A Review on Adsorption of Cationic Dyes using Activated Carbon

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Abstract. In this article efficiency of activated carbon as a potent adsorbent of cationic dyes has been reviewed. Non-biodegradable nature of pollutants and their removal in the present generation is a great challenge. Therefore, extensive study on adsorption of these classes of pollutants from water bodies is being carried out. Methylene blue (majorly) a dye seen in the effluent streams of textile, printing, paper industries along with some of the commonly used cationic dyes in process industries and their sorption on activated carbon are reviewed here. High cost of commercially activated carbon which is a limitation to its extensive use have paved way for study of adsorption by naturally obtained and extracted activated carbon from agricultural wastes and various other sources. The purpose of this review paper is to summarize the available information on the removal of cationic dyes using naturally extracted and commercially obtained activated carbon. Various parameters such as temperature, initial dye concentration, pH, contact time, adsorbent dosage, particle size, stirring, agitation etc. were studied and the optimum parameters were determined based on the experimental outcomes. Equilibrium data was examined using Langmuir, Freundlich, Temkin and Dubinin–Radushkevich and few other isotherm models. Kinetic studies also have been carried out to find the most suitable way of expressing the adsorption process.

Keywords: Adsorption, Cationic, Langmuir, Isotherm, Activated carbon.

1 Introduction

Urbanization has been taking place rapidly in recent years which has resulted in increase of all forms of pollution one of which is water pollution. Exhaust and waste water streams being let out from industries carry huge amount of various toxic substances. Dyes are one of the main pollutants of textile industries. They are composed of two main components: chromophone one which imparts color and the other is auxophone this not only behaves as a supplement to the former component but also gives the water-soluble property to the dye and enhances the affinity of the dye to the cloth material. There are different classes of dye depending upon various factors. One of the classification of dyes is based on the charge the molecule carries. Some of the dyes are cationic in nature (e.g., methylene blue) and some are anionic in nature (e.g., methyl orange). Dyes present in effluent streams that are emptied in water bodies can have adverse effects on human and marine life.

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Presence of methylene blue reduces the diffusion of light and thereby photosynthesis [1]. Concentration of dyes higher than 1mg/l in water streams make it unfit for consumption and therefore quality testing and treatment of water becomes important [2]. But overall there are about 100,000 commercial dyes which are produced and account for massive amounts ranging from 7×10^5-1×10^6 tons annually of which 65-70% of dyes are azo dyes [3]. Its low biodegradability [1] makes it a challenging task to eliminate it from water bodies. There are various methods that are used to treat dye contaminated water, some of them are osmosis, reverse osmosis, filtration, membrane filtration etc. In any process certain factors are to be taken to consideration such as economic feasibility, time required, availability of materials, design of the process. Adsorption is one of the recent methods that has gained attention for treatment of waste water streams as it is efficient compared to other existing methods. A good adsorbent is one that is highly porous and has a large surface area. Depending on the availability, its properties and ease of usage, activated carbon can be classified as a good adsorbent. Activated carbon can be produced or extracted by various waste materials such as organic wastes (coconut husk, rice husk, pomegranate peels, olive stones, apricot stones etc.) Activated carbon is known for its high adsorptivity.

Researches have been conducted to study the effect of activated carbon on adsorption of various dyes depending upon the source from which activated carbon is obtained. Some research have been carried out by using activated carbon from olive stones [4], tea waste [2], sugarcane bagasse, apricot stones [5], date stones [6], banana peel [7], tamarind seeds [7], orange peels [6], etc. For studies on adsorption and its efficiency there are some basic requirements: rate of adsorption and equilibrium data [1]. Parameters such as concentration of adsorbent, pH, agitation temperature at which experiments are carried out can be varied to study the effect of adsorption on dyes [1].

1.1 Cationic dyes

As mentioned in the introduction dyes can be classified as cationic and anionic in nature depending upon the charge they carry. Cationic dyes possess a positive charge on its molecule and are also called as basic dyes. They are usually found along with a $ZnCl_2$ or HCl complexes [2] Some of these dyes on which extensive studies have been carried out are methylene blue, malachite green [8], rhodamine 6G[9] basic yellow[10]. All these dyes are known to be toxic, capable of causing mutation, carcinogenic in nature. These dyes are capable of imparting color to water and are soluble with it [6]. Prolonged exposure to methylene blue can cause eye irritation [6], tachycardia [2], nausea, vomiting, slower the mental growth or retardation. Malachite green a cationic dye widely used in clothing industries, fish industries and at a large scale used as disinfectants in medical sector [8]. This pollutant too is known for having carcinogenic properties and cause mutation. Rhodamine 6G a dye which gives a dark reddish-brown appearance is from the rhodamine family known for stunting the growth in plants due to its adherence to lipid and phosphate molecules present in the cell membrane of plants.
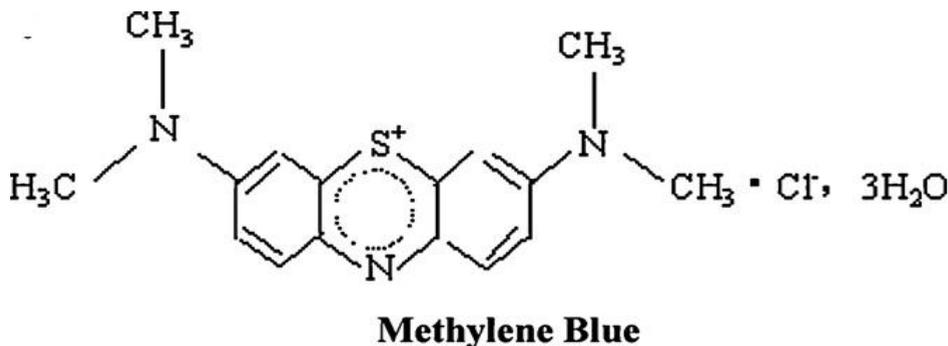
Fig. 1. Methylene Blue structure [11]

1.2 Different methods of dye removal

Few of the common techniques used for treatment of waste water streams polluted by dye are discussed below:

1.2.1 Filtration

There are different types of filtration process such as ultra-filtration, micro filtration, reverse osmosis, nano-filtration etc. Each of them are used for different purposes. Nano and ultra-filtration are the two types of processes that are generally used for treatment of waste water stream for removal of dyes. Drawback of this method is clogging of the pores which makes it an inefficient process. [3]

1.2.2 Chemical treatment

In this method coagulating and flocculating agents are used for dye removal. Ions such as Aluminium (Al^{3+}), Calcium (Ca^{2+}) etc. induces flocculation. Though the process is very feasible, the disadvantage of this method is the production of concentrated sludge due to which disposal becomes a problem. [3]

1.2.3 Oxidation process

Oxidizing agent are used in treatment of effluent streams. Chemical oxidation and UV assisted oxidation are the two common types in this process. These use low quantities of agent and short time for reaction. But the drawback of this process is formation of sludge [3], and (H_2O_2) agent need activation for efficient performance [2].

1.2.4 Adsorption using activated carbon

Of the various methods explained and enlisted above adsorption is one of the most commonly used methods for removal of cationic dyes from industrial effluents. In this process the adsorbate or dye molecules adhere to surface of adsorbent. Adsorption is widely applicable for removal of wide range of dyes. The disadvantage of adsorption is the cost of adsorbent which makes it economically infeasible. In this paper we are reviewing different sources of agricultural waste from which activated carbon is prepared and can be used as adsorbent. By this method the process can be made economical.

Table 1. Studies on adsorption of cationic dyes using activated carbon from different sources

Adsorbents	Dye	Source
F400 commercial activated carbon	Methylene blue	[12]
Pinewood (AC)	Methylene blue	[2]
Activated carbon from textile sludge	MB	[13]
CAC	MG	[8]
Rice husk activated carbon	MG	[2]
Carbon from jute fibers	MG	[8]
Acorn AC	MB	[1]
Oil palm wood AC	MB	[1]
A C peanut shell	MG	[3]
A C from pinedust	MG	[3]
A C plum kernel	Basic red 22	[3]
A C bagasse	Basic red 22	[3]
A C corncob	MB	[6]
A C rice husk	MB	[6]
A C date stones	MB	[6]
A C orange peels	MB	[6]

1.3 Activated carbon

Activated carbon (AC), as the name suggests, is conventionally prepared from carbon from its various physical forms such as coal, coconut shell, wood etc., using physical or chemical activation methods and for all its virtues is the oldest known adsorbent to mankind. Physical and chemical activations [14]**,** as discussed below**,** have their own merits and drawbacks. On one hand physical activation is more dependent or inclined towards use of elevated temperature and prolonged activation time and on the other hand chemical activation needs a rigorous and exhaustive cleaning of substrate because of exposure to chemical reagents [12].

1.3.1   Physical activation:

Initially, the substrate or source material is subjected to hot gases to be further developed into activated carbon. After the hot air treatment, the source material is then required to be burnt out of gases, giving way to a graded, concealed and dustless form of activated carbon. To achieve such an outcome from a relatively complicated process, a combination of techniques is used that are discussed below:

- *Carbonization*: It is the term for the conversion of an organic substance into carbon or a carbon-containing residue through destructive distillation, commonly known as pyrolysis, at 600–900 °C, conventionally with inert gases such as argon or nitrogen.

- *Activation/Oxidation*: Material obtained from carbonization is subjected to oxidization (oxygen or steam) with temperatures ranging well above 300°C, is in the vicinity of 600-900°C

1.3.2 Chemical activation: It acts as a precursor to carbonization. Here, the raw material is typically injected with an acid, base or salt. After this process, the previous step of carbonization is repeated but this time at a slightly lower temperature range of 400-900°C. The raw material is then carbonized at lower temperatures (450–900 °C). Although there is no certain proof for it but scientists widely agree that the activation step proceeds parallel to chemical activation.

Activated charcoal has been used for over 100 years for the treatment of toxic ingestions, and continues to be the most common form of gastrointestinal decontamination for the poisoned patient [15]. Though commercially available activated carbon (CAC) are usually derived from natural materials such as biomass, lignite or coal, but almost any carbonaceous materials may be used as precursor for the preparation of carbon adsorbents because of its commercial availability and cheapness, coal is the most widely used precursor to produced activated charcoal [10,16].

1.3.3 Properties [17]

1 gram of activated carbon has surface area ranging from 500 m^2 to 1500 m^2 which is available commercially. Carbon aerogels, which have higher surface areas are expensive, and are used in specific applications. Electron microscope, reveal the structure of high surface area of activated carbon. Particles that are extremely complicated exhibit innumerable kinds of porosity; but there can be regions where flat planes of graphite-like material run parallel to each other, which may be disconnected by few nanometers. These micro-pores provide excellent conditions for adsorption such that adsorbing material can interact with various surfaces concurrently. Testing of adsorption behavior are generally carried out with nitrogen gas at 7 K under high vacuum condition. On a general basis activated carbon is perfectly capable of producing its equivalent, by adsorption from its environment, liquid water from steam at 100°C (212 °F) and a pressure of 1/10,000 of an atmosphere.

1.3.4 Applications of activated carbon

The unique properties of activated carbon find its way to following applications:
1. Water purification
2. Gas purification
3. Gold and precious metal recovery
4. Pharmaceuticals and drug industry
5. Thermal and nuclear power stations
6. Waste water treatment
7. Petroleum

Coal is a mixture of carbonaceous materials, formed by the degradation of plants and formation of fossils over ages. The adsorption properties of each coal are determined by the manner by which the plants cultivated and the extent of the physical–chemical changes occurring after deposition. Coal adsorption capacities are given below.

Table 2. Adsorption capacities of commercially activated carbon for MB [18-20]

Adsorbents	Adsorption capacity (mg/g)
Commercial activated carbon	980.3
Activated carbon produced from New Zealand coal	588
Filtrasorb 400	476
Activated carbon	400
Activated carbon produced from Venezuelan bituminous coal	380
Peat	324
Coal	323.68
Filtrsorb 400	299
Norit	276
Picacarb	246
Filtrasorb 300	240
Coal	230
Commercial activated carbon	200
Bituminous Coal	176
Charcoal	62.7

1.3.5 Classification

Depending upon size of particle, methods of preparation and industrial applications activated carbon can be classified as follows:

1. Powdered activated carbon (R1, PAC)

Activated carbon is generally prepared in particulate form as fine granules which have a size of 1mm having an average diameter ranging from 0.15 to 0.25 mm. With this structure achieving higher surface to volume ratio and small diffusion distance becomes easier. Activated carbon (R1) are those particles of activated carbon which retain on a 50-mesh sieve (0.297mm).

2. Granular activated carbon (GAC)

Granular activated carbon, these comparatively have larger particle size than powdered activated carbon and hence represent a smaller external surface. GAC are classified depending on their dimensions where particles having sizes 8×20, 20×40, or 8×30 are used for liquid phase applications and 4×6, 4×8 or 4×10 are used for vapor phase applications.

3. Bead activated carbon (BAC)

Petroleum pitch is used for the production of bead activated carbon and are available in diameter ranging between 0.35mm to 0.8mm. It is also known for its low ΔP, high mechanical strength and low dust content, with a smaller pellet size. It is widely used in fluidized bed applications such as water filtration which could be credited to its spherical structure.

2 Effect of parameters

2.1 Effect of temperature

Temperature is an important parameter in adsorption studies. For any process it is essential to know to what extent does temperature bear an effect on the efficiency of adsorbent. Experiments are conducted at different temperatures ranging from 293K-333K by keeping all other parameters constant [1]. The nature of the process can be understood depending upon the way process reacts with variation in applied temperature. A process or a reaction is said to be endothermic in nature if the sorption of dye on the adsorbent sees a rise due to increase in temperature and exothermic if there is a fall in the adsorption capacity with increase in temperature. Adsorption of methylene blue dye on commercially activated carbon is an endothermic process. Two main effects of temperature on this process are increase in the rate of diffusion of the dye molecules on the outer surface of AC and the other increased movement of molecules thereby leading to reduced viscosity [1]. The same was seen in adsorption of MB using olive stone and olive stone activated carbon (OSAC) [4]. Increasing the temperature beyond a certain limit to achieve better adsorptivity is also not advisable since it has an effect on the operating cost [5]. It is seen that for most of the adsorbent used for uptake of MB (whatever the source of activated carbon used) had an endothermic natured process [11, 2, 21-23].

2.2 Effect of contact time

Contact time refers to the amount of time the adsorbent is in contact with the dye solution. Amount of MB that was adsorbed onto OSAC increased with the rise in contact while keeping the other parameters constant [4]. For a dye solution of 50mg/l a contact time of 15min was sufficient whereas for a dye of about 120mg/l concentration the time to attain equilibrium was about 30 minutes [4]. With increase in dye concentration the contact time required to reach equilibrium gets higher. The adsorption of MG was rapid till 120 min of contact and thereafter plateau is observed until equilibrium. And no further dye could be adsorbed [8]. The uptake of MG-5 increased continuously until 30 min of contact time after which removal rate decreased slightly and plateaued after 120 min. The quick adsorption from 50.1 to 72.8% within 1 min suggests strong affinity for the cationic dye molecule [24].The same trend was followed when C-PAN (*Persean Americana* nuts)was introduced in basic yellow 28 dye solution where during the first 15 min the adsorbing capacity was high followed by low adsorption rate until equilibrium was established at 30 min. depending upon the type of adsorbent being used and the removal % expected from the adsorbent the optimal contact time can range from few min to few hours[25].

2.3 Effect of pH

pH refers to the acidity or basicity of a solution. Solution having pH value below 7 are termed as acids/acidic in nature and pH above 7 are alkaline in nature where neutrality is at pH 7. pH gives an account of degree of ionization of acidic or basic compounds in adsorption process [1]. pH values are generally altered by using NaOH and HCl [5]. pH value can alter the surface charge of A C and functional group of the dye [23]. In the experiment of MB uptake using olive stone AC it was seen that there was increase in the amount adsorbed from 6.4-8.3 mg/g but optimum value was found at pH 5 having 9.5 mg/g uptake. There is no significant change in the adsorption capacity of adsorbent with variation in pH [22]. The

same is in accordance with adsorption of MB dye using CAC by varying pH between 2-11[1], but there was a significant change in the surface charge the drop in the pH value shows reduced hydrolysis of the groups, simultaneous increase in the stability of $(MB)^+$ was seen. In adsorption process of MB using ASAC there was an evident rise in the efficiency of adsorption with increase of pH credited to the protonation dye in the acidic medium and presence of excess H^+ ions showing optimum value at pH 5[5]. Whereas in adsorption of MG using CO_2 activated carbon it was seen that max adsorption (35.5%-93.2%) took place at pH 2-8 but further increase from 8-12 showed no such effect and was almost negligible impact due to the increased negative charges on CO_2 activated carbon surface at this pH [8].

2.4 Effect of initial dye concentration

Initial dye concentration studies and its effects on adsorption can be understood by treating different concentration dye with adsorbent dose maintained constant. For experiment of AC treatment of MB dye by varying the initial dye concentration, it was seen that achieving equilibrium with lower concentration of dye was much easier compared to higher concentration levels. It is to be mentioned that the rate at which dye is adsorbed is faster at high concentration initially and then steadily attains equilibrium [1]. The same was seen in textile sludge activated carbon used as adsorbent also indicating the faster rate is due to high driving force initially which gradually reduces [13]. In most of the cases it's seen that the initial dye concentration and removal % are inversely related to each other as active sites are saturated in the presence of higher initial concentration [2].

Table 3. Adsorption capacity on varying initial dye concentration

Adsorbents	Dye	Initial dye concentration (mg/l)	% removal	Adsorption Capacity (mg/g)	References
Sawdust Carbon	MB	50-250	99%-82.2%	12.49-51.4	[2]
Apricot Stone AC (ASAC)	MB	5-100	99%-67%	----	[5]
Olive Stones AC	MB	50-150	------	4.8-12.4	[4]
Ficus Carica Bast AC (FCBAC)	MB	40-90	80-50	30-45	[26]
Coconut shell AC	MB	10-50	87.8-39.6	--	[21]

2.5 Effect of adsorbent dosage and particle size

Optimal amount of adsorbent to be used for adsorption can be studied extensively by carrying out experiments where the adsorbent dosage is varied when other conditions are maintained constants. In an experiment of removal of MB dye using CAC it was seen that a dosage of 0.1 g was sufficient to get maximum removal % where initial dye concentration was 10mg/l with agitation speed of 200rpm at 298K were maintained [5]. This was in correspondence with removal of MB using FCBAC when the adsorbent dosage was varied from 0.1/100ml to 0.5/100ml [26]. Same was seen that with an increase in dosage from 2-12g/l the removal % varied from35-90% for CP13[27]. Generally, it is seen that with rise in the adsorbent dosage the removal % or its efficiency gets better as the number of vacant sites available for uptake of dye are more [2]. But to achieve better adsorption we cannot keep increasing the

adsorbent dose as cost becomes a limiting factor and therefore finding an optimal dosage for any process of dye adsorption has to be considered.

The CAC used for removal of MB dye had the following physical parameters [1]

Table 4. Physical properties of commercially activated carbon

BET surface area (m^2)	900
Particle size (μm)	150
Mesopore vol. (cm^3/g)	0.058
Micropore vol. (cm^3/g)	0.294

It is seen in an adsorption process study of MB uptake using PAC2 the adsorption capacity of the adsorbent did rise with smaller particle size of PAC2. The solution of 600mg/dm^3 showed an increase in adsorption from 253-325mg/g as the particle size of adsorbent was varied between 106-180μm when compared to particle size which was maintained below 106μm [10].

2.6 Effect of stirring /agitation speed

Adsorption of MB using CAC as adsorbent was studied at different mixing rates experiments were carried out at 293K by varying stirring speed from 90-150rpm for a solution of 120mg/l concentration. From the experiment, it was concluded that this parameter did not have any significant effect on removal % of dye [1]. Depending upon the agitation speed of a solution it can be understood that the rate controlling step could either be film diffusion or pore diffusion. On agitating MB solution between 50-300rpm with initial dye concentration of 10mg/l adding 0.01g of adsorbent at 298K following were concluded [5].

Table 5. Optimum stirring speed for MB adsorption

Adsorbent	Optimum Stirring speed (rpm)	Efficiency/ removal %
CAC	200	97.4
ASAC	100	99.2

3 Adsorption isotherms

There are different types of adsorption isotherms such as: Freundlich, Langmuir, and Temkin, Harkins-jura, R-D isotherms among which the former two are widely used. Depending on the type of data available any of them could be used for best fitting of the data. Adsorption isotherm in general refers to a graphical representation giving a relation between amount of adsorbate adsorbed on to surface of an adsorbent. There are basically two types of isotherm depending on the parameters

1.   Two parameter isotherms: Langmuir, Freundlich, Temkin, R-D isotherms, hill isotherms.

2.   Three parameter isotherms: this include Redlich-Peterson, sips model, khan isotherm, Radke–Prausnitz isotherm [28].

3.1 Two Parameter Models [4]

3.1.1 Langmuir isotherm

Langmuir isotherm assumes that a single layer of adsorption takes place on the surface of adsorbent having certain number of vacant sites for adsorption of uniform strategies of adsorption. The expression for Langmuir isotherm is given as follows

$$\frac{C_e}{q_e} = \frac{1}{Q_o K_L} + \frac{C_e}{Q_o} \tag{1}$$

Where C_e refers to concentration of adsorbate at equilibrium.
q_e refers to adsorbate that has been adsorbed /unit mass of adsorbent
Q_O, K_L are the adsorptivity rate constant of adsorption process
A dimensionless parameter R_L gives the essential characteristics of Langmuir isotherm and can be given as

$$R_L = \frac{1}{1 + K_L C_e} \tag{2}$$

3.1.2 Freundlich isotherm

In this isotherm heterogeneous/non-homogenous surface with a non-uniform distribution of heat of sorption over surface is assumed. This is given by

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \tag{3}$$

K_F, n are Freundlich isotherm constants where n values generally range from 1-10. Increased value of n shows better adsorption

3.1.3 Temkin isotherm

Here it is assumed that heat of adsorption of all molecules in the layer reduces linearly with coverage. This is due to the interactions that exist between the dye and activated carbon molecules in this case. It is given by:

$$q_e = B_T \ln K_T + B_T \ln C_e \tag{4}$$

K_T is equilibrium binding constant,

$$B_T = RT/b$$

R is the gas constant, T absolute temperature.

3.1.4 Dubinin-Radushkevic: The model is given as follows:

$$\ln q_e = \ln Q_s - B\dot{\varepsilon}^2 \tag{5}$$

Where $\dot{\varepsilon}$ is known as Polanyi potential

$$\dot{\varepsilon} = RT \ln \left(1 + \frac{1}{C_e}\right) \tag{6}$$

The relation between mean energy for sorption and B is given as

$$E = \frac{1}{\sqrt{2B}}$$ (7)

The E value gives relation of physical and chemical nature of adsorption

3.1.5   *The Harkins-Jura isotherm* [4]

$$\frac{1}{qe^2} = \frac{B_2}{A} - \frac{1}{A}\log C_e$$ (8)

Where q_e -adsorption at equilibrium and C_e is the concentration at equilibrium
A is Harkins-Jura isotherm parameter and B_2 is the isotherm constant.
In this isotherm it is assumed that multilayer adsorption takes place in an heterogenous pore distribution.

3.2 Three Parameter Models [28]

3.2.1 Redlich-Peterson isotherm

$$q_e = \frac{K_R C_e}{1 + a_R C_e^g}$$ (9)

A combination of both Langmuir and Freundlich isotherms, which three parameter isotherm. The isotherm is linearly dependent on concentration in the numerator and an exponential function in the denominator to represent adsorption equilibria. This could be done over a wide concentration range in both homogeneous or heterogeneous systems due to its versatility.

3.2.2 Sips isotherm
Just like Redlich-Peterson isotherm this also is a combination of both Langmuir and Freundlich isotherm which is generally applicable to heterogeneous adsorption systems. This isotherm is influenced by the working conditions of the adsorption process such as pH, temperature and concentrations.

$$q_e = \frac{K_s C_e^{\beta s}}{1 + C_e^{\beta s} a_s}$$ (10)

Following is a table of various adsorbent and adsorbate combination and their relation with adsorption isotherms.

Table 6. Adsorption isotherms for dyes using different adsorbents

Adsorbent	Dye/adsorbate	Isotherm	Constants	Source
CAC	MB	Langmuir	q_m=146.46;K=1.11; R^2=0.998(293K)	[1]
Olive stone activated carbon	MB	Temkin	R^2=0.997	[4]
Olive stone	MB	Temkin	R^2=0.995	[4]
Textile sludge AC	MB	Freundlich	K_F=0.165; n=1.280	[13]
Apricot stones AC	MB	Langmuir	q_m= 36.68 ;K_L=23.3 ;R^2=0.961	[5]
CAC	MB	Langmuir	q_m=199.60 ; K_L=2.97; R^2=0.964	[5]
Pinewood AC	MB	Langmuir	q_m=5.56	[2]
AC from pinedust	MG	Langmuir	q_m= 370.37	[3]
A C peanut shell	MG	Langmuir	q_m =222.22	[3]
Mesoporous A C	MB	Langmuir	q_m=336.3,K_L=1.004; T=293K	[23]
AC rice husk	MB	Freundlich	T=303K; q_L=9.8mg/g	[6]
AC sunflowerhulls	MB	Langmuir	T=303K; q_L=473.4mg/g	[6]
AC walnut shells	MB	Redlich-Peterson	T=298K; q_L=355.5mg/g	[6]
AC Date stones	MB	Sips	T=303K ;q_L=369.4mg/g	[6]

4 Adsorption kinetics

The rate of adsorption is given by adsorption kinetics in terms of order of the rate constant [2]. This adsorption rate is essential to decide the type or the best suited adsorbent for a specific process and this is governed by two main properties of adsorbent. One is the adsorption capacity and the other is the rate of adsorption. Most of the adsorption kinetics fall under one of the two types:

1. Pseudo- first order
2. Pseudo-second order

The adsorption process is then evaluated and is checked for the best kinetics that is applicable.

4.1 Pseudo- first order (PFO)

The adsorption rate for this kinetics is given by Lagergren; [4]

$$\ln (q_e-q) = \ln q_e - k_1 t \qquad (11)$$

where q_e refers to the dye adsorbed (mg/g) at equilibrium and q is the amount of dye adsorbed at any time t

k_1 is the rate constant for pseudo first order kinetics (min^{-1})

when the adsorption is characterized by diffusion through a boundary the following equation applies when n=1 [2].

$$-r_A = C_A^n$$

4.2 Pseudo-second order model   [2]

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} \qquad (12)$$

4.3 Intraparticle diffusion model [4]

The adsorption process has three steps: Film diffusion, Pore diffusion, intra-particle transport.
The slowest step among the three is called as the rate determining step. Intraparticle diffusion is given by

$$q_t = k_{diff} \, t^{0.5} + C \qquad (13)$$

where k_{diff} is the intraparticle diffusion rate constant (mg/g min) and C is the intercept (mg/l) indicating that the line does not pass through the origin which is attributed to the difference in the initial and final mass transfer rates. The intercept gives an idea about the thickness of the boundary layer higher the value of which greater is the thickness.

Where q_t and q_e are the amount of dye adsorbed at time t and at equilibrium respectively.
k_2 is the rate constant for pseudo second order kinetics (g/mg min).
This model shows or follows a linear path. Depending upon the linear regression coefficient R^2 the best model for process can be inferred.
Generally, for cationic dye adsorption pseudo second order represents the system better [2].

For adsorption of MB from macore fruit shells revealed that the R^2 value was max for pseudo second order kinetics [22]. The same was seen in adsorption of the MB dye using OSAC and OS as adsorbent suggesting that overall rate was controlled by chemical adsorption. But in contrast the MB dye adsorption onto surface of ASAC should better results for intraparticle diffusion [2]. An experiment of malachite green adsorption using CO_2 activated carbon gave the best result for intraparticle diffusion model [8].

5 Regeneration of activated carbon

Regeneration of the adsorbent is essential as excess amounts untreated can lead to problems in disposal. The adsorbent used can be reused for future applications. It is seen that regeneration of adsorbents from different agricultural sources show good amount of adsorption. The different methods of regeneration are biosorbents [25], carbonization of

activated carbon, thermal regeneration [8]. It is seen that as we increase the regeneration cycles the adsorption capacity decreases.

Table 7. Adsorption capacity of adsorbents on regeneration

Adsorbent	Dye	Adsorption Capacity (mg/g)	References
C-PAN	MB	235-37.3	[25]
A C from fuel oil	MB	37-28	[9]
A C from fuel oil	Rhodium 6G	27-18	[9]
CAC	MB	210.18-148.51	[8]

6 Conclusions

Adsorption has been extensively studied and still research is being continued on efficient methods of dye removal.in this review paper various works have been compared and following are some of the findings

- Most of the agriculture based AC have good potential for adsorption of cationic dyes
- On uptake of MB dye varying pH over certain range and stirring did not show any significant changes.
- Initially for higher dye concentration the uptake of dye by the adsorbent is high and then slowly reaches equilibrium
- Depending upon the agitation and the process response towards it one can identify the rate limiting step between film and pore diffusion
- Adsorption isotherms of two and three parameter were used for studies and it was observed that most of them gave good results for Langmuir isotherms.
- Adsorption kinetics for the adsorption processes were not very satisfying for pseudo-first order kinetics when compared to the second order or intraparticle diffusion.

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