Removal of dye by adsorption on various adsorbents: A review

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***Abstract*— Dye removal from industrial effluents is an important environmental concern. Various physical and chemical treatment methods can serve this purpose, of which the most economical and effective one is adsorption. A variety of adsorbents are available naturally- bagasse, rice husk, neem bark, clays etc. that can be used to remove dye from the discharged waste. In this review, we look at the various adsorbents available and see how effectively they can be utilized to meet our requirements.The adsorption followed pseudo first order and/or pseudo second order kinetics. The dye removal process followed Freundlich isotherm in most of the cases and in few investigations , it followed Langmuir isotherm also.**

***Index Terms*— bagasse, isotherm, kinetics, efficiency, uptake**

I. Introduction

Dyes are natural or synthetic, organic compounds that provide bright and lasting color to other substances. They are used in various industries like the textile, leather, paper, rubber, plastic, cosmetics, pharmaceuticals, and food industries. Textile industries lie first in the dye usage.The wastewaters discharged from dyeing processes exhibit a high BOD, high COD, visible pollutants and high amounts of dissolved solids. Effluents discharged from dyeing industries are highly colored and are toxic to aquatic life. Some dyes are mutagenic, carcinogenic and teratogenic. Therefore, it's a must to treat dye effluents before being discharged into the environment. Thus, there is a need to control an emission of dyes into the environment. The maximum permissible Chemical Oxygen Demand (COD) limit is 4.0 mg/L The maximum permitted Biological Oxygen Demand (BOD) content of < 100 to 300 mg/L according to USPH Standard. The conventional wastewater treatment, which rely on aerobic biodegrading have low removal efficiency for reactive and other anionic soluble dyes. Therefore, due to inefficient biodegradation of dyes, this may not be an ideal choice for treating dyes in polluted water.

Various treatment methods for removal of dyes from industrial effluents like coagulation using alum, lime, ferric chloride, ferric sulfate, chemical oxidation methods using chlorine and ozone; and membrane separation methods are in vogue. Many of them do not operate at low concentration of colored compounds in the effluent. Also, these are very expensive and are not feasible for treating wide range of dyes in water. Special measures therefore are necessary to be taken to remove them from the effluents. Adsorption has received considerable attention for color removal from wastewaters as it offers the most economical and effective treatment method.

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II.ADSORPTION AS DYE REMOVAL TECHNIQUE

Adsorption is a phenomenon in which gas or liquid molecules get adhered on the surface of porous solid. It is a surface phenomenon. The fluid molecule which gets adsorbed is called adsorbate. The porous solid on which the adsorbate gets adsorbed is called adsorbent. The process of adsorption involves separation of a substance from one phase accompanied by its accumulation or concentration at the surface of another. The exact nature of the bonding depends on the details of the species involved, but the adsorbed material is generally classified as exhibiting physisorption or chemisorption. An adsorbent is a substance, usually porous in nature with high surface area that can adsorb substances onto its surface by intermolecular forces. Adsorbents are used usually in the form of spherical pellets, rods, moldings, or monoliths with hydrodynamic diameters between 0.5 and 10 mm. They must have high abrasion resistance, high thermal stability and small pore diameters, which results in higher exposed surface area and hence high surface capacity for adsorption. The adsorbents must also have a distinct pore structure that enables fast transport of the gaseous vapors.

In this review paper, we have studied about adsorption of various dyes onto various adsorbents to see its effectiveness in lowering adsorbent concentration.

III. DYE REMOVAL BY VARIOUS ADSORBENTS

Dye from effluent waste can be removed using various adsorbents. The adsorbents that we have reviewed are bagasse; activated carbon; mango bark and neem bark powder, rice husk carbon, wheat straw carbon, saw dust carbon, Cucumis sativa, Organoclay, raw and activated prawn shell, activated rice husk and rice husk ash, alumina, spent brewery grains, cellulose-based wastes, feldspar, Pseudomonas putida and bentonite.

A. Bagasse

Mahesh et.al studied the removal of violet dyes using raw bagasse and chemically activated bagasse. This group of dye and adsorbent followed Freundlich isotherm. The percent adsorption of dye was decreased with increase in dye

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concentration. Raw bagasse was found more efficient than chemically activated form. The equilibrium is attained between 30-60 mins. The effect of increase in temperature was studied and it was found that increase in temperature decreases the rate of dye uptake [1].

Sharma and Kaur performed batch experiments to find out the effect of parameters like initial dye concentration, pH, contact time, weight of adsorbent and system temperature on the removal dyes by bagasse. It was found that adsorption increases with increase in pH value and adsorbent dosage. As the contact time increases, rate of adsorption first increases and then becomes almost constant. The amount of dye removed was found to decrease with increase in concentration of the adsorbate while the amount adsorbed at equilibrium increases with increase in dye concentration. The experimental data was well represented by Langmuir and Freundlich adsorption isotherms [2].

Filhoa et.al studied the equilibrium and kinetics of Methylene Blue(MB) over reticulated formic lignin from sugar bagasse. The different parameters studied were pH, temperature, ionic strength. Buffered solute at pH 5.8 and 4.5 was found much faster than unbuffered solution. At the temperature of 40°C and 50°C was determined to be the optimum for MB adsorption. The rate of adsorption was dependent on ionic strength. The adsorption values well fitted in Langmuir adsorption isotherm [3].

Raghuvanshi et.al studied equilibrium as well as the rate of adsorption of basic dye (Methylene Blue) in aqueous solution and efficiency of cellulose based adsorbents prepared from Bagasse in different forms i.e., Raw and Chemically Activated form and found The removal is better and more effective with chemically activated bagasse in comparison to the raw bagasse. An average percent removal difference between the two adsorbents of around 18% was achieved under the different conditions in the experiment. The adsorption data fitted well in Freundlich isotherm [4].

B. Activated Carbon

Yasin et.al used KOH treated activated carbon (30%-ACKOH) and untreated activated carbon (AC) to adsorb Methylene Blue (MB). Various parameters such as contact time, solution pH and adsorbent dosage were studied. It was found that the capacity uptake of MB at equilibrium on both adsorbents at 50 and 100 ppm were fairly similar with the capacity uptake of 80-90 %. The results showed that the contact time required to attain equilibrium was about 120 minutes for adsorption by ACKOH and 180 minutes by AC. At 28^0 C, pH value was varied from 1.5-12 and adsorption of MB at 50 and 100 ppm using AC and 30%-ACKOH showed that adsorption increased with pH value. Also it was found that the percentage adsorption increases with increase in adsorbent dose. The adsorption data fitted well in Langmuir isotherm. The study concludes that MB can be effectively removed by activated carbons, especially the KOH treated (30%-ACKOH) in which great reduction of colour and contact time was observed [5].

Abechi et.al studied the removal of Methylene Blue dye on Activated carbon prepared from palm kernel shell. The various parameters studied by them were contact time, initial concentration of dye and temperature. The kinetics followed pseudo second order equation. Adsorption was well described by largergren model. The initial concentration of MB of 20 ppm was found optimum with 99.7% of dye adsorbed at 25°C [6].

Santhi and Manomani adsorbed a textile dye; Methylene Blue was onto carbon prepared from the epicarp of Ricinus communis. The effect on adsorption was studied by varying the agitation time, dye concentration, adsorbent dose and pH. At pH 7 and adsorbent size of 125-250 μm the adsorption capacity was found to be 62.5 mg/g at room temperature (32 $\pm$ 2^0C). The adsorption data fitted the Langmuir and Freundlich isotherm model. Results showed that the process followed pseudo-first-order rate kinetics [7].

Chaudhari et.al used activated carbon prepared from coconut coir as an adsorbent for adsorption of reactive dyes- Remazol Red F-3B and Remazol Blue. It was found that adsorption was dependent on dye concentration, pH, contact time and carbon dose. Results showed maximum color removal occurred in the pH range of 1-3 and that equilibrium was attained in 3 hours of time. By Langmuir and Freundlich isotherms, the coconut coir activated carbon showed higher capacity for adsorption of Remazol Red F-3B than the commercially available activated carbon whereas, for Remazol Blue, comparable adsorption capacity was shown by both activated carbons [8].

Ahmad et.al prepared activated carbon by chemically activating bamboo waste precursor using phosphoric acid which was used to study the adsorption of C.I. Reactive Black 5 (RB5) onto its surface. Various parameters such as contact time, initial dye concentration, pH an temperature were studied. Equilibrium data very well fitted the Freundlich equation. The adsorption process was found to follow the pseudo-second-order rate kinetics. The intraparticle diffusion model was used to determine the mechanism of the adsorption process. Various thermodynamic parameters like standard entropy, standard enthalpy, standard free energy, and activation energy were also determined [9].

Bello and Ahmed prepared activated carbon from mango peels using K_2CO_3. It was found effective for adsorption. In this way this method can be commercialized using waste raw material [10].

C. Mango bark and Neem Bark powder

Srivastava and Rupainwar did comparative study for adsorption of Machelite Green dye on Mango bark and Neem bark powder. The data fitted well in linear form of Langmuir and Freundlich isotherms. The results indicated Langmiur adsorption isotherm fitted the data better than Freundlich isotherm. The adsorption kinetics of Machelite Green on to Mango bark and neem bark powder followed Pseudo second order model. The data showed perfect fit with Langmuir isotherm for both the adsorbents this suggest monolayer coverage of Machelite Green with adsorption capacity 0.36 and 0.53 mol/g at 298 K for NBP and MBP respectively. The results implied both neem bark and mango bark act as promising adsorbent for dye removal [11].

D. Rice husk carbon, wheat straw carbon, saw dust carbon.

Verma and Mishra used low cost adsorbents like rice husk carbon, Wheat Straw Carbon and Saw Dust Carbon. 70% of crystal violet dye was removed in 15 mins and was increased 82.5% in 60 mins. The amount of direct orange and magenta was 47% and 77% in 15 mins. pH was varied from 2 to 8 and the optimum was found to be 6. Effect of temperature was

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studied and equilibrium was found to attain at 60'C. These dyes are found to follow pseudo first order kinetics [12].

E.Cucumis sativa

Santhi et.al studied the adsorption of dyes like Methylene Blue, Methyl Red and Malachite Green by Cucumis Sativa. Different parameters were studied such as influence of initial pH, dye concentration, effect of adsorbent dose, effect of adsorbent particle size. pH 6 was found optimum for adsorption. The equilibrium was reached approximately 1 at hour. With increase in dye concentration the percentage of dye concentration and it was found that they follow Langmuir and Freundlich isotherm. The increase in concentration of adsorbent increased the rate of adsorption. With increase in granular size of adsorbent the adsorption decreased [13].

F. Organoclay

Andreo dos Santos et.al studied the adsorption of orange dye using organoclay which was prepared from commercial sodium bentonite. Various parameters like effects of pH, dose of adsorbents, effect of contact time, initial dye concentrations and temperature were studied by them. The experiments were carried with same dye concentration and at room temperature. It was observed that there is very little effect of pH on the dye adsorption. The amount of dye adsorbed was almost the same even for varying pH. Adsorbent dosage at 1 g/L was found to be optimum. There was no effect of adsorbent dosage. The dye adsorbed was almost the same for 1.0, 2.0, 3.0 and 5.0 g/L. Another parameter studied was effect of contact time, and it was found that contact time necessary for initial low concentration (50-70 mg/L) of dyes was about 60 minutes, whereas for initial concentration of 100 mg/L it was 120 minutes and for 200 mg/L it was 300 minutes. Effect of initial dye concentration was also studied at room temperature and keeping the pH 6. When initial dye concentration increased from 50 to 200 mg/L, the amount adsorbed was 46.33 to 190.31mg/L. With increase in temperature the amount of dye adsorbed also increased. Studying the isotherms it was observed that for low concentration of dyes the values fitted into Freundlich isotherm [14].

G. Raw and activated prawn shell

Santhi and Manonmani studied the adsorption of Methylene Blue from aqueous solution onto prawn shell in raw as well as acid treated form. They studied effects of pH, dye and solid concentration and contact time on adsorption. Experimental data were analyzed using Langmuir model, Freundlich model and Dubinin-Radushkevich model. It was found that the Langmuir model fitted better to the adsorption data compared to the other isotherms studied. It followed a pseudo-second-order kinetic model. The activated form was better than raw prawn waste form with an average difference of 20% in the removal of dye. pH 7 and 8 were optimum for activated form and raw form respectively. The raw form and activated form took about 110 minutes and 90 minutes to reach adsorption equilibrium. The amount of dye adsorbed was found to be the maximum for initial dye concentration of 25 ppm [15].

H. Activated rice husk and rice husk ash

Oidde et.al studied different parameters like pH, contact time, adsorbent dosage and initial concentration of dyes on adsorption of Methylene Blue on activated rice husk and rice husk ash. Optimum pH for adsorbent activated rice husk and rice husk ash was determined to be 7. Contact time of 40 minutes was found to be optimum for both the adsorbents. For the MB concentration of 50 mg/L, optimum adsorbent dose for RHA was 2.5 mg/L and that for ARH was 20 mg/L the experimental data was found to fit well in Langmuir adsorption isotherm [16].

I. Alumina

Iqbal and Ashiq analyzed the removal of various industrial dyes on Alumina at different shaking times, amount of adsorbent used, temperature and pH. The optimum shaking time was found to be 40 minutes. The optimum amount of adsorbent used was found to be 0.2 g for dyes like bromophenol blue, malachite green, Methylene Blue, Methyl Blue and Methyl Violet and 0.3g for phenol red and eriochrome black T. The Langmuir adsorption isotherm fitted well for this adsorption. Dyes were adsorbed maximum at lower pH. Most dyes followed pseudo second order kinetics [17].

J. Spent Brewery grains

Jaikar et.al studied adsorption of acid dyes (Acid Yellow – AY 17 and Acid Blue – AB 25) onto spent brewery grains (SBG) from brewery industry waste. Various parameters were studied like, the influence of time, pH, adsorbent dosage, temperature and initial dye concentration. It was found that the uptake was the maximum at pH value of 2 and thereafter the uptake decreased with increase in pH for both the dyes. Colour removal was found to increase with increase in biosorbent dosage and time, while it decreased with decrease in dye concentration and temperature. The equilibrium data was best represented by the Freundlich adsorption isotherm. For both the dyes, adsorption process followed the pseudo-second-order rate expression [18].

K.Cellulose-based wastes

Annadurai et.al used banana and orange peels as adsorbents for adsorption of dyes from aqueous solutions. The kinetic and equilibrium studies were carried out in the concentration range 10-20 mg/l at30^{0}C. The effect of pH value and initial dye concentration were studied. For both peels it was found that the adsorption capacities decreased in the order: methyl orange > methylene blue > Rhodamine B > Congo red > methyl violet >amido black 10B. The Freundlich equation showed a better fit for adsorption by banana peel,and it was the Langmuir equation for adsorption by orange peel. Adsorption was the maximum at pH 6-7 using banana peel, and at pH > 7 using orange peel. The Langergren rate constant and the intraparticle diffusion rate constant were also determined [19].

L. Feldspar

Awala and Jamal in their objective to access the use of feldspar to remove dyes from aqueous solutions investigated the adsorption of three dyes Methylene Blue, Methyl Red and Fluoresceine onto feldspar. Methyl Red and Fluoresceine (acid-base properties) did not show adsorption due to absence of attraction between dyes and adsorbent. Methylene Blue

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(ox-red properties) showed low adsorption reports to be Psuedo second order chemical reaction kinetics. According to Langmuir isotherm adsorption capacity was estimated as 0.66 mg/g adsorbent at 313 K [20].

M. Pseudomonas putida

Ratnamala and Brajesh studied biosorption of remazol navy blue dye from an aqueous solution using pseudomonas putida. Biosoprtion of Remazol navy blue dye, from an aqueous solution was studied by adsorption on powdered Pseudomonas putida. The equilibrium data satisfied both Langmuir and Freundlich models with freundlich model to fit the data better. The biosoprtion capacity of pseudomonas putida was found to be 20 mg dye per gram of adsorbent. The experimental data were analyzed using the pseudo-first-order and pseudo-second-order adsorption kinetic models. The experimental data fit the second-order kinetic model [21].

N. Bentonite

Hong et.al studied the effect of temperature on the equilibrium adsorption of MB using bentonite. It was found that adsorption increases with increasing temperature. The analysis of equilibrium adsorption data was done using isotherms: Langmuir, Freundlich, and Redlich-Peterson. A non-linear method was used and the best fit was found to be Redlich-Peterson adsorption isotherm. Various thermodynamic parameters like standard entropy, standard enthalpy and standard free energy were also determined. The negative values of ΔG° indicated that the spontaneous nature of adsorption and the positive value of ΔH° indicated that the adsorption reaction was endothermic. The value of ΔS° was found to be positive, this implied increasing randomness at the solid/liquid interface during the adsorption of MB on bentonite [22].

IV.CONCLUSION

This study shows that there are various adsorbent options available to choose from in order to remove dye from aqueous media using adsorption method. The effect of different parameters like contact time, adsorbent dosage, initial concentration of dye, pH and temperature on the adsorption rate using these adsorbents revealed that with increase in contact time, the adsorption rate increases first then remains constant when the equilibrium is reached. The adsorption rate increased with increasing adsorbent dosage and pH but showed a decreasing trend with increase in initial adsorbent concentration while the effect of temperature was dependent on the type of adsorbent and adsorbate used. The equilibrium data fitted Freundlich and Langmiur isotherms in majority of cases. Although the rate of adsorption depends upon the affinity of adsorbent towards the adsorbate, the bioadsorbent showed a good adsorption rate for majority of commonly used dyes and have been found to be quite effective in dye removal.

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