchite Green	0.36	[11]
Mango Bark	Malchite Green	0.53	[11]
Neem leaf powder	Congo red	72	[12]
Teak tree bark	Methylene Blue	333.3	[13]
Sunflower seed husk	Methylene Blue	45.25	[14]
Hazlenut shell	Methylene Blue	76.9	[15]
Tree fern	Basic red 13	408	[16]
Pine sawdust	Acid yellow 132	398.8	[17]
Peanut hull	Methylene Blue	68.03	[18]
Coir pith	Acid violet 1.6	1.6	[19]
Rice husk	Methylene Blue	40.588	[20]

Research for Regeneration, Recovery and Desorption

In many case adsorbate may be a resource and need to be recovered or concentrated to earn recovery credits [21]. Considering all above arguments it is evident that spent adsorbent needs to be stabilized after being discarded. Because of involvement of high cost of production, stabilizing or proper disposal seems unwilling operation. Under such circumstances reuse by regeneration of adsorbent could prove double rewarding by stabilizing adsorbents and recovering resource by reutilization and thereby minimizing demand for virgin adsorbents. Thus regeneration assumes essential importance for economical use of adsorption technique Techno economical viability of regeneration has been established and it is current research thrust area in this field. Many methods of regeneration are currently being researched which include, thermal regeneration, steam regeneration, pressure swing regeneration, vacuum regeneration, micro wave regeneration, ultrasound regeneration, chemical regeneration, oxidative regeneration, ozone regeneration, bio-regeneration. Apart from these regeneration methods combined effects of these methods have been also explored *e.g.* thermo chemical regeneration, electro-chemical *etc*.

Method and types of regeneration

Selection of method of regeneration depends upon the priority of regeneration. If adsorbate or both adsorbent and adsorbate recovery is desired physical means of regeneration are generally employed *e.g.* thermal, pressure, vacuum, microwave *etc*. If adsorbent recovery or adsorbent recovery with destruction of adsorbate is required then oxidative or chemical regeneration may be preferred. However this is not hard and fast rule but techno-economics generally dominates the selection of procedure for regeneration. Regeneration have been also referred as reactivation [22,23], Literature survey suggests that regeneration is better term for reuse of adsorbents as it includes both desorption and activation and also carves difference between desorption and regeneration. In better case the agent of desorption is also candidate for activation and hence activation step is skipped and hence regeneration can be explained as combination of desorption and activation. In the regeneration process the following factors influence on the effectiveness of the installation performance: the degree of solution purification, the separation of a mixture into the components, adsorbent stability, the degree of recovery of adsorbed components and energy consumption. The chosen regeneration method should ensure [24].

- The highest possible degree of desorption of the adsorbed compound
- The least possible erosion and the mechanical destruction of used adsorbent
- Easy access and the ecological safety of used regeneration agent
- Ease of separation of recovered or removed compounds from desorbate
- Invariable qualitative composition of desorbed components

Thermal regeneration

In case of thermal regeneration which is most common the temperature of regeneration decides the site for regeneration, offsite regeneration in such case [24] in only preferred when regeneration temperature is between 700^0C-1000^0C, moreover because of liability and economic concerns, many design manuals recommend that regeneration should be done offsite whenever possible, regardless of whether land and utilities are available on-site [25]. The adsorbent losses due to attrition have been estimated as 5-10% for *in situ* regeneration and 10-15% for offsite regeneration [26]. However in actual practice the method adopted depends upon the cost of adsorbent and the nature of adsorbate.

Steam regeneration

Discovery of steam power has been turning point of human history. Steam has been used in industry since long time now. This industrial familiarity of steam thus is not new. Most industrial setups are well acknowledged with steam operation and maintenance units and hence prefer steam regeneration. Steam regeneration is widely popular and cheap [27]. Even though steam is readily available in industry it can also be generated by skid mounted boiler units which are available at relatively low cost. Steam works especially well with hydrophobic organics, such as chlorinated solvents. Hydrophobic adsorbents have an added advantage in that they can be separated from the condensed water by gravity. Steam is less useful for hydrophilic contaminants such as alcohols, aldehydes, or ketones. If steam is used for these types of contaminants, the contaminants can be separated from the condensate by distillation. However, distillation raises the Operation and Maintenance costs of the system. Hydrophobic adsorbate desorbs at temperature approaching steam distillation temperature and hydrophilic adsorbate desorbs at temperature approaching their boiling points [28]. After regeneration of adsorbent bed, the condensed adsorbate can be recovered by separation techniques, multiplying benefits of steam regeneration. Steam regeneration has been repeatedly shown to be very effective and economic to regenerate active carbons and hydrophobic zeolites [29]. Heating and purging properties of steam are important for regeneration and contribute equally to the regeneration of adsorbents [30]. The source of energy for regeneration is heat of steam and heat of adsorption of water. The heat generated by adsorption of water cannot be neglected as a driving force for regeneration of adsorbents [31]. During steam regeneration unlike purge gas regeneration the temperature don't drop significantly along the length of bed as the heat released due to adsorption is uniform throughout the bed [31]. In Steam regeneration, the high heat of condensation of steam allows the bed to be heated up rapidly, allowing for a faster desorption from the adsorbent; the desorbate is however only swept out of the bed when the latter is hot enough such that at least some steam remains in gaseous form and can sufficiently purge the adsorbate. Steam also activates adsorbent and do not cause polymerization of adsorbate.

Electrochemical regeneration of a carbon-based adsorbent loaded with crystal violet dye

Electrochemical processes have been widely investigated as methods of treating dissolved organics in water [33], with significant interest being shown in the removal of colour from dye house waste [34–36]. These wastes are highly coloured and electrochemical processes can be used to eliminate colour as the waste is highly conductive due to the presence of large quantities of sodium chloride. Whilst the treatment of wastewater in electrochemical cells has been the subject of many reports, electrochemical regeneration of adsorbents has not been widely studied. Electrochemical regeneration refers to the regeneration of loaded adsorbent inside an electrolytic cell. The regeneration involves desorption and/or destruction of the adsorbed organic matter restoring the adsorptive capacity. Whilst a number of other researchers have undertaken some research into electrochemical regeneration of activated carbon [37,38], Tsai [32] has undertaken the most detailed investigations using granular activated carbons (GAC) loaded with phenol, achieving regeneration efficiencies of up to 95%. Regeneration was found to be greatest with the loaded GAC being placed on the cathode. Tsai [32] suggested that the electrochemical effects are restricted to the external surface of the carbon and for regeneration at the cathode surface the process consisted of initial phenol desorption followed by phenol destruction. Both research groups used undivided cells. The rate of adsorption and desorption of organics from activated carbons is often governed by intra-particle diffusion. This requires long adsorption and regeneration periods. For example Tsai [32] reported that 6-8 days were required to achieve equilibrium using GAC (Filtrasorb F-400) and several hours were needed for electrochemical regeneration. An alternative approach is to adsorb onto a non-porous material which would eliminate the intra-particle diffusion. If this material had a high electrical conductivity it would facilitate its electrochemical regeneration. The use of such a material should significantly reduce the time required to achieve both equilibrium and regeneration, at the expense of greatly reduced adsorbent capacity due to the lack of internal surface area. As well as increased rates of adsorption and electrochemical regeneration, this approach shares the same benefits as direct electrochemical treatment of waters, notably the minimal use of chemicals with no sludge produced.

CONCLUSION

Adsorption is very important unit pollution abatement. Efficiency of adsorption process, its diverse applicability and its operator friendliness make it more favorites process in industry for compliance and recovery purpose. However disposal of spent adsorbents is still a topic of debate. With strict legislation surfacing for treatment and storage of spent adsorbent many industries would like to shift to regeneration. The review presented various technical aspects of steam regeneration of adsorbents. Owing to availability and familiarity of steam in industry, it is highly beneficial to utilize steam for regeneration. Regeneration is very important aspect of the adsorption from economy and environmental point of view. The disposal of adsorbent is one of the problems associated with the adsorption processes. The regeneration can reduce the need of new adsorbent and also reduce the problem of disposal of used adsorbent. Various regeneration methods have been used with different degrees of success. These methods includes solvent washing, thermal, chemical and electrochemical regeneration. The recovery of many solutes was possible by using solvent washing. Use of non thermal plasma instead of electric heater showed promising results in terms of energy efficiency.

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