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Dye and its Removal from aqueous solution by Adsorption: A review

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Abstract

The removal of dyes from waste water is a matter of great interest in the field of waste water treatment. The effluents from many industries often contain one or more toxic dyes. Therefore, an increased interest has been focused on removing such dyes from wastewaters. In general, several methods are used for the removal of dyes from waste water. Different techniques including chemical oxidation, precipitation, membrane filtration, ion exchange, biosorption and adsorption are adopted to remove dyes from aqueous solution. Adsorption has gained attraction in the treatment of dyes from coloured wastewater compared to other techniques due to the bulk availability of adsorbents, higher dye uptake capabilities, robustness and economical desorption cycles and excellent resistance towards degenerative action of a target contaminant (Gupta *et al.,* 2013). Also, adsorption using bio-derived, renewable sorbent materials can be seen as environmental friendly and can provide us with a trouble –free, commercially cheap operation. This chapter describes the comparative dye adsorption potential of various waste biomass adsorbents reported in the literature for treatment of basic (cationic), acidic, direct and reactive dyes.

Keywords – wastewater, biosorption, aqueous solution, biomass, dye.

1. Introduction

Nowadays, large amounts of wastewater are produced in dye production and usage. This kind of wastewater would cause serious pollution to environment. It would impart a significant color to water even at a very low concentration, and reduce sunlight transmission through water (Rodríguez et al., 2010). Furthermore, it would increase the biological oxygen demand and do harm to the aquatic organisms (Al-Qodah et al., 2007). Different techniques including chemical oxidation, precipitation, membrane filtration, ion exchange, biosorption and adsorption were adopted to remove dyes from aqueous solution (Ayad and El-Nasr, 2010). Among these methods, biosorption has been suggested as a potential alternative for detoxification and recovery of toxic dyes from wastewater due to the low operational cost, low maintenance and simplicity (Akar et al., 2008, Juhasz et al., 2002).

Different types of modified and unmodified biosorbent such as peat, rice husk, pinus sylvestris and ash had been used for the removal cationic dyes (Sun and Yang, 2003, Zou et al., 2011, Vijayaraghavan et al., 2008, Gupta, 2006, Aksakala and Ucunb, 2010, Srinivasan and Viraraghavan, 2010). In order to determine the effectiveness of adsorption as well as the maximum adsorption capacity of the modified and unmodified sorbents, the adsorption experiments including adsorption isotherms, kinetics, competitive adsorption and the other conditional experiments were often carried out by using batch model (Ata et al., 2012, Alencar et al., 2012).

1.1.Dyes

Dye is a colored substance that has an affinity to the substrate to which it is being applied. The dye is generally applied in an aqueous solution, and may require a mordant to improve the fastness of the dye on the fiber.

Both dyes and pigments are colored, because they absorb only some wavelengths of visible light. Dyes are usually soluble in water whereas pigments are insoluble. Some dyes can be rendered insoluble with the addition of salt to produce a lake pigment.

1.2. Types of dyes

Dyes are classified according to their solubility and chemical properties.

a) Direct Dyes

Direct dyes are inexpensive and easy to apply, but they are of poor fastness. These dyes are also known as 'salt dyes' or cotton colours, which dye cotton, other vegetable fibres and viscose rayon. They are readily soluble in water. Colours of cotton fabrics dyed with direct dyes are not fast. They are applied to cellulose fibres from aqueous liquor in which an electrolyte is added, which is usually sodium chloride as it accelerates the rate at which the dye is chosen up by the fibre. They generally bleed. To make them fast on fabric, sodium bicarbonate is added for warm colours and copper sulphate for cool colours. They are excellent fast to perspiration and dry cleaning.

b) Acid Dyes

These are soluble in water and are applied under acidic conditions. The acid dyestuff is typically used for wool and silk and to a less amount for nylon and acrylic fibres. The maximum quantity of dye absorbed depends on the amount of H_2SO_4 present in the bath. Acid dyes are inexpensive dyes. They are fast to light, but they are not fast to washing. Attachment to the fibre leads partly to salt formation between anionic groups in the dyes and cationic groups in the fibre. Acid dyes are not substantive to cellulosic fibres. Most synthetic food colours fall in this category. Examples of acid dye are Alizarin, Pure blue B_1, Acid red 88 etc. They are generally water soluble. The principal chemical classes of these dyes are azo, anthroquinone, triphenylmethane, azine, xanthene, nitro and nitroso groups.

c) Vat Dyes

They are insoluble in water, but they are made soluble by the use of a strong reducing agent, such as sodium hydrosulphite dissolved in sodium hydroxide. These are the fastest dyes for cotton, linen and rayon. They also may be applied to wool, nylon, polyester etc. Vat dyes are hot water dyes and are available in both powder and liquid form. The first synthetic vat dye was Indigo produced in 1879. Vat dyes are costly because of the initial cost as well as the method of application.

d) Azoic Dyes

The Azoic dyes are applied to cotton in two stages. The first stage consists of treatment with naphthol and the second stage is by treatment of the naphtholated material with diazotized base or diazotized salt. The colour development takes place in-situ by the coupling reaction between naphthol and diazo component. They are quite fast to washing and have poor to excellent light fastness. Azoic colours are used mostly on cotton and for special purposes on nylon. Azoic colours are sometimes referred to as ice dyes because ice is frequently used to bring the dyes to low temperatures. Azoic colours give bright and high intensity colours than the common dye classes. These are cold water dyes and are most appropriate for cold dyeing techniques such as Batik, Tie-Dye etc.

e) Basic Dyes

The first coal tar dye was basic dye. Basic dyes are water soluble cationic dyes and are mostly applied to arylic fibres, but find some uses for wool and silk. They give good fastness and bright shades to acrylics. Usually acetic acid is added to the dye bath to help the uptake of the dye onto the fibre. Basic dyes are also used in the colouration of paper. Example of cationic dyes are Methylene blue, Malachite green, Gentian violet etc.

f) Reactive Dyes

They were first developed in 1954 by Rattee and Stephens. The dye is retained by means of a chemical reaction between the dye and the fibre. As such their fastness properties are excellent. The fibres most readily coloured with reactive dyes are natural and man made cellulosic fibres, natural protein fibres and polyamide fibres. With some reactive dyes, the dyeing can be carried out at room temperature. However with most reactive dyes, the dyeing is carried out at high temperatures. They have a chromophore attached to a substituent that is capable of directly reacting with the fibre substrate. The prime reason to make them classified among the permanent dyes is the covalent bond that attaches reactive dyes to natural fibres. They find their uses for cotton, wool and nylon.

g) Disperse Dyes

The fibres that are most commonly dyed with disperse dyes are cellulose diacetate, cellulose triacetate and polyester fibres. To a lesser extent acrylic and nylon fibres are also dyed with disperse dyes. The wash fastness of disperse dyes differ with the types of fibres used. Examples are, Disperse red, disperse blue, Disperse violet, Disperse yellow, Disperse green, etc.

h) Sulphur Dyes

Natural and man made cellulosic fibres are readily dyed with sulphur dyes. These dyes are water insoluble dyes containing sulphur or sodium suphide.The dyes are usually applied at high temperatures (60^0c to 100^0c). They are applied in a soluble reduced form from sodium sulphide solution, which are then reoxidised to insoluble form on the fibre.These dyes have excellent resistance to washing but poor resistance to sunlight.

i) Solvent Dyes

These dyes are non-ionic compounds soluble in organic solvents. They are used as a solution in an organic solvent. For example, Solvent red 24, Solvent yellow 124, Solvent blue 35, Solvent orange 5, Solvent black 3, etc. are solvent dyes.

1.3. Methods of Dye Removal

Technologies for treating wastewater polluted with dyes can be divided into three categories: biological methods, chemical methods and physical methods. Biological methods are those that involve living organisms using organic, or in some cases, inorganic substances for food, totally changing their chemical and physical characteristics (Woodard, 2001). Chemical methods rely upon the chemical interactions of the contaminants from water and the application of chemicals that either assist in the destruction or neutralization of harmful effects associated with contaminants. Physical treatment methods include sedimentation, adsorption, ion exchange, filtration and other processes that accomplish removal of dissolved and undissolved substances without essentially changing their chemical structures (Nicholas & Cheremisinoff, 2002).

i) Biological Methods for Dye removal

Biological methods are gaining more importance nowadays because of their low cost, effectiveness and eco-friendly nature. The metabolites produced after biodegradation are mostly non toxic or comparatively less toxic in nature (Jadhav *et al*., 2010). Biological decolorization methods use several classes of microorganisms including bacteria, algae and fungi to degrade the dyes and industrial wastewater. The end products of biological methods are fully mineralized through the process of biodegradation (Shertate & Thorat, 2013). The main disadvantage of this method is that they are less flexible in design and operation as they require a large land area and microorganisms are sensitive towards variants. Besides, some of the dyes are resistant to aerobic digestion. The usage of activated sludge for biological treatments do not effectively remove colour as the oxidation rate is too low but it can reduce the BOD of the wastewater (Pathiraja, 2014).

ii) Chemical Methods for Dye Removal

Chemical methods include coagulation / flocculation, oxidation, ozonation, electrochemical and photocatalysis. These chemical techniques are costly, and a disadvantage is that it produces secondary pollution (Musstafa &Yagub 2013). In most chemical methods, chemical reactions occur for the separation of contaminants from water or neutralization of the harmful compounds present in the contaminants. In these methods, oxidizing agents such as ozone, hydrogen peroxide and permanganate are needed for the removal of dyes. But these oxidizing agents produce harmful disinfection by-products. Moreover, chemical methods will involve high cost, limited versatility, low efficiency and utilize a significant amount of energy.

iii) Physical Methods for Dye Removal

Different physical methods are widely used to remove dye, such as Membrane filtration process. Adsorption, Ion exchange and Electro coagulation, Membrane technique was applied on a number of applications mainly for the treatment of complex industrial wastewater (Benito *et al.,* 1998).

Membrane filtration process such as Microfiltration, Ultrafiltraion, Reverse osmosis and Nanofiltration is used to remove colour, COD, heavy metals and total dissolved solids (TDS) from wastewater. Additionally, membrane separation processes offer various advantages like the usage of a compact system, easy control of operation, maintenance and low need for chemicals.

Reverse Osmosis (RO) is a membrane-based demineralization technique. The main function of reverse osmosis is to isolate dissolved solids such as ions from aqueous solution. Reverse Osmosis is believed to remove hardness, colour, many kinds of bacteria and viruses and organic contaminants (Abid *et al.,* 2012).

2.4. Adsorption

Adsorption is used as top quality treatment procedures for the removal of dissolved organic pollutants like dyes from industrial waste water. Adsorption is defined as concentration of materials on the surface of solid bodies. Adsorption is a surface phenomenon which deals primarily with the utilization of surface forces. When a solution having absorbable solute, also called as adsorbate, comes into contact with a solid, called as adsorbent, with highly porous surface structure liquid-solid intermolecular forces of attraction causes the solute to be concentrated at the solid surface. Adsorption is one of the unit operations in the chemical engineering processes used for the separation of industrial wastewater pollutants.

2.5.Adsorbents

Adsorbents are mainly derived from sources such as zeolites, charcoal, clays, ores, and other waste resources. Adsorbents prepared from waste resources used include coconut shell, rice husk, petroleum wastes, tannin-rich materials, sawdust, fertilizer wastes, fly ash, sugar industry wastes, blast furnace slag, chitosan and seafood processing wastes, seaweed and algae, peat moss, scrap tyres, fruit wastes, etc.

2.6. Reviews of Some Recent Works on Removal of Dyes by Adsorption

2.6.1 Adsorbents from Forest and Agriculture Biomass

Agricultural waste materials have little or no economic value and often pose a disposal problem. The utilization of agricultural waste is of great significance. A number of agricultural waste materials are being studied for the removal of different dyes from aqueous solutions at different operating conditions. Raw agricultural solid wastes and waste materials from forest industries such as sawdust and bark have been used as adsorbents. These materials are available in large quantities and act as potential sorbents due to their physico-chemical characteristics and low-cost.

Sawdust is an abundant by-product of the wood industry that is either used as cooking fuel or as packing material. Sawdust is easily available in the countryside at zero or negligible price (Garg *et al.,* 2004). It contains various organic compounds (lignin, cellulose and hemicellulose) with polyphenolic groups that might be useful for binding dyes through different mechanisms (Chikri *et al.*, 2020). Sawdust has proven to be a promising effective material for the removal of dyes from textile effluent (Eletta *et al.*,2018) and the results showed, a maximum adsorption capacity 98.5% of textile dye was obtained at the optimized conditions of 1.5g, 90 min and 275 rpm for adsorbent dose, contact time and agitation speed respectively. Muhammad *et al*., (2019) studied the sorption ability of both raw sawdust and chemically activated sawdust carbon on the removal of chrysoidine dye (azo dye) from the aqueous solutions. Adsorption isotherms of the chrysoidine dye on sawdust were determined and correlated with usual isotherm equations like Freundlich and Langmuir. Experimental results showed that sawdust has a high adsorption efficiency and the adsorption of chrysoidine dye on saw dust followed Freundlich's isotherm.

The use of low-cost locally available adsorbent, sawdust for the removal of methylene blue dye in a batch adsorber system has been investigated by Markandeya *et al*., (2015). The experimental data fitted best in Langmuir isotherm as compared to Freundlich and Temkin isotherms, showing maximum adsorption capacity of 76.92 mg/g. The study revealed that the adsorption of MB dye onto sawdust follows pseudo-second-order kinetic model and the same has been used in design of a two-stage batch adsorber by minimizing total contact time to attain a fixed percentage of MB dye removal. The minimum contact time required for the removal of MB dye with 99% efficiency has been found as 37.54 min. Chemical pretreatment of sawdust has been shown to improve the sorption capacity and to enhance the efficiency of sawdust adsorption (Chikri *et al.*, 2020). Hanane Tounsadi *et al.*, (2020), studied the adsorption of methylene blue and brilliant blue on the sawdust of acacia tree from waste water. Sawdust of acacia tree has been successfully used to remove textile dyes from wastewater due to its good sorption properties and its good chemical stability. Two materials were prepared by chemical treatment, including acidic and basic sawdust of acacia. Efficient removal of both dyes has been achieved by the basie treated sawdust acacia. Langmuir biosorption capacities are 8.13 mg/g and 267.04 mg/g onto basic sawdust acacia and 6.19 mg/g and 230.76 mg/g onto acidic sawdust acacia, respectively, for methylene blue and brilliant blue sorption.

Bhanuprakash and Belagali (2016) studied the efficient removal of dyes using almond husk as a natural adsorbent. The results showed that, almond husk is a very good adsorbent for the removal of dyes such as Fuschin basic, Janus green B, Indigo caramine and Metanil yellow from the aqueous medium. The adsorption isotherms like Freundlich and Langmuir isotherms were studied and found to be favourable. Date pits carbon was studied by Khaled Mahmoudi *et al.*,(2016) for the removal of methylene blue and methyl orange from aqueous solution. Equilibrium adsorption data followed both Langmuir and Freundlich isotherms. The adsorption capacity of date pits carbon was found to be 434 mg/g and 455 mg/g of methyl orange and methylene blue respectively. Acidic pH is favourable for the adsorption of methyl orange against a basic medium which is favourable for the adsorption of MB.

2.6.2. Adsorbents from Rice and Wheat Wastes

Rice is one of the major crops grown throughout the world and most important staple food for the human population. Rice husk, rice hull and rice bran are the byproducts of rice industry which have been used to prepare low cost adsorbents for the removal of heavy metals and dyes from wastewater. Rice husk has been used as an effective adsorbent for the removal of dyes such as reactive orange 16, reactive yellow 2, reactive blue 2 , direct blue 67, direct red 23, acid yellow 36, acid violet 54, acid violet 17, acid blue 15, acid violet 49 and acid red 119 from wastewater.

Wheat is another important stable food which produces products such as wheat bran, wheat husk etc. It was studied by Khalid and Alla Hussein (2015) on the ability of natural and modified wheat straw to remove reactive blue dye. In this study, adsorption process was carried out for both batch (kinetic and isotherm) studies using natural wheat straw as low cost adsorbent, modified wheat straw and activated carbon for comparing the results. Batch adsorption experiments were conducted on a shaker at 200 rpm with 100 mL of dye solution at room temperature. The effect of pH was determined by adjusting pH values (2.5- 10.5). The results showed that the removal percent using natural wheat straw, modified wheat straw and activated carbon are 68%, 92.17% and 90.5% respectively. Equilibrium isotherm experiment were carried at different dosages (0.1 – 1 g) to predict the isotherm model - Langmuir, Freundlich and BET. The experimental data showed that reactive blue is fitted with Freundlich isotherm (1/n=1.25, 0.67) for both natural wheat straw and modified wheat straw respectively and (activated carbon) is fitted with Langmuir isotherm. Three kinetic models, were selected to fit the kinetic data - pseudo first, second order and intraparticle diffusion. Reactive blue is fitted with intra-particle diffusion model with (natural wheat straw) and (modified wheat straw) and pseudo second order for (activated carbon).

2.6.3. Adsorbents from Seed Shell and Seeds of Agricultural Products

Many researchers have investigated seed shells and seeds of various agricultural products as adsorbent for the removal of toxic pollutants from waste water. Fruit seeds have not received serious consideration as sorbents. However, there are considerably high amounts of waste arising from human consumption or food-processing plants. Seeds of many fruits have also been investigated as the inexpensive adsorbents for the removal of dyes from waste water. Adsorption of reactive black 5 and congo red from aqueous solution by coffee waste modified with polyethylenimine was investigated. The removal percentages of reactive black 5 and congo red dyes increased with the amount of polyethylenimine in the modified adsorbent. The modelling result showed that anionic dyes adsorption occurred via monolayer adsorption and chemisorption was the rate-controlling step. The adsorbent possesses higher maximum adsorption capacity towards reactive black 5 (77.52 mg/g) than congo red (34.36 mg/g), due to the higher number of functional groups in reactive black 5 that interact with the adsorbent. This study reveals the potential of adsorbent derived from coffee waste in textile wastewater.

Hard shell of rubber seed (RSS) was selected from the agricultural solid wastes to prepare effective and low cost adsorbents for sorption of methylene blue dye from aqueous solution (Mohd.Azani *et al.*,2019). RSS was prepared through the conduction of a chemical activation process primarily using potassium hydroxide in the ratio of 1:1 followed by carbonisation at 400°C with N_2 under a steady flow rate of 1 ml min^{-1} for 3 hrs. The produced RSS activated carbon (RSSAC) was characterised using Fourier transform infrared (FTIR) spectroscopy, scanning electron microscopy-energy dispersive X-ray (SEM-EDX) spectroscopy, BET analysis and thermogravimetric analysis (TGA). The SEM image revealed the presence of a highly porous RSSAC surface, with an average pore diameter of 3.35 nm, indicating a mesoporous structure. EDX analysis depicted that C and K were major elements found in RSSAC with a compound percentage of 99.73% and 0.27%, respectively. Batch adsorption studies were conducted to investigate the adsorption properties of RSSAC towards the removal of methylene blue (MB) dye. The optimum dosage of RSSAC was determined to be 5.0 g per 100 ml. The effect of contact time revealed that the highest percentage removal of MB (99.62%) by RSSAC was obtained at a concentration of 100 mg/g during a time period of 1 hour. In comparison, the effect of pH study affirmed that RSSAC achieved an average removal of 99% of MB in both acidic and basic media at 100 mg/g. Kinetic studies revealed that the adsorption process abides by the pseudo second-order kinetic model.

The adsorption capacity of a biosorbent, dried sunflower seed hull (DSSH), was investigated by Gbekeloluwa and Oguntimein (2016). Adsorption kinetics was examined by first and second order rate models and intra particle diffusion models, while equilibrium studies were examined by Langmuir, Freundlich and Dubinin-Radushkevich (D-R) isotherm models. D-R model fitted the data best with a biosorption capacity of 0.0365 mg/g. The standard Gibbs free energy change was also calculated to define the nature of biosorption process. These results revealed that the utilization of sunflower seed hull residues as a dye biosorbent could be an interesting option from both environmental and economic point of view. Rajesh Dandge *et al.*, (2016) investigated the removal of congo red dye from aqueous solution by using green peas shell (GPS) as low-cost biowaste adsorbent under various experimental conditions. The adsorption study reveals that congo red has the affinity to get adsorbed onto the surface of GPS. Equilibrium isotherms were analyzed and Freundlich isotherm described the isotherm data with high-correlation coefficients.

Shells of kernel was investigated by Phyo Phyo Kyi *et al.*,(2020) for the removal of crystal violet from waste water. Kinetic, equilibrium, and thermodynamic studies were carried out to evaluate the adsorption of crystal violet onto biocar derived –palm kernell shell. The kinetics of adsorption process followed the pseudo-second-order model, indicating that the rate of adsorption is principally controlled by chemisorption. The adsorption equilibrium data were better fitted by the Langmuir isotherm model with a determination coefficient of 0.954 and a maximum adsorption of 24.45 mg/g.

2.6.4. Adsorbents from Fruit Peels of Agricultural Products

Fruit peel waste (FPW) is abundantly available from the agricultural and food processing industry. It has been studied in recent past as an adsorbent. Nuriya Jemal (2015) studied reactive azo dye removal from aqueous solution using orange peel as bio adsorbent. It was found that maximum adsorption of the dye took place at an acidic pH. The effective solution pH, orange peel adsorbent dose and contact time were found to be 3, 0.2mg/100mL and 80 min, respectively for the dye adsorption studies at constant room temperature of 27°C. At these experimental conditions, the dye removal efficiency of 90% was achieved.

2.6. 5.Adsorbents from Stem and Leaves of Agricultural Wastes

Banana stem was used as adsorbent for the removal of colour from aqueous solutions by Akbar *et al.,*(2019). Analysis on adsorption isotherm was done using Langmuir and Freundlich model. In addition to it, the behaviour and mechanism of adsorption were analysed using kinetic model, namely pseudo-first order and pseudo-second order kinetics. The result showed that more than 90% of the colour was removed at an optimum dosage of 1 g of banana stem adsorbent in 100 mL of synthetic dye at optimum contact time of 90 min. Hence banana stem adsorbent has a good potential for colour removal in textile wastewater treatment because of low cost. Thus, it is an alternative adsorbent to overcome problems related to excessive colour in dye wastewater treatment plant.

Seed husk of bengal gram were used as adsorbent for the removal of congo red, two basic dyes (methylene blue and rhodamine B) and an acidic dye namely acid blue 25 from aqueous solutions by Somasekhara Reddy and Nirmala (2017). Cotton stalk has been explored as a bioadsorbent for the removal of methylene blue from aqueous solutions in batch mode system by Ertas *et al.*, (2010). Mango leaf has been effectively used as an adsorbent for the removal of methylene blue from aqueous solutions (Tamez Uddin *et al.,* 2017).The pH at the point of zero charge of the adsorbent was determined by titration method and was found to be 5.6 ± 0.2. The adsorption of MB on by electrostatic attraction was further confirmed by desorption study. Initialy the adsorption was observed by increasing the pH from 2.3 to 10. The desorption was then carried out by decreasing the solution pH . The adsorption equilibrium time required for the adsorption of methylene blue on mango leaf powder was almost 2 h and 85 ± 5% of the total amount of dye uptake was found to occur in the first rapid phase (30 min). The experimental equilibrium data could be well interpreted by Langmuir isotherm with maximum adsorption capacity of 156 mg/g. The above findings suggested that mango leaf powder can be effectively used for decontamination of dye containing wastewater.

2.6.6. Adsorbents from Algal Biomass

Algal biomass is one of the most efficient photosynthetic and CO_2 sequestering organism on earth. Its adsorption potential can be enhanced considerably in a CO_2 rich environment (Song *et al.,* 2015). Bio fixation of carbon dioxide using microalgae is becoming a potential option as they have the ability to fix CO_2 using solar energy with efficiency ten times greater than that of terrestrial plants. It has numerous additional technological advantages and one such is the adsorption capacity (Sara *et al.,* 2014).

The powder of the algae, *Chara* has been used as a biosorbent for removal of naphthalene (Khairi *et al.,* 2018). The optimum conditions for naphthalene removal were found to be pH 7 and biosorbent dosage of 0.15 g for each 50 ml of naphthalene solution. The rate of biosorption of naphthalene was found to be rapid during the initial 30 min and equilibrium was established after 240 min. The results of equilibrium isotherm study showed that the data properly fit to Freundlich isotherm model within the investigated concentrations ranged 10-50 mg/L. The peak capacity of adsorption of the biosorbent was 5 mg/g. The pseudo-second order kinetic model yielded the optimum fit to the experimental results. This study proved the applicability of *Chara sp., algae*, for the removal of naphthalene from waste water.

Fungi is proved to be a suitable organism for the treatment of textile effluents and in dye removal (Weber and Stickney, 1993). The fungal biomass effectively removes dyes due to faster growth in addition to adsorption by its dead immobilized state. Waste fungal biomass, which is a byproduct of industrial fermentation, can be used as a cheap source of biosorbent. Tao Lu *et al.*,(2017) investigated removal of dyes from wastewater by growing fungal pellets in a semi-continuous mode. The mycelia pellets were prepared by marine fungus Aspergillus niger. Eight dyes were tested as dye targets for the adsorption capacity of mycelia pellets and good removal results were obtained. Eriochrome black T was selected as a model dye for characterizing the adsorption processes in detail.

2.8. Adsorbents from Industrial / Domestic Wastes or byproducts

Lignin a waste / byproduct discharged from paper mills in larger quantities has been used in its raw state as well as modified state for removal of contaminants by researchers. A lignin- based adsorbent was prepared by Xianzhi Meng *et al.*, (2020**)** from a bamboo pulp mull byproduct. The adsorbent was investigated for the removal of methylene blue and direct blue from aqueous solution. It had a maximum adsorption capacity of 502.7 mg/g for direct blue dye and the kinetic study suggested that the adsorption process follows a pseudo- second order kinetic model. The isotherm result also showed that the modified lignin – based adsorbent exhibited monolayer adsorption. Sugar industry generates a significant amount of byproducts such as sugar beet pulp and sugarcane bagasse and their handling and management is a matter of great concern. Among their uses such as fuel and fertilizer, the valorization of biowastes from sugar industry as adsorbents for the removal of various aquatic pollutants presents promising features in terms of cost reduction for waste disposal and environmental protection (Loannis *et al.*,2017). Adsorption of reactive black 5 and congo red from aqueous solution by coffee waste modified with polyethylenimine was investigated by Syieluing Wong *et al.*,(2020). The removal percentage of both dyes increased with increase in the amount of polyethylenimine in the modified adsorbent. The adsorbent possesses higher maximum adsorption capacity towards reactive black 5 (77.52 mg/g) than congo red (34.36 mg/g), due to the higher number of functional groups in reactive black 5 that interact with the adsorbent. This study revealed the potential of adsorbent derived from coffee waste in textile wastewater treatment.

2.9 Inorganic Materials as Adsorbents

Clay is defined as a mineral which is helpful in making up the colloid fraction of rocks, soils, sediments and water. It has been studied that normal clay minerals are well known to mankind because of the properties of clay like high sorption, potential for ion exchange and abundant in nature. Clay is cheaply available and clay mineral work as an effective adsorbent, because of layered structure and called as hosting material for adsorbates and counter ions. Clay has strong affinity towards both cations and anions. It helps in removal of dyes from waste water.

There are several classes of clay such as Smectites (Montmorillonite, Sponite), Mica (illite), Kaolinite, Serpentine, Pylophyllite (talc), vermiculite and sepiolite (Shichi and Takagi, 2000). The adsorption capabilities result from a net negative charge on the structure of minerals. This negative charge gives clay the capability to adsorb positively charged species.

In recent years, there has been an increasing interest in utilizing clay minerals such as bentonite, kaolinite, diatomite and Fuller's earth to adsorb not only inorganic but also organic molecules. Clay minerals exhibit a strong affinity for both heteroatomic cationic and anionic dyes. However, the sorption capacity for basic dye is much higher than for acid dye because of the ionic charges on the dyes and the character of the clay. The adsorption of dyes on clay minerals is mainly dominated by ion exchange process. They show that the adsorption capacities are substantially improved upon modifying their surfaces with quaternary amines.

Ifelebuegu *et al.,* (2020) investigated the effectiveness of waste recycled bricks as adsorbent for phosphate removal during wastewater treatment. The kinetics, isotherms and thermodynamics of adsorption were investigated to establish the mechanism of adsorption. The results showed that the adsorption capacities were increased with an increase in contact time, adsorbent dosage and initial phosphate concentration. The kinetic study indicated that adsorption was governed by several mechanisms with various processes dominating different stages of the adsorption. The adsorption process was better represented by the pseudo-second-order kinetics and the Langmuir isotherm adequately described the adsorption of phosphates onto brick particles with a maximum adsorption capacity of 5.35 mg/g. The thermodynamic studies showed that the adsorption process was exothermic and proceeded spontaneously, demonstrating that waste bricks can be used as a sustainable alternative for the effective removal of phosphates from wastewater.

Mn- mica was studied by Mohamed *et al.,*(2020), for the efficient removal of methyl orange dye. Mn–mica was characterized and tested as a new adsorbent for the removal of methyl orange dye from aqueous solution. Compared to naturally occurring mica, the Mn–mica with manganese in the octahedral sheet resulted in enhanced methyl orange uptake by four times at pH 3.0 and 25°C. The pseudo-second order equation for kinetics and Freundlich equation for adsorption isotherm fitted well to the experimental data at all adsorption temperatures (i.e., 25^{o}C, 40^{o}C and 55^{o}C). The decrease of Langmuir uptake capacity from 107.3 mg/g to 92.76 mg/g within the temperature range of 25 ^{o}C –55 ^{o}C suggested that methyl orange adsorption is an exothermic process.

Shashikala *et al*., (2014) used activated carbon prepared from Chitosan as an adsorbent for adsorption of methyl orange dye. Batch experiments were conducted to study the effect of pH, initial dye concentration, various adsorbent dosage and these were analyzed using both pseudo first order and pseudo second order equations. The equilibrium adsorption data were analyzed by using the Freundlich and Langmuir isotherms. The maximum adsorption of methyl orange dye occurred at pH 4 by taking the optimum values for adsorbent dosage as 1g and initial dye concentration as 10 ppm. Adsorption kinetics were best described by the pseudo-second order model. The equilibration data for methyl orange dye fitted well with Langmuir isotherm model and the adsorption capacity for methyl orange dye is 99.04%. Multiwalled carbon nanotubes can be effectively for the removal of Bismarck brown G dye from aqueous solution. 20 mg is the optimum dosage of multiwalled carbon nanotubes to adsorb Bismarck brown G. The adsorption of Bismarck brown G on multiwalled carbon nanotubes has been described by the Langmuir and Freundlich adsorption isotherm models. The equilibrium data were fitted with the Langmuir isotherm.

Fella –Naouel Allouche *et al.*, (2015) investigated the adsorption behaviour of methyl orange from aqueous solution on chitosan biomass. The equilibrium data of methyl orange fitted to both Langmuir and Freundlich isotherms, but the experimental data of methyl orange were found to be better fitted by the Freundlich model. Maximum sorption capacity of 29 mg/g at pH 3 was achieved within 60 min. The sorption data was best fitted with the pseudo- second –order kinetic model.

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