RESEARCH ARTICLE OPEN ACCESS

Adsorptive Removal Of Dye From Industrial Dye Effluents Using Low-Cost Adsorbents: A Review

Mehali J. Mehta[1], Karishma K. Chorawala[2]
[1](Assistant Professor, Civil Engineering Department, Sarvajanik College of Engineering & Technology, Gujarat, India)
[2] (Student, Masters in Environmental Engineering, Sarvajanik College of Engineering & Technology, Gujarat, India)

ABSTRACT
Industrial, agricultural, and domestic activities of humans have affected the environmental system, resulting in drastic problems such as global warming and the generation of wastewater containing high concentration of pollutants. As water of good quality is a precious commodity and available in limited amounts, it has become highly imperative to treat wastewater for removal of pollutants. In addition, the rapid modernization of society has also led to the generation of huge amount of materials of little value that have no fruitful use. Such materials are generally considered as waste, and their disposal is a problem. The utilization of all such materials as low-cost adsorbents for the treatment of wastewater may make them of some value. An effort has been made to give a brief idea about the low-cost alternative adsorbents with a view to utilizing these waste/low-cost materials in the treatment of wastewater.
***Keywords* -** Adsorption, color, dye effluent, isotherms, low- cost adsorbents.

I. INTRODUCTION

The textile industry is one of the largest manufacturing industries. In every stage of textile industry various types of dyes are used to color their products. The dye containing wastewater is usually released directly into the nearby drains, rivers, stagnant, ponds or lagoons. Such wastewater disposal may cause damage to the quality of the receiving water bodies, the aquatic eco-system and the biodiversity of environment. The dyeing industry effluents contain high BOD and COD value, suspended solids, toxic compounds and the color that is perceived by human eyes at very low concentration. Moreover, dyes may adversely affect the aquatic life because of the presence of aromatic materials, metals and chlorides etc. The color removal was extensively studied using different methods such as coagulation, flocculation, ultra-filtration, nano-filtration, photo oxidation, activated carbon etc [1].

Industrial waste constitutes the major source of various kinds of metal pollution in natural water. Wastewaters generated from industrial treatment plant contain considerable metal contaminants. Their concentrations must be reduced to safe levels before being released into the environment. Rapid industrialization has led to increase disposal of heavy metal into the environment. The metals are of special concern because of their persistency [8].

physicochemical technique includes adsorption, coagulation, chemical precipitation, ultra filtration, etc. Among of these methods, adsorption is the most effective and economical because of their relative low cost. The adsorbents may be of minerals, organics, or biological origin, zeolites, industrial bi products, agriculture wastes, biomass and polymeric materials. The major advantage of an adsorption system for water pollution control are less investment in terms of both initial cost and operational cost, simple design, easy operation and no effect of toxic substances compared to conventional biological treatment processes [3].

1.1 Adsorption

Adsorption is a fundamental process in the physiochemical treatment of wastewaters, a treatment which can economically meet today's higher effluent standards and water reuse requirements. Adsorption is a mass transfer process which involves the accumulation of substances at the interface of two phases, such as, liquid–liquid, gas–liquid, gas–solid, or liquid– solid interface. The substance being adsorbed is the adsorbate and the adsorbing material is termed the adsorbent [1]. The driving force for adsorption process is Surface affinity. Chemical reactivity, pH, surface area for adsorption per unit volume and reduction in surface tension is key parameter for adsorption.

Adsorption is a sorption operations, in which certain components of a fluid phase, called solutes, are selectively transferred to insoluble, rigid particles suspended in a vessel or packed in a column. Adsorption is a separation process in which certain components of the fluid phase are transferred to the surface of the solid adsorbents.

The phenomenon of the enrichment of chemical substances at the surface of a solid is called adsorption. All adsorption performance processes are depends on solid-liquid equilibria and on mass transfer rates. The adsorption operation can be batch, semi-batch and continuous [12].

Among the unit operations in water and wastewater treatment adsorption occupies an important position.

Adsorption operations exploit the ability of certain solids preferentially to accumulate specific substances from solution onto their surfaces. Sorption, includes selective transfer to the surface, and for into the bulk of liquid. In a general adsorption process, the adsorbed solutes are referred to as adsorbate and the adsorbing agent is the adsorbent.
Theoretically, the adsorption of solute on to solid particles normally takes four essential steps:
a) Solutes diffuses through the fluid to an area near the solid particle surface,
b) Solute diffuses to the external surface of the particle,
c) Solute diffuses to the pore wall,
d) Solute adsorbs to the internal surfaces of the pore wall.

1.1.1 Types of Adsorption:

At molecular level, adsorption is due to attractive interactions between a surface and the species being adsorbed.

• **Physical adsorption**: It is a result of intermolecular forces of attraction between molecules of the adsorbent and adsorbate. Physical adsorption occurs when the intermolecular attractive forces between molecules of a solid and the gas are greater than those between molecules of the gas itself. Furthermore, it occurs lower or close to the critical temperature of the adsorbed substance.

• **Chemisorptions**: It is a result of chemical interaction between the solid and the adsorbed substance. It is also called activated adsorption. Commercial adsorbents rely on physical adsorption; catalysis relies on chemisorptions.

• Chemisorptions occur only as a monolayer and substances chemisorbed on solid surface are hardly removed because of stronger forces

II. Natural Adsorbents Used For Color Removal

2.1 Clay:

Clay are natural adsorbent classified based on their difference in layered structure. The available classes of clay materials include smectites (montmorillonite, saponite), mica (illite), kaolinite, serpentine, pylophyllite (talc), vermiculite and sepiolite [4]. The process by which adsorption takes place is as a result of net negative charge on the structure of minerals, and it's this negative charge that gives the clay mineral the capability to adsorb positively charged species. Most of Their sorption properties depends their high surface area and high porosity.

2.2 Siliceous Materials:

Natural Siliceous materials are one of the most availability and low price adsorbent. It includes silica beads, perlite and dolomite, and glasses. The use of these minerals was based on chemical reactivity of their hydrophilic surface and mechanically stable, which results from the presence of silanol groups. But among all this, silica beads is given particular attention in the use of the material as adsorbent. However, it is reported that, a major problem with this kind of application is their low resistance toward alkaline solutions their usage is limited to media of pH less than 8.

2.3 Zeolites:

Zeolites occur naturally as porous alumino silicates consisting of different cavity structures and are linked together by shared oxygen atoms. Zeolite has a wide variety of species. More than 40 natural species are available which includes clinoptilolite and chabazite[5]. But, clinoptilolite, a mineral of the heulandite group is the most and frequently studied material, due to its have high selectivity for certain pollutants. Intensive research has been done on the use and application of zeolite as adsorbent in removing trace quantities of pollutants such as heavy metal ions and phenols with regards to their cage-like structures suitable for ion exchange.

2.4 Color Removal Using Activated Carbons From Waste Water:

Activated carbons are derived from natural materials such as wood, lignite or coal, which are commercially available. But almost any carbonaceous material may be used as precursor for the preparation of carbon adsorbents. Coal is the most commonly used precursor for AC production because of its availability and cost effective [5]. Coal comprises of different mixtures of carbonaceous materials and mineral matter, which results from the degradation of plants. The nature, origin and the extent of the physical–chemical changes occurring after deposition of vegetation, determines the sorption properties of each individual coal.

Attention has been drawn on the use of coal as a successful sorbents for dye removal. Additionally, coal is not a pure material, and thus will have different sorption properties due to its large variety of surface properties. Recently there has been report on the use of activated carbon in the treatment of dye and heavy effluents. Materials such as peanut shell, raw pine and acid-treated pine cone powder. Neem leaf, coconut shell has been proved in reducing the concentration of pollutants in wastewater successfully. Their sorption capacity increases with increasing in adsorbent dosage.

TABLE 1
Low-Cost Adsorbents [12]

Sr No	Adsorbents
1.	Ferric oxide
2.	Aluminium oxide
3.	Chitosan
4.	Cotton
5.	Orange peel
6.	Saw dust
7.	Neem leaf
8.	Sugarcane bagasse
9.	Rice husk
10.	Fly ash
11.	Chitin
12.	Banana peel
13.	Maize cob
14.	shell

III. METHODS OF ADSORPTION[15]

Adsorption is carried out by two systems:

3.1 Batch Reactor: In batch-type contact processes a quantity of carbon is mixed continuously with a specific volume of water until the contaminants have ben decreased to a desired level. The carbon is then removed and either discarded or regenerated for use with another volume of solution. If finely powdered carbon is used in this type of system, separation of the spent adsorbent from the water may be difficult. Conversely, the use of large particles of carbon, which are removed more rapidly when exhausted, requires longer periods of contact between solution and adsorbent, necessitating larger basins or tanks in which to retain the water during treatment.

3.2 Column Type Reactor: Column-type continuous-flow operations have an advantage over batch type operations because rates of adsorption depend on the concentration of solute in the solution being treated. For column operation the carbon is continuously in contact with afresh solution. Consequently, the concentration in the solution in contact with a given layer of carbon in a column changes very slowly. For batch treatment, the concentration of solute in contact with a specific quantity of carbon decreases much more rapidly as adsorption proceeds, thereby decreasing the effectiveness of the adsorbent for removing the solute[14].

The rate of exhaustion of carbon in most waste treatment applications is usually not high enough to justify moving-bed adsorbers for column or bed type systems. Thus a fixed-bed adsorber is generally preferred. Up-flow expanded operation of fixed beds of activated carbon permits the use of small particles for faster adsorption rates without the associated problems of excessive head-los, air-binding, and fouling with particulate matter common to packed-bed operation with fine media[14]. In expanded-bed operation, the water flows upward through a column of relatively fine granular carbon at a velocity sufficient to suspend the carbon. Packed-bed adsorption techniques have conventionally ben used for water treatment. Expanded-bed technology is relatively new**.**

For fixed-bed (either packed or expanded) adsorption operations with activated carbon the water or wastewater to be treated is passed through a stationary bed. Non steady-state conditions prevail in that the carbon continues to remove increasing amounts of impurities from solution over the entire period of useful operation.

IV. EFFECT OF LOW-COST ADSORBENTS ON VARIOUS WASTEWATERS

Based on various researches, it has been proved that eco- friendly adsorbents have been satisfied as an alternative substitution of activated carbon for the removal of dyes from wastewater. Adsorbents prepared from sugarcane, baggase- an agro industries waste has been successfully used to remove the methyl red from an aqueous solution.

Maximum removal efficiency achieved up to 85% for biosorbent prepared from Neem Leaves at the optimum values of parameters such as pH, dosage, contact time, etc. The analyses of the results indicate that egg shell, chitosan, etc. like most other natural absorbents can be used in the treatment process of heavy metals and the treatment efficiency may be as high as 100% by choosing the adsorbent amount precisely. The concentration of heavy metals has also an important effect on the treatment outcome. Chitosan, egg shell wastes are cheap material and thus it would be convenient to use it in industrial wastewater treatment plants.

Saw dust an agriculture by-product acts as an effective adsorbent for the removal of basic dye like congo red from its aqueous solution.

Low-cost adsorbents like peanut husk charcoal, fly ash and natural zeolite are effective for the removal of Cu^{2+} and Zn^{2+} ions from aqueous solutions.

Wood apple shell, a fruit-food solid waste, was successfully utilized as a low cost alternative adsorbent for the removal of hazardous dye Malachite Green MG. The removal of MG dye was found to be 98.87%.

V. PROPERTIES OF LOW-COST ADSORBENTS

4.1 Chitosan: Chitosan and its derivatives are examples of value-added materials. They are produced from chitin, which is a natural carbohydrate polymer found in the skeleton of crustaceans, such as crab, shrimp. Chitosan is a polymer obtained from deacetylation of chitin.

4.2 Egg shell: Egg shell is largely-crystalline calcium carbonate. The calcium comes partly from the hen's bones and when necessary the hen can mobilize 10 percent of her bone for the purpose.

4.3 Rice husk: Rice husk is an agricultural waste material generated in rice producing countries, especially in Egypt. The annual world rice production is approximately 500 million metric tons, of which 10–20% is rice husk [5]. Dry rice husk contains 70–85% of organic matter (lignin, cellulose, sugars, etc.) and the remainder consists of silica, which is present in the cellular membrane. In recent years, attention has been focused on the utilization of unmodified or modified rice husk as an adsorbent for the removal of pollutants.

4.4 Fly ash: Fly Ash is a naturally-cementations coal combustion by-product. It is extracted by the precipitators in the smokestacks of coal-burning power plants to reduce pollution Since the fly ash disposal problem emerged with the advent of pollution control systems in the 1960's and 1970's, extensive research has been done to understand how it performs in its orthodox capacity – as a soil stabilizer and structural concrete admixture[5].

VI. ADSORPTION ISOTHERMS AND MODELS

An adsorption isotherm is the presentation of the amount of solute adsorbed per unit weight of adsorbent as a function of the equilibrium concentration in the bulk solution at constant temperature. Langmuir and Freundlich adsorption isotherms are commonly used for the description of adsorption data[8].

The Langmuir equation is expressed as:

$C_e/q_e= 1/bX_m+Ce/X_m$

Where,

C_e is the equilibrium concentration of solute (mmolL^{-1}).

q_e is the amount of solute adsorbed per unit weight of adsorbent (mmol g^{-1} of clay).

X_m is the adsorption capacity (mmol g^{-1}) or monolayer capacity, and *b* is a constant (L mmol^{-1}).

The Freundlich isotherm describes heterogeneous surface adsorption. The energy distribution for adsorptive sites (in Freundlich isotherm) follows an exponential type function which is close to the real situation. The rate of adsorption/desorption varies with the strength of the energy at the adsorptive sites.

The Freundlich equation is expressed as:

$\log q_e= \log k+ 1/n \log C_e$

Where,

k (mmol g^{-1}).

1/*n* are the constant characteristics of the system.

VII. ADVANTAGES OF ADSORPTION PROCESS

- Cheap: The cost of adsorbent is low since they are often made from locally, abundantly and easily available materials.
- Metal Selective: The metal adsorbing performance of different types of bio-mass can be more or less selective on different metals.
- Regenerative: Sorbent material can be possible to reuse after regeneration.
- No Sludge Generation: Unlike the problems in other techniques (ex: precipitation), there is no issue of sludge generation in adsorption process.
- Metal Recovery: If adsorbate is a metal ion, it is possible to recover the metal ion after being desorbed from the adsorbent materials.
- Competitive Performance: Performance of adsorption process in terms of efficiency and cost is comparable with the other methods available.

VIII. CONCLUSION

In this review, a wide range of non-conventional low- cost adsorbents has been presented. Inexpensive, locally available and effective materials could be used in place of commercial activated carbon for the removal of dyes from aqueous solution. Undoubtedly low-cost adsorbents offer a lot of promising benefits for commercial purposes in the future. In particular, from the recent literature reviewed, chitosan-based sorbents have demonstrated outstanding removal capabilities for certain dyes in comparison to activated carbon [1]. However, despite a number of papers published on low-cost adsorbents, there is as yet little information containing a full study of comparison between sorbents. Although much has been accomplished in the area of low-cost sorbents, much work is necessary (i) to predict the performance of the adsorption processes for dye removal from real industrial effluents under a range of operating conditions, (ii) to better understand adsorption mechanisms and (iii) to demonstrate the use of inexpensive adsorbents at an industrial scale.

REFERENCES

[1] A. Buekens and n. X. Zvavkiua, "*Adsorbents and Adsorption processes for pollution control*"pollution control technologies - vol. 2.

[2] D.A. Nimkar, S.K. Chavan, "*Removal of congo red dye from aqueous solution by using saw dust as an adsorbent*", International Journal of Research and Applications, ISSN: 2248-9622, Vol. 4, Issue 4, April 2014, pp. 47-51.

[3] D. Suteu, C. Zaharia, "*Saw dust as biosorbent for removal of dyes from wasterwaters. Kinetics and thermodynamic study", Chemical Bulletin of "Politehnica*" University of Timisoara, Romania,Vol. 56(70), 2, 2011, pp. 85-88.

[4] Dr. Hoda Roushdy Guendy "*Treatment and reuse of wastewater in the textile industry by means of coagulation and adsorption techniques*"journal of applied science research, 2010, pp 964-972.

[5] F.Z. Mahjoubi, H.Tounsadi, J. Moustadraf, M. Abdennouri, A. Zouhri A. El Albani, N. Barka, "*Adsorption of textile dyes on raw and decanted Moroccan clays: Kinetics, equilibrium and thermodynamics*", Water Resources and Industry.

[6] Hajira tahir, uzma hammed, Muhammad sultan and qazi jahanzeb, " *Batch adsorption techniques for the removal of malachite green and fast green dyes by using montmorillonite clay as adsorbent*", African journal of biotechnology, vol.9(48) November 2010, pp. 8206-8214.

[7] M.J.W. Frank, J.B. Westerink, A. Schokker, "*Recycling of industrial waste water by using a two-step Nano filtration process for the removal of colour*", Desalination 145 (2002) 69-74

[8] Mohammed Faouzi Elahmadia, Nasr Bensalahb, Abdellatif Gadria, "*Treatment of aqueous wastes contaminated with Congo Red dye by electrochemical oxidation and ozonation processes*", Journal of Hazardous Materials 168 (2009) 1163–1169.

[9] Mohamed Nageeb Rashed, *Adsorption Technique for the Removal of Organic Pollutants from Water and Wastewater*, INTECH, pp. 167-194.

[10] Nader Al-Bastaki, "*Removal of methyl orange dye and Na_2SO_4 salt from synthetic waste water using reverse osmosis*" Department of Chemical Engineering, College of Engineering, University of Bahrain, Bahrain.

[11] Nargish Jahan Ara, Md. Abu Hasan, Mohammad Arifur Rahman,Md. Abdus Salam, and A.M. Shafiqul Alam, "*Removal of Remazol Red from Textile Waste Water Using Treated Saw dust- An Effective Way of Effluent Treatment*", Bangladesh Pharmaceutical Journal 12(1), 2013, pp. 93-98.

[12] Selene Maria de Arruda Guelli Ulson de Souza∗, Karin Angela Santos Bonilla, Antônio Augusto Ulson de Souza, "*Removal of COD and color from hydrolyzed textile azo dye by combined ozonation and biological treatment*", Journal of Hazardous Materials 179 (2010) 35–42.

[13] Simphiwe P. Buthelezi, Ademola O. Olaniran and Balakrishna Pillay "*Textile Dye Removal from Wastewater Effluents Using Bioflocculants Produced by Indigenous Bacterial Isolates* ", Molecules 2012, 17 ISSN 1420-3049, PP. 14260-14274.

[14] Suman Mann, Dr.Anubha Mandal, *Performance of Low-Cost Adsorbents for the Removal of fluoride ions – An overview*, International Journal of Engineering Science and Innovative Technology (IJESIT) Volume 3, Issue 3, May 2014, ISSN: 2319-5967, pp. 437-443.

[15] Walter J. Weber Jr, "*Adsorption Processes*", The University of Michigan, College of Engineering, Arbor, Michigan 48104, USA.