

Removal of dyes using agricultural waste as low-cost adsorbents: a review

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Abstract Color removal from wastewater has been a matter of concern, both in the aesthetic sense and health point of view. Color removal from textile effluents on a continuous industrial scale has been given much attention in the last few years, not only because of its potential toxicity, but also mainly due to its visibility problem. There have been various promising techniques for the removal of dyes from wastewater. However, the effectiveness of adsorption for dye removal from wastewater has made it an ideal alternative to other expensive treatment methods. In this review, an extensive list of sorbent literature has been compiled. The review evaluates different agricultural waste materials as low-cost adsorbents for the removal of dyes from wastewater. The review also outlines some of the fundamental principles of dye adsorption on to adsorbents.

Keywords Dyes · Low-cost adsorbents · Adsorption · Wastewater treatment

Introduction

Dyes are widely used in industries such as textiles, rubber, plastics, printing, leather, cosmetics, etc., to color their products. As a result, they generate a considerable amount of colored wastewater. There are more than 10,000 commercially available dyes with over 7×10^5 tonnes of dye stuff produced annually. It is estimated that 2 % of dyes

produced annually is discharged in effluents from associated industries (Allen and Koumanova 2003). Among various industries, textile industry ranks first in usage of dyes for coloration of fiber. The total dye consumption of the textile industry worldwide is in excess of 107 kg/year and an estimated 90 % of this ends up on fabrics. Consequently, 1,000 tones/year or more of dyes are discharged into waste streams by the textile industry worldwide (Marc 1996). Discharge of dye-bearing wastewater into natural streams and rivers poses severe problems to the aquatic life, food web and causes damage to the aesthetic nature of the environment.

Dyes absorb and reflect sunlight entering water and so can interfere with the growth of bacteria and hinder photosynthesis in aquatic plants. The problems become graver due to the fact that the complex aromatic structures of the dyes render them ineffective in the presence of heat, light, microbes, and even oxidizing agents and degradation of the dyes become difficult (Pearce et al. 2003). Hence, these pose a serious threat to human health and water quality, thereby becoming a matter of vital concern. Keeping the essentiality of color removal, concerned industries are required to treat the dye-bearing effluents before dumping into the water bodies. Thus, the scientific community shoulders the responsibility of contributing to the waste treatment by developing effective dye removal technique.

Dyes can have acute and/or chronic effects on exposed organisms depending on the exposure time and dye concentration. Dyes can cause allergic dermatitis, skin irritation, cancer, mutation, etc. Dyes can be classified as (Mishra and Tripathy 1993): anionic (direct, acid and reactive dyes), cationic (basic dyes) and non-ionic (dispersive dyes).

Many treatment processes have been applied for the removal of dye from wastewater such as: Fenton process

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(Behnajady et al. 2007), photo/ferrioxalate system (Huang et al. 2007), photo-catalytic and electrochemical combined treatments (Neelavannan et al. 2007), photo-catalytic degradation using UV/TiO₂ (Sohrabi and Ghavami 2008), sono-chemical degradation (Abbasi and Asi 2008), Fenton-biological treatment scheme (Lodha and Chaudhari 2008), biodegradation (Daneshvar et al. 2007), photo-Fenton processes (Garcia-Montano et al. 2007), integrated chemical–biological degradation (Sundarjanto et al. 2006), electrochemical degradation (Fan et al. 2008), adsorption process (Tan et al. 2007; Hameed et al. 2007a, b), chemical coagulation/flocculation, ozonation, cloud point extraction, oxidation, nano-filtration, chemical precipitation, ion-exchange, reverse osmosis and ultra-filtration (Lorenc-Grabowski and Gryglewic 2007; Malik and Saha 2003; Malik and Sanyal 2004; Banat et al. 1996).

Among treatment technologies, adsorption is rapidly gaining prominence as a method of treating aqueous effluent. Some of the advantages of adsorption process are possible regeneration at low cost, availability of known process equipment, sludge-free operation and recovery of the sorbate (Kapdan and Kargi 2002). Activated carbon is the most widely used adsorbent for dye removal because of its extended surface area, micro-pore structures, high adsorption capacity and high degree of surface reactivity. However, commercially available activated carbon is very expensive and has high regeneration cost while being

exhausted. Furthermore, generation using solution produces a small additional effluent while regeneration by refractory technique results in a 10–15 % loss of adsorbent and its uptake capacity (Waranusantigul et al. 2003). This has led to search for cheaper substances. Researchers are always in a hunt for developing more suitable, efficient and cheap and easily available types of adsorbents, particularly from the waste materials.

Agricultural waste materials have little or no economic value and often pose a disposal problem. The utilization of agricultural waste is of great significance (Geopaul 1980). A number of agricultural waste materials are being studied for the removal of different dyes from aqueous solutions at different operating conditions. Agricultural waste includes coir pith (Namasivayam and Kavitha 2002), orange peel (Rajeswari et al. 2001), banana peel (Annadurai et al. 2002), rice husk (Malik 2003), straw (Kannan and Sundaram 2001), date pit (Banat et al. 2003a), oil palm trunk fiber (Hameed and El-Khaiary 2008a), durian (*Durio zibethinus* Murray) peel (Hameed and Hakimi 2008), guava (*Psidium guajava*) leaf powder (Ponnusami et al. 2008), almond shell (Ardejani et al. 2008), pomelo (*Citrus grandis*) peel (Hameed et al. 2008a), broad bean peel (Hameed and El-Khaiary 2008b), peanut hull (Tanyildizi 2011), *Citrullus lanatus* rind (Bharathi and Ramesh 2012). The adsorption capacity of these sorbents is listed in Table 1.

Table 1 Reported adsorption capacities q_m (mg/g) of different agricultural wastes

Adsorbent	Dye	Maximum adsorption capacity (mg/g)	References
Coir pith	Congo red	2.6	Namasivayam and Kavitha (2002)
Orange peel	Aid violet	19.88	Rajeswari et al. (2001)
Banana peel	Basic blue 9	20.8	Annadurai et al. (2002)
Rice husk	Acid yellow 36	86.9	Malik (2003)
Straw	Basic blue 9	19.82	Kannan and Sundaram (2001)
Date pit	Basic blue 9	17.3	Banat et al. (2003a)
Oil palm fiber: activated carbon	Malachite green	149.35	Hameed and El-Khaiary (2008a)
Durian shell: based activated carbon	Methylene blue	289.26	Hameed and Hakimi (2008)
Guava (<i>Psidium guajava</i>) leaf Powder	Methylene blue	185.2	Ponnusami et al. (2008)
Almond shell	Direct red 80	90.09	Ardejani et al. (2008)
Pomelo (<i>Citrus grandis</i> peel)	Methylene blue	344.83	Hameed et al. (2008a)
Broad bean peel	Methylene blue	192.7	Hameed and El-Khaiary (2008b)
Peanut hull	Reactive dye	55.5	Tanyildizi (2011)
<i>Citrullus lanatus</i> rind	Crystal violet	11.9	Bharathi and Ramesh (2012)

Removal of dyes by low-cost sorbents

Garlic peel was investigated by Hameed and Ahmad (2009) for the removal of Methylene blue from aqueous solution. Equilibrium isotherms were determined and analyzed using the Langmuir, Freundlich and Temkin isotherms. The maximum monolayer adsorption capacities were found to be 82.64, 123.45 and 142.86 mg g⁻¹ at 303, 313 and 323 K, respectively. Batch studies were carried out to explore the potential use of garlic peel as low-cost adsorbent for Methylene blue removal from aqueous solution. The kinetic data were analyzed using pseudo-first-order and pseudo-second-order models. For Methylene blue author observed that the adsorption capacity was higher due to the presence of polar functional group. Dogan et al. (2009) studied hazelnut shell, an agricultural waste, without any pretreatment for the removal of Methylene blue. Pine apple stem was studied by Hameed et al. (2009) for the adsorption of Methylene blue (basic dye) from aqueous solution. The process was studied at different concentration of dyes, contact time, and pH and was found to obey the Langmuir isotherm. The authors suggested that the acidic pH is favorable for the adsorption. The maximum adsorption capacity on pine apple stem for the removal of Methylene blue was found to be 119.05 mg g⁻¹.

Jack fruit peel has been investigated as adsorbents for removal of Methylene blue by Hameed (2008a). The effect of different system variables like adsorbent dose, initial dye concentration, contact time and pH were evaluated and found that as the amount of adsorbent increased, the percentage of dye removal increased accordingly. Low concentrations of Methylene blue favored high adsorption percentages and the optimum pH value for dye adsorption was found to be 4.0. The equilibrium biosorption data were analyzed using four different types of linearized Langmuir isotherm, the Freundlich isotherm and the Temkin isotherm. Best fits were obtained with the type 2 Langmuir model. The sorption capacity of Methylene blue on jack fruit peel was found to be 285.713 mg g⁻¹.

Oil palm trunk fiber as an adsorbent was investigated by Hameed and El-Khaiary (2008a) who studied the removal of Malachite green, thereby making an attempt to overcome the economic disadvantages of activated carbon. The adsorbent was studied without any pretreatment and was sieved into different size ranges prior to use. The monolayer coverage of Malachite green on oil palm trunk fiber was found to be 149.35 mg g⁻¹ at 30 °C.

Wang et al. (2008) reported on the capacity and mechanism of adsorption of two basic dyes, namely Malachite green and Methylene blue by rice bran and wheat bran. Rice bran and wheat bran are by-products. The adsorption of both basic dyes was pH dependent. Both the dyes are basic in nature, which upon dissociation release colored

dye cations into solution. The adsorption of these positively charged dye groups on to the adsorbent is primarily influenced by the surface charge on the adsorbent, which in turn is influenced by the surface charge on the adsorbent, which in turn is influenced by the solution pH. As the pH is increased, greater cation removal is facilitated. The kinetic experimental data were analyzed using four kinetic equations including pseudo-first-order equation, pseudo-second-order equation, external diffusion model and intra-particle diffusion model. The experimental data were fitted with Langmuir and Freundlich isotherms and the results showed that the Langmuir isotherm exhibited a little better fit to the Methylene blue adsorption data by both adsorbents. While, the Freundlich isotherm seemed to agree better with the Malachite green adsorption, the effects of particle size, adsorbent concentration and solution ionic strength on the adsorption of the two dyes were studied and it was found that the adsorption capacity decreases with an increase in the adsorbent concentration. This is due to the fact that some of the adsorption sites remained unsaturated during the adsorption process and due to inter-particle interaction.

Broad bean peel an agricultural waste chopped, sieved, washed and oven dried at 60 °C for 48 h was used by Hameed and El-Khaiary (2008b) for removal of cationic dye (Methylene blue) and adsorption capacity of 192.7 mg g⁻¹ was found. It was noted that adsorption of dye decreases with an increase in the initial Methylene blue concentration. The adsorption of dyes was reported to follow Langmuir adsorption model and pseudo-first-order kinetic model.

Groundnut shell, an agricultural solid waste has been used as an adsorbent by Malik et al. (2007), for the removal of Malachite green from aqueous solution. The material is largely available and can be used as a potential sorbents due to their physico-chemical characteristics and low cost. Groundnut shell is easily available at zero prices. Nut shell is carbonaceous, fibrous solid waste, which creates a disposal problem and is generally used for its fuel value. Further, in order to know the effect of chemical treatment and improve its efficiency, the authors also tested the potential of the adsorbents by treating it with ZnCl₂. Besides this, the simulation studies for effect of contact time, adsorbent dose and initial dye concentration were also studied. The experimental results indicated that at a dose of 0.5 g L⁻¹ and initial concentration of 100 mg L⁻¹, groundnut shell powder activated carbon showed 94.5 % removal of the dye in 30 min equilibrium time, while commercially available powdered activated carbon removed 96 % of the dye in 15 min. The experimental isotherm data were analyzed using the linearized form of Freundlich, Langmuir and BET equations to determine the maximum adsorptive capacities. The equilibrium data fit well to the Freundlich isotherm.

Raw agricultural solid wastes and waste materials from forest industries such as sawdust have been used as adsorbents. These materials are available in large quantities and may have potential as adsorbents due to their physico-chemical characteristics and low cost. Sawdust is an abundant by-product of the wood industry, which is available in country side at zero or negligible price. It contains various organic compounds (lignin, cellulose and hemicellulose) with poly phenolic groups that might be useful for binding dyes through different mechanisms. The role of sawdust material in the removal of pollutants from aqueous solutions has been reviewed recently by Shukla et al. (2002). Sawdust has proven to be a promising effective material for the removal of dyes from wastewater. Garg et al. (2003) studied Rose wood sawdust a low-cost adsorbent for the removal of Malachite green from aqueous solution. Further, in order to know the effect of chemical treatment and to improve its efficiency the authors also tested the potential of the adsorbent by treating it with formaldehyde and sulphuric acid. Besides this, studies on the effect of pH, initial concentration, adsorbent dose and contact time were also carried out by Garg et al. (2003). The authors determined that an initial pH in the range of 6–9 was favorable for dye removal. The low adsorption of Malachite green at acidic pH was suggested to be due to the presence of H^+ ions that compete with the dye cation for adsorption sites. With the increase of the pH of the system, the number of positively charged sites decreases while the number of the negatively charged increases.

Dulman and Cucu-Man (2009) investigated the effect of Beech wood sawdust on the adsorption of six reactive dyes in aqueous solution, namely C.I. Direct Blue 6, C.I. Direct Brown 2, C. I. Direct Green 26, C.I. Direct Brown, C.I. Reactive Red 3, C.I. Basic Blue 86. The percentage removal of the reactive dyes Direct Brown 2 and Direct Brown decreased with increase in pH (above pH 10) and the maximum removal rate was occurred at pH 3. Consequently, the percentage color removal of Direct Brown 2 and Direct Brown dropped from 98.6 to 34.7 % and 94.4 to 28.5 %, respectively. For Basic Blue the sorption has a maximum value of 97 % at pH 4.43–7.06. At lower pH ($pH < p_{H_{zpc}}$), the percentage color removal of hydrolyzed reactive dyes was relatively high. Malik (2003) investigated Mahogany sawdust and rice husk as adsorbents for the removal of (acidic dye) Acid yellow 36. The adsorbents were activated by means of steam. The kinetics of the process was found to be dependent on contact time, adsorbent dose and pH. The authors found that an acidic pH is favorable for the adsorption of acid dye. It was observed that adsorption obeys both Freundlich and Langmuir isotherms and the intraparticle diffusion of dye molecule within the particle is the rate-limiting step. The monolayer coverage of acid yellow 36 on Mahogany

sawdust was found to be 183.3 mg g^{-1} of the adsorbent. Hameed et al. (2007a) studied rattan sawdust as adsorbent for the removal of Malachite green from aqueous solution. The adsorbent was studied without any physical or chemical treatment. The equilibrium data fit with the Langmuir isotherm with a monolayer capacity of 62.71 mg g^{-1} . The authors found that for a short time period the rate of adsorption is controlled by film diffusion. However, at longer adsorption times, pore diffusion controls the rate of adsorption

Hameed (2009a), studied papaya seeds a novel non-conventional low-cost adsorbent for the removal of (cationic dye) Methylene blue. The effect of dye adsorption increased with increase in adsorbent dosage and pH. In terms of the initial rate of adsorption, the uptake of the cationic dye on to papaya seeds was found to occur more rapidly. The intraparticle diffusion indicated that more than one process affected the adsorption. The removal of Methylene blue by papaya seeds suggested that the sorption interaction obeyed the pseudo-second-order kinetics. The equilibrium data for Methylene blue on papaya seeds were modeled with the Langmuir, Freundlich, and Temkin models. The data fitted well with the Langmuir model with a maximum monolayer capacity of $555.557 \text{ mg g}^{-1}$.

Leaf biomass, an agricultural waste, widely available was studied as an alternative adsorbent for different pollutants as well as dyes by various investigators (Ponnusami et al. 2009; Weng et al. 2009; Han et al. 2007; Immich and Ulson de Souza 2009). The plant leaves have porous structure which can effectively adsorb dye molecules. The functional groups on the leaf surface can attract ionic dye molecules of opposite charge which lead to increase in dye removal efficiency. Ponnusami et al. (2009) studied Gulmohar (*Delonix regia*) as adsorbent for the removal of Methylene blue from aqueous solution. The materials were studied without chemical treatment. Authors found the adsorption was favorable at higher pH and lower temperature. The equilibrium data were well fitted by the Langmuir isotherm an appreciable Langmuir capacity of 0.3 mg g^{-1} was found out.

A Phoenix tree leaf has also been studied as an adsorbent by Han et al. (2007), for the removal of Methylene blue from aqueous solution. The Phoenix tree leaves contain abundant floristic fiber, protein and some functional groups such as carboxyl, hydroxyl and amidogen, etc., which make biosorption process possible. The leaf is a waste product with practically no cost but its adsorption capacity is 80.90, 83.80, 89.70 mg g^{-1} at 295, 305 and 323 K, respectively, makes it an adsorbent of a little importance for dye removal from wastewater. Neem leaf has proven to be a promising effective material for the removal of Remazol Blue RR dye from aqueous solution (Immich and Ulson de Souza 2009). Pine apple leaf powder

an agricultural waste, has been recently investigated to remove Methylene blue from aqueous solutions by Weng et al. (2009). Pine apple leaf powder is a complex material containing 70–80 % cellulose, lignin (5–12 %) and hemicellulose. The maximum adsorption capacity varied from 0.15 mg/g only. The capacity increased as the initial Methylene blue concentration increases. The adsorption increases with decreasing temperature suggesting that the adsorption reaction is exothermic in nature.

Namasivayam et al. (2001) investigated coir pith, an agricultural solid waste, as an adsorbent for the adsorption of Rhodamine B and Acid violet dyes. The adsorbent was used after drying, sieving and carbonizing at 700 °C. It was found that Rhodamine B adsorption reached equilibrium stage at 5, 7, 10 and 10 min for dye concentration 10, 20, 30 and 40 mg L⁻¹, respectively, while crystal violet (CV) was found to have equilibrium time of 40 min for all the concentrations. The adsorption capacity was found to be 2.56 and 8.06 mg g⁻¹ of adsorbent for Rhodamine B and Acid violet, respectively. Coir pith has also been investigated as an adsorbent by Kavitha and Namasivayam (2007) for the removal of Procion Orange from wastewater. The sorption capacity of 2.6 mg g⁻¹ makes it an adsorbent of little importance for dye removal from wastewater. Banana stalks were studied as adsorbents by Hameed et al. (2008b) for basic dyes in aqueous solutions with equilibrium isotherms and kinetic adsorptions. High adsorption capacity of 243.90 mg g⁻¹ was observed and authors suggested that banana stalks consists of cellulose and lignin; it is the polyol structure of cellulose-based materials that has relatively strong chemical adsorption of cations such as metal ions and organic bases as well as physical adsorption of other material such as acidic and anionic compounds.

Mall et al. (2006) utilized bagasse fly ash for the removal of Orange-G (OG) and Methyl violet (MV) from aqueous solution. Results indicated that OG is strongly adsorbed at pH 4.0, whereas MV is strongly adsorbed at pH 9.0. The percentage of dye removal was higher at low initial concentration and increased in amount of adsorbent used. The adsorption data have been correlated with Freundlich, Langmuir, Redlich–Peterson, Dubinin–Radushkevich and Temkin adsorption models. The authors observed that the Freundlich isotherm gave the best correlation for the adsorption of Orange-G-bagasse fly ash system and Redlich–Peterson isotherm better fits the Methyl violet-bagasse fly ash system. The adsorption of Methylene violet and Orange Green followed pseudo-second-order kinetics. Manaskorn et al. (2004), studied bagasse pith from sugarcane industry without any pretreatment for the removal of three reactive dyes, Remazol Black B, Remazol Brilliant Blue and Remazol Brilliant Red from aqueous solutions. High percentage removal was

observed for the adsorption of reactive dyes in the order of 58.48–98.03 % for RR Black, 46.15–93.47 % for RB Blue and 46.30–94.60 % for RB Red, respectively.

Agricultural solid waste such as seed hull has been used as adsorbents for the removal of dye from wastewater. These materials are available in large quantities and may have potential as adsorbents due to their physico-chemical characteristics and low cost. Sunflower seed hull activated with sulphuric acid has been used for the removal of Acid violet 17 by Thinakaran et al. (2008). The Langmuir adsorption capacity was found to be 116.27 mg g⁻¹. The same material has been used for the removal of Methyl violet by Hameed (2008b), without any physical or chemical treatment. The equilibrium data were analyzed using the Langmuir, Freundlich and Temkin isotherm models and the equilibrium process was described well by the Freundlich isotherm model. The maximum sorption capacity was found to be 92.59 mg L⁻¹ at 30 °C. Pumpkin seed hull as low-cost adsorbent has been investigated by Hameed and El-Khaiary (2008a), for the removal of basic dye (Methylene blue) from aqueous solutions. Authors noted that adsorption of dyes was rapid on the outer surface, followed by slower adsorption inside the porous. The removal of Methylene blue was high at pH 6–9. The results obtained by the workers indicated that the multilayer adsorption isotherm was found to have the best fit to the experimental data, suggesting multilayer adsorption on a homogeneous surface. The adsorption capacity was determined from the parameters of adsorption isotherms and was found to be 141.92 mg g⁻¹.

Hevea brasiliensis seed coat was studied by Hameed and Daud (2008), for the adsorption of basic blue from aqueous solutions with different contact time and initial concentration. The monolayer adsorption capacity was found to be 227.27 mg g⁻¹ at 30 °C. Authors reported that adsorption process obeyed the pseudo-second-order kinetic model and the adsorption isotherm followed Freundlich isotherm model. Thinakaran et al. (2008) investigated gingelly (sesame) (sp), cotton (cp), pongam (pp) seed hulls, an agricultural waste for the adsorption of Acid Red 114 from aqueous solution. The materials were used after cleaning, drying, soaking in 18 N H₂SO₄ and carbonizing at 80 °C. It was found that the optimum condition for AR114 removal was at a pH of 3, adsorbent dose of 3 g L⁻¹ and at an equilibrium time of 4 h. The adsorption capacity was in the order of sp > cp > pp. Another agricultural product is bamboo, a grass, the most diverse group of plants in the grass family. Bamboo is an abundant natural resource which has been found to be effective in retaining dyes from aqueous solutions. Because of its low cost and high availability, bamboo is very attractive as an adsorbent. Like sawdust, the cost of forest waste is only associated with the transport cost from the storage place to

the site where they will be utilized. The adsorption of Methylene blue on to bamboo-based activated carbon was studied by Hameed et al. (2007b). In order to improve the efficiency, the authors also tested the potential of the adsorbent by treating it with potassium hydroxide and CO₂. Besides this, the simulation studies for the effect of agitation time and concentration of dye were also carried out. The equilibrium data for Methylene blue adsorption well fitted to the Langmuir equation, with maximum monolayer adsorption capacity of 454.2 mg g⁻¹. Hameed (2009b), studied grass an agricultural waste without any pretreatment for the removal of basic dyes (Methylene blue) from aqueous solution. The agricultural waste was found to have high adsorption capacity of 457.60 mg g⁻¹. Other agricultural solid wastes from cheap and readily available resources such as de-oiled soya (Mittal et al. 2005) date pits (Banat et al. 2003b), coir pith, sawdust, sugarcane fiber (Parab et al. 2009), banana pith (Kadirvelu et al. 2003; Ho and McKay 1999; Chen et al. 2001), corncob (Robinson et al. 2002b, c) and orange peel (Namasivayam et al. 1996) have also been successfully employed for the removal of dyes from aqueous solutions.

Adsorption kinetics

Adsorption kinetics depends on the adsorbate–adsorbent interaction and system condition and has been investigated for their suitability for application in water pollution control. Two vital evaluation elements for an adsorption process operation unit are the mechanism and the reaction rate. Solute uptake rate determines the residence time required for completing the adsorption reaction and can be enumerated from kinetic analysis. Numerous attempts were made in formulating a general expression to describe the kinetics of adsorption on solid surfaces for the liquid–solid adsorption system (Ho 2004). The adsorption rate is an important factor for a better choice of material to be used as an adsorbent; where the adsorbent should have a large adsorption capacity and a fast adsorption rate. Most of adsorption studies used pseudo-first-order and pseudo-second-order models to study the adsorption kinetics (Salleh et al. 2011).

Lagergren (1898) presented a first-order rate equation to describe the kinetic process of liquid–solid phase adsorption of oxalic acid and malonic acid onto charcoal, which is believed to be the earliest model pertaining to the adsorption rate based on the adsorption capacity (Qiu et al. 2009). To distinguish kinetic equations based on adsorption capacity from solution concentration, Lagergren's first-order rate equation has been called pseudo-first-order (Ho and McKay 1998). The pseudo-first-order equation is generally expressed as (Lagergren 1898),

$$\log(q_e - q_t) = \log(q_e) - \frac{k_1}{2.303}t, \quad (1)$$

where q_e and q_t are the adsorption capacity at equilibrium and at time t , respectively (mg g⁻¹), k_1 is the rate constant of pseudo-first-order adsorption (L min⁻¹). The values of $\log(q_e - q_t)$ were linearly correlated with t . The plot of $\log(q_e - q_t)$ versus t should give a linear relationship from which k_1 and q_e can be determined from the slope and intercept of the plot, respectively.

The second-order Lagergren equation was given by (Ho and McKay 1999). It is expressed as

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}(t), \quad (2)$$

where k_2 is the rate constant of pseudo-second-order adsorption (g mg⁻¹ min⁻¹). The plot of (t/q_t) and t should give a linear relationship from which q_e and k_2 can be determined from the slope and intercept of the plot, respectively.

In 1934, the kinetic law of chemisorptions was established though the work of Zeldowitsch. The rate of adsorption of carbon monoxide on manganese dioxide decreasing exponentially with an increase in the amount of gas adsorbed was described by Zeldowitsch (1934). It has commonly been called the Elovich equation in the following years:

$$\frac{dq_t}{dt} = \alpha e^{-\beta q_t}, \quad (3)$$

where α is the initial adsorption rate (mg g min⁻¹) and β is the desorption constant (mg g⁻¹ min) during any experiment. To simplify the Elovich equation, Chien and Clayton (1980) assumed $\alpha\beta \gg t$ and by applying the boundary conditions $q_t = 0$ at $t = 0$ and $q_t = q_t$ at $t = t$ Eq. (3) becomes:

$$q = \frac{\ln(\beta\alpha)}{\beta} + \frac{\ln t}{\beta}(t). \quad (4)$$

If the adsorption fits the Elovich model, a plot of q_t versus $\ln(t)$ should yield a linear relationship with a slope of $(1/\beta)$ and an intercept of $(1/\beta) \ln(\alpha\beta)$.

Natarajan and Khalaf (Kannan and Vanangamudi 1991) developed a relation between the initial concentration and the concentration at any time t . The equation is given as

$$\log\left(\frac{C_0}{C_t}\right) = \frac{k}{2.303}(t), \quad (5)$$

where C_0 and C_t are the concentrations of dye solution (in mg L⁻¹) at time zero (initial concentration) and at time t , respectively.

Bhattacharya and Venkobachar (1984) develop a relation between adsorbate uptake on to the adsorbent and time t . The equation is given as

$$\log [1 - U(T)] = -\frac{k_B}{2.303} (t), \quad (6)$$

where

$$U(T) = \frac{C_0 - C_t}{C_0 - C_e} (t), \quad (7)$$

where C_e is the equilibrium dye concentration (mg L^{-1}), C_0 and C_t are the concentrations of dye (mg L^{-1}) at time zero (initial concentration) and at time t , respectively; k_B is the first-order adsorption rate constant (min^{-1}).

The power function kinetic equation (Dalal 1974) develops a relation between dye uptake on to the adsorbent and time t , the equation is given as

$$\log q_t = \log a + b \log t. \quad (8)$$

A linear plot between $\log q_t$ versus $\log t$ gives the constants of power functions a and b . The constant a represents the initial rate and refers to the y intercept of the straight line plot of $\log q_t$ vs. $\log t$. The constant b is the slope of the plot, and is the rate constant of the reaction. It is generally known that a typical liquid/solid adsorption involves film diffusion, intraparticle diffusion, and mass action. For physical adsorption, mass action is a very rapid process and can be negligible for kinetic study. Thus, the kinetic process of adsorption is always controlled by liquid film diffusion or intraparticle diffusion, i.e., one of the processes should be the rate-limiting step (Meng 2005). Therefore, adsorption diffusion models are mainly constructed to describe the process of film diffusion and/or intraparticle diffusion (Qiu et al. 2009). The mechanism of adsorption of a sorbate on a sorbent follows a series of steps. The slowest of these steps controls the overall rate of the process. Generally, pore and intraparticle diffusion are often rate limiting in a batch reactor while, for a continuous flow system, film diffusion is more likely the rate-limiting step (Goswami and Ghosh 2005). This possibility was tested in terms of a graphical relationship between q_t and the square root of time, $t^{1/2}$, according to the intraparticle diffusion model proposed by Weber and Morris (1963). The intraparticle diffusion model is expressed as

$$q_t = k_{id}t^{1/2} + C, \quad (9)$$

where C is the intercept and k_{id} is the intraparticle diffusion rate constant ($\text{mg g}^{-1} \text{min}^{0.5}$), which can be evaluated from the slope of the linear plot of q_t versus $t^{1/2}$.

The film diffusion mass transfer rate equation presented by Boyd et al. (1947) is

$$\ln(1 - F) = -R^1 t, \quad (10)$$

where

$$F = \frac{q_t}{q_e} \quad (11)$$

$$R^1 = \frac{3D_e^1}{k^1 r_0 \Delta r_0}, \quad (12)$$

where R^1 (min^{-1}) is liquid film diffusion constant, D_e^1 (cm^2/min) is effective liquid film diffusion coefficient, r_0 (cm) is radius of adsorbent beads, Δr_0 (cm) is the thickness of liquid film, and k^1 is equilibrium constant of adsorption. A plot of $\ln(1 - F) \sim t$ should be a straight line with a slope $-R^1$ if the film diffusion is the rate-limiting step.

Adsorption isotherms

Equilibrium isotherm is described by a sorption isotherm, characterized by certain constants whose values express the surface properties and affinity of the sorbent sorption equilibrium is established when the concentration of sorbate in the bulk solution is in dynamic balance with that at the sorbent interface (Oladoja et al. 2008). The analysis of equilibrium adsorption data by fitting them to different isotherm models is an important step to find the suitable model that can be used for design purposes (Haghserehs and Lu 1998). The adsorption isotherm is important for the description of how the adsorbate will interact with the adsorbent and gives an idea of the adsorption capacity of the adsorbent. The surface phase may be considered as a monolayer or multilayer (Salleh et al. 2011). The two well-known adsorption isotherm models are Langmuir and Freundlich isotherms. The Langmuir isotherm assumes monolayer adsorption onto a surface containing a finite number of adsorption sites of uniform strategies of adsorption with no transmigration of adsorbate in the plane of surface (Fytianos et al. 2000). While the Freundlich isotherm model assumes heterogeneous surface energies, in which the energy term in the Langmuir equation varies as a function of the surface coverage (Weber and Chakkravorti 1974); the Langmuir isotherm is developed by assuming that a fixed number of adsorption sites are available, and that the adsorption is reversible. The Langmuir isotherm may be used when the adsorbent surface is homogeneous. The Langmuir isotherm is expressed as (Langmuir 1915).

$$\frac{1}{X/M} = \frac{1}{q_{\max}} + \frac{1}{q_{\max} b C_e}, \quad (13)$$

where b is the constant that increases with increasing molecular size, q_{\max} is the amount adsorbed to form a complete monolayer on the surface (mg g^{-1}), X is the weight of substance adsorbed (mg), M is the weight of adsorbent (g), C_e is the concentration remaining in solution (mg L^{-1}).

The essential features of the Langmuir isotherm may be expressed in terms of equilibrium parameter R_L , which is a dimensionless constant referred to as separation factor or equilibrium parameter (Weber and Chakkravorti 1974):

$$R_L = \frac{1}{1 + bC_0}. \quad (14)$$

The value of R_L indicates the type of the isotherm to be either unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$) or irreversible ($R_L = 0$).

The Freundlich equation is an empirical equation that is very useful as it accurately describes much adsorption data (Freundlich 1906). The Freundlich isotherm is expressed as

$$\log q_e = \log K + \frac{1}{n} * \log C \quad (15)$$

where, K , n are constants depending on temperature.

The Harkins and Jura (1944) adsorption isotherm can be expressed as:

$$\frac{1}{q_e^2} = \frac{B}{A} - \frac{\log C_e}{A}, \quad (16)$$

where B and A are the isotherm constants. The isotherm equation accounts for multilayer adsorption and can be explained by the existence of a heterogeneous pore distribution (Venkatesh et al. 2010). The plot between $\log C_e$ and $1/q_e^2$ gives a straight line with slope of $1/A$ and intercept of B/A .

The Halsey adsorption isotherm (Halsey 1948) can be given as:

$$\ln C_e = \frac{\ln k}{n_H} - \frac{\ln C_e}{n_H}, \quad (17)$$

where n_H and k are Halsey isotherm constants. This equation is suitable for multilayer adsorption and the fitting of the experimental data to this equation attest to the heteroporous nature of the adsorbent. The Halsey isotherm parameters are obtained from the plot of $\ln q_e$ versus $\ln C_e$.

The Temkin isotherm assumes that the fall in the heat of adsorption is linear rather than logarithmic as stated in Freundlich expression (Teles de Vasconcelos and Gonzalez Beca 1993). The heat of sorption of all the molecules in the layer would decrease linearly with coverage due to sorbate/sorbent interactions. The Temkin isotherm is applied in the following form (Wang and Qin 2005):

$$q_e = B_T (\ln A_T + \ln C_e) \quad (18)$$

T is the absolute temperature in Kelvin and R is the universal gas constant, $8.314 \text{ J mol}^{-1} \text{ K}^{-1}$. The constant B_T is related to the heat of adsorption, A_T is the equilibrium binding constant (L g^{-1}) corresponding to the maximum binding energy. The slope and intercept from a plot of q_e versus $\ln C_e$ determines the isotherm constants A_T and B_T .

The adsorption capacity for cationic dye adsorption is higher than anionic dye adsorption on the same adsorbent (Salleh et al. 2011). Since the carboxyl group is one of the major functional groups in agricultural wastes, it will have an effect on the adsorption capacity according to the dye class. The carboxyl group bears a negative charge, and therefore it is the major functional group in the adsorption of cationic dyes. On other hand, it will inhibit the adsorption of anionic dyes (Gong et al. 2005).

Factors affecting adsorption

Effect of initial dye concentration

The initial dye concentration of an effluent is important since a given mass of sorbent material can only adsorb a fixed amount of dye (Benaïssa 2005). The effect of initial dye concentration can be carried out by preparing adsorbent–adsorbate solution with fixed adsorbent dose and different initial dye concentration for different time intervals and shaken until equilibrium (Salleh et al. 2011). The effect of the initial of dye concentration factor depends on the immediate relation between the concentration of the dye and the available binding sites on an adsorbent surface (Salleh et al. 2011). Normally the dye removal will decrease with increase in initial dye concentration. This is because for a given mass of adsorbent; the amount of dye it can adsorb is fixed. The higher the concentration of the dye, the smaller the volume it can remove (Low and Lee 1990). At a low concentration there will be unoccupied active sites on the adsorbent surface, and when the initial dye concentration increases, the active sites required for adsorption of the dye molecules will be lacking (Kannan and Sundaram 2001). Low and Lee (1990) also reported that the time taken to reach equilibrium increased with increasing concentration. But the actual amount of dye adsorbed per unit mass of adsorbent increased with increase in dye concentration. This may be due to the high driving force for mass transfer at a high initial dye concentration (Bulut and Aydin 2006). Bello et al. (2010) reported that the adsorption capacity of treated sawdust at equilibrium increases from 67.5 to 410.2 mg g^{-1} with an increase in the initial dye concentration from 100 to 500 mg L^{-1} . But Garg et al. (2004) reported that dye removal by Granular activated carbon was 100% at all the studied dye concentrations. Adsorption and initial dye concentration correlation was exponential for formaldehyde-treated *Prosopis cineraria* sawdust and sulphuric acid-treated *Prosopis cineraria* sawdust as in Fig. 1. Thus the adsorption is highly dependent on the initial concentration of dyes. The capacity of the adsorbent material gets exhausted sharply with increase in initial dye

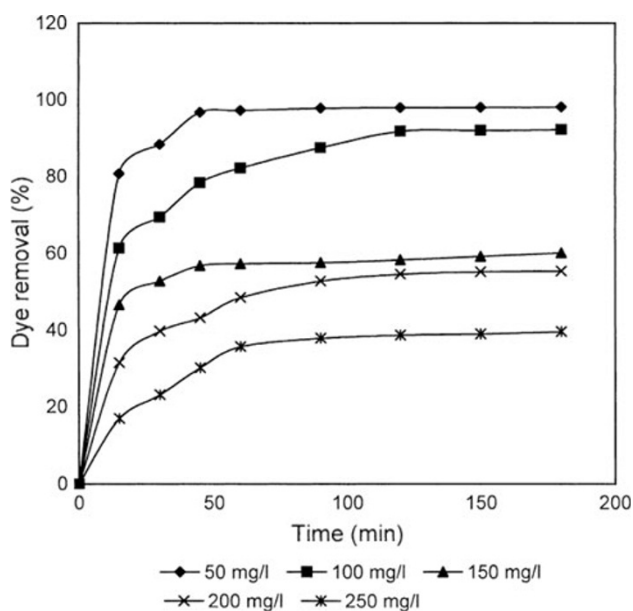


Fig. 1 Effect of initial dye concentration on the adsorption of Malachite green on formaldehyde-treated *Prosopis cineraria* sawdust (Garg et al. 2004)

concentration. This may be probably as a result of the fact that for a fixed adsorbent dose, the total available adsorption sites remain invariable for all the concentrations checked. With increasing concentration the available adsorption sites become fewer and hence the percent removal of dye is dependent upon the initial concentration.

Effect of adsorbent dosage

The effect of adsorbent dosage on the adsorption process can be carried out by preparing adsorbent–adsorbate solution with different amount of adsorbents added to fixed initial dye concentration and shaken together until equilibrium time (Salleh et al. 2011). Generally, the percentage of dye removal increases with increasing adsorbent dosage. Initially the rate of increase in the percent dye removal has been found to be rapid which slowed down as the dose increased. This phenomenon can be explained, based on the fact that at lower adsorbent dose the adsorbate (dye) is more easily accessible and because of this, removal per unit weight of adsorbent is higher. With rise in adsorbent dose, there is less commensurate increase in adsorption, resulting from many sites remaining unsaturated during the adsorption (Jain et al. 2003). But after a certain dosage the increase in removal efficiency is insignificant with respect to increase in dose. This is due to the fact that, at higher adsorbent concentration there is a very fast superficial adsorption onto the adsorbent surface that produces a lower solute concentration in the solution than when adsorbent dose is lower. Thus, with increasing adsorbent dose, the

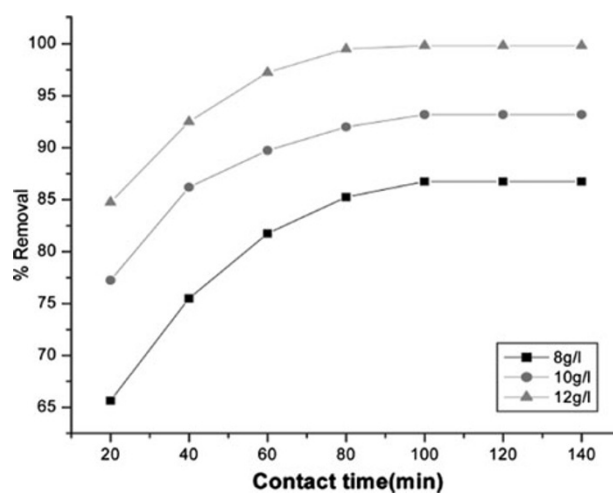


Fig. 2 Effect of adsorbent dose on the percent removal of methylene blue on rice husk activated carbon (Sharma and Uma 2010)

amount of dye adsorbed per unit mass of adsorbent is reduced, thus causing a decrease in q_e value (Han et al. 2007). Sharma and Uma (2010) carried out an experiment by taking different adsorbent doses (0.40–0.60 g) in 50 mL of dye solution in order to find the effect of different doses of rice husk activated carbon on the removal of Methylene blue. They reported that the removal increased from 86.75 to 99.83 % with increasing adsorbent dose from 0.40 to 0.60 g as in Fig. 2

Effect of contact time

The effect of contact time on adsorption of dye can be carried out by preparing adsorbent–adsorbate solution with fixed adsorbent dose and initial dye concentration for different time intervals and shaken until equilibrium. Generally the rate of removal of dye increases with an increase in contact time to a certain extent. Further increase in contact time does not increase the uptake due to deposition of dyes on the available adsorption site on adsorbent material (Ansari and Mosayebzadeh 2010). At this point, the amount of the dye desorbing from the adsorbent is in a state of dynamic equilibrium with the amount of the dye being adsorbed onto the adsorbent. The time required to attain this state of equilibrium is termed the equilibrium time, and the amount of dye adsorbed at the equilibrium time reflects the maximum adsorption capacity of the adsorbent under those operating conditions (Bello et al. 2010).

Effect of pH

pH is a measure of acidity ($\text{pH} < 7$) or basicity ($\text{pH} > 7$) of an aqueous solution. The pH factor is very important in the adsorption process especially for dye adsorption. The pH of

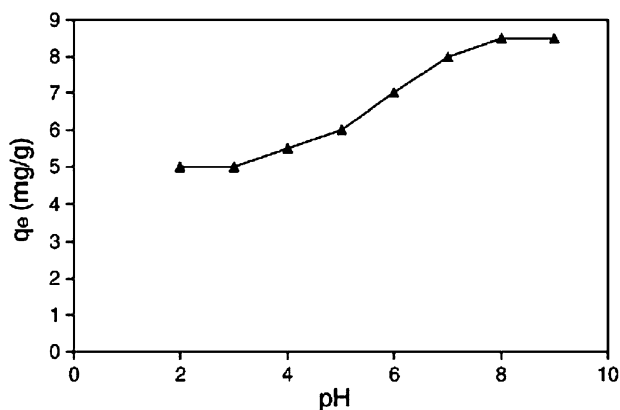


Fig. 3 Effect of pH onto crystal violet biosorption (Kumar and Ahmad 2011)

a medium will control the magnitude of electrostatic charges which are imparted by the ionized dye molecules. As a result, the rate of adsorption will vary with the pH of an aqueous medium (Önal et al. 2006). The pH of initial dye solution can be adjusted by the addition of dilute 0.1 N HCl or 0.1 N NaOH. Generally, at low pH solution, the percentage of dye removal will decrease for cationic dye adsorption, while for anionic dyes the percentage of dye removal will increase. In contrast, at a high pH solution the percentage of dye removal will increase for cationic dye adsorption and decrease for anionic dye adsorption (Salleh et al. 2011). For cationic dyes, lower adsorption of dye at acidic pH (as in Fig. 3) is probably due to the presence of excess H^+ ions competing with the cation groups on the dye for adsorption sites. As surface charge density decreases with an increase in the solution pH, the electrostatic repulsion between the positively charged dye and the surface of the adsorbent is lowered, which may result in an increase in the extent of adsorption (Wang et al. 2006). With an increase in the solution pH, the electrostatic repulsion between the positively charged cationic dyes and the surface of adsorbent is lowered and consequently the removal efficiency is increased (Ansari and Mosayebzadeh 2010). Garg et al. (2004) reported that the dye adsorption by coconut-based carbon was unaffected by pH changes in the range of 2–10. Sulphuric acid-treated sawdust had maximum dye adsorption (96 %) over the pH range of 6–10 which decreased to 70 % at pH of 2.0. By formaldehyde-treated sawdust, dye removal was minimum (26.8 %) at the pH of 2.0, which increased to 99 % at pH 10. Many researchers studied the isoelectric point (pH_{IEP}) of adsorbents that prepared from agricultural solid wastes in order to better understand of adsorption mechanism. Cationic dye adsorption is favored at $pH > pH_{pzc}$, due to the presence of functional groups such as OH^- , COO^- groups. Anionic dye adsorption is favored at $pH < pH_{pzc}$ where the surface becomes positively charged (Radovic

et al. 1997; Savova et al. 2003). At high pH solution, the positive charge at the solution interface decreases and the adsorbent surface appears negatively charged (Özcan et al. 2007). As a result, the cationic dye adsorption increases and anionic dye adsorption shows a decrease (Salleh et al. 2011). Zawani et al. (2009) reported that adsorption of Remazol black 5 on the palm kernel shell activated carbon has optimum pH of 2 with maximum uptake at 27.44 mg g^{-1} , and then, the uptake was declined significantly. Solution pH influences both the carbon surface dye binding sites and the dye chemistry in water. At lower pH values, the carbon will have a net positive charge. Higher uptakes obtained at lower pH may be due to the electrostatic attractions between negatively charged functional groups located on the reactive dye and positively charged adsorbent surface. Hydrogen ion also acts as a bridging ligand between the adsorbent wall and the dye molecule (Aksu and Tezer 2005).

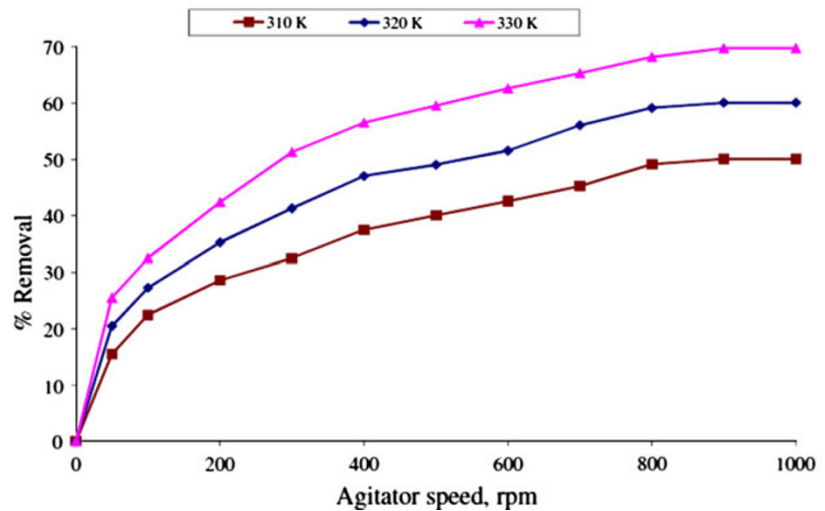
Effect of agitation speed

In the batch adsorption systems, agitation speed plays a significant role in affecting the external boundary film and the distribution of the solute in the bulk solution (Crini et al. 2007). The effect of agitation speed on adsorption of dye can be carried out by changing the speed of rotation of adsorbate–adsorbent solution and samples withdrawn at different intervals, while keeping other parameters constant. Generally removal of dyes increases with agitation speed. The mechanism of adsorbate removal involved four steps: (1) migration of adsorbate molecules from the bulk solution to the surface of the adsorbent; (2) diffusion through the boundary layer to the surface of adsorbent; (3) adsorption at a site; and (4) intraparticle diffusion into the interior of the adsorbent. Increasing agitation speed decreases the boundary layer resistance of the transfer of adsorbate molecules from the bulk solution to the adsorbent surface. Due to this, the adsorbate is forced towards the adsorbent surface and it leads to an increase in the diffusion of adsorbate into the surface of the adsorbent (Mane et al. 2005). Patel and Vashi (2010) reported that as agitation speed increases, percentage of crystal violet adsorption significantly also increases up to 15.5–50.0, 20.5–60.0 and 25.5–69.7 % at 50–900 rpm, respectively, with different temperatures (310, 320 and 330 K), but then gradually approaches a constant value after 900 rpm as in Fig. 4.

Effect of ionic strength

The wastewater containing dye has commonly higher salt concentration, and effects of ionic strength are of some importance in the study of dye adsorption onto adsorbents

Fig. 4 Effect of agitation speed with various temperatures (Patel and Vashi 2010)



(Han et al. 2007). The effect of ionic strength on adsorption can be carried out by adding different doses of salts (normally NaCl) to the adsorbent–adsorbate solution and shaking up to equilibrium time. Theoretically, when the electrostatic forces between the adsorbent surface and adsorbate ions were attractive, as in this system, an increase in ionic strength will decrease the adsorption capacity. Conversely, when the electrostatic attraction is repulsive, an increase in ionic strength will increase adsorption (Newcombe and Drikas 1997; Alberghina et al. 2000; Germa'n-Heins and Flury 2000). Wang et al. (2008) reported that the extent of adsorption is sensitive to changes in concentration of supporting electrolyte (chloride sodium) indicates that electrostatic attraction may be a significant component of the overall adsorption in this system. The electrostatic free energy change, ΔG contributes to the total free energy change of adsorption, ΔG and depends on the ionic strength of solution. When the ionic strength was increased, the electrical double layer surrounding the adsorbent surface was compressed, which would lead to a decrease in the electrostatic potential. This indirectly resulted in a reduction in the coulombic free energy, and a decrease in basic dye ions adsorption. Arivoli et al. (2009) reported that the low concentration NaCl solution had little influence on the adsorption capacity. When the concentration of NaCl increases, the ionic strength is raised. At higher ionic strength, the adsorption of Malachite green will be higher owing to the partial neutralization of the positive charge on the carbon surface and a consequent compression of the electrical double layer by the Cl^- anion. The chloride ion also enhances adsorption of Malachite green ion by pairing their charges, and hence reducing the repulsion between the Malachite green molecules adsorbed on the surface. This initiates carbon to adsorb more positive Malachite green ions (Arivoli 2007; Guo et al. 2005). Wang et al. (2008) examined three

competitive modes (competitive mode, uncompetitive mode and noncompetitive mode) to quantify the ionic strength effects. According to the competitive mode, the sodium ions interact directly with the active sites on the adsorbent surface, competing with basic dye for the available sites. For the competitive isotherm, the intercept term of the linearized Langmuir isotherms remains constant. For uncompetitive inhibition, the sodium ions do not react with the active sites on the adsorbent surface directly, but instead react with the adsorbent surface–dye complexes. In this case, the linearized Langmuir adsorption isotherms remain parallel to each other. Noncompetitive mode mechanism is a combination of the above two modes. Both the sodium ions and basic dye adsorb independently at different sites on the adsorbent surface. In other words, sodium ions react with the adsorbent surface sites and dye molecules adsorbent surface complexes, while dye molecules react with the adsorbent surface active sites and sodium ions–adsorbent surface complexes. In this case, the linearized Langmuir isotherms converge at x axis.

Effect of temperature

A study of the temperature dependence of adsorption reactions gives valuable knowledge about the enthalpy and entropy changes during adsorption (Alkan and Doğan 2003). Temperature is an indicator for the adsorption nature whether it is an exothermic or endothermic process (Salleh et al. 2011). If the adsorption capacity increases with increasing temperature then the adsorption is an endothermic process. This may be due to increasing the mobility of the dye molecules and an increase in the number of active sites for the adsorption with increasing temperature (Senthilkumaar et al. 2006). Senthilkumaar et al. (2006) reported that the enhancement of adsorption

capacity of the activated carbon at higher temperatures is attributed to the enlargement of pore size and activation of the adsorbent surface. During the adsorption there, some structural changes in the dyes and the adsorbent occur (Hema and Arivoli 2007). The adsorbed water molecules, which are displaced by the adsorbate species, gain more translational entropy than it is lost by the adsorbate molecules, thus allowing the prevalence of randomness in the system. Increasing temperature may decrease the adsorptive forces between the dye species and the active sites on the adsorbent surface as a result of decreasing adsorption capacity (Ofomaja and Ho 2007).

Mechanism of adsorption

Mathematical treatment given by Reichenberg (1953) and Boyd et al. (1947) is used to distinguish between the particle, film diffusion, and mass-action-controlled mechanisms of exchange have laid the foundations of sorption/ion-exchange kinetics (Singh et al. 2003). Usually, external transport is the rate-limiting step in systems, which have (a) poor mixing (b) dilute concentration of adsorbate (c) small particle size and (d) high affinity of the adsorbate for adsorbent. In contrast, the intraparticle step limits the overall transfer for those systems that have (a) high concentration of adsorbate; (b) good mixing; (c) large particle size of adsorbent; and (d) low affinity of the adsorbate for adsorbent (Singh et al. 2003). It is now well established that during the adsorption of a solid chemical substance over a porous adsorbent following three consecutive steps taking place (Gupta et al. 2004).

1. Transport of the adsorbate ions to the external surface of the adsorbent (film diffusion).
2. Transport of the adsorbate particles within the pores of adsorbent, excluding the small amount of adsorption occurring at the external surface of the adsorbent (particle diffusion).
3. Adsorption of the adsorbate ions on the interior surface of the adsorbent.

If external transport < internal transport, particle diffusion will take place and while external transport > internal transport, adsorption is governed by film diffusion process. If external transport \approx internal transport, the transport of the adsorbate ions to the boundary may not be possible with a significant rate because of which there is a possibility of formation of a liquid film around the solid adsorbent particles (Gupta et al. 2004).

The quantitative treatment of the sorption dynamics is in accordance with the observations of Reichenberg (1953), as given by the following equation.

$$F = \frac{q_t}{q_e} = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp(-n^2)Bt \quad (19)$$

where, F is the fractional attainment of equilibrium at time t and n is Freundlich constant of the adsorbate.

$$B = \frac{\pi^2 D_i}{r_0^2} \quad (20)$$

where, D_i is the effective diffusion coefficient of adsorbate in the adsorbent phase and r_0 is the radius of adsorbent particles assumed to be spherical. The Bt values were obtained for each observed value of F , from Reichenberg's table (1953). The linearity test of Bt versus time plots was employed to distinguish between the film diffusion- and particle diffusion-controlled adsorption. If the plot of Bt versus time (having slope B) is a straight line passing through the origin, then the adsorption rate is governed by the particle diffusion mechanism; otherwise, it is governed by film diffusion (Singh et al. 2003). Gupta et al. (2004), applied Reichenberg analysis for removal of Malachite green and reported that film diffusion and particle diffusion mechanisms as the rate-controlling step at lower ($<5 \times 10^{-5}$ M) and higher ($\geq 5 \times 10^{-5}$ M) concentrations, respectively.

Kumar and Ahmad (2011) reported the removal mechanism of CV on treated ginger waste (TGW). There were many factors that may influence the biosorption behavior, such as dye structure and size, biosorbent surface properties, steric effect and hydrogen bonding, van der Waals forces, etc. The structure of the CV molecule was a prominent factor for its biosorption. The complexation between CV and TGW can take place through the weak and strong forces. The weak interactions occur due to the van der Waals forces while the strong interactions occur due to (1) hydrogen bonding interaction between the nitrogen containing amine groups of CV and TGW surface (2) hydrophobic–hydrophobic interactions between the hydrophobic parts of CV and TGW (3) electrostatic interaction between the cationic dye [due to the presence of $+N(CH_3)_2$ group] and negatively charged TGW surface in basic medium. A proposed mechanism for the biosorption of the CV onto TGW is shown in Fig. 5. Sivakumar and Palanisamy (2010) reported a four-stage adsorption mechanism for removal of Acid Blue 92, Basic Red 29, Reactive Red 4 and Direct Blue 53 by precursor wood (Fig. 6).

Modifications of adsorbents

In order to increase the adsorption capacity of the adsorbent, researchers have followed different activation methods and they usually used the Langmuir isotherm to

indicate the effectiveness of the activation process. Activation methods involve physical activation such as carbonization of material and chemical activation such as using chemical activating agents (Salleh et al. 2011). Abdelwahab et al. (2005) treated rice husk with citric acid for treating synthetic Direct F. Scarlet (Direct Red 23) containing industrial wastewater. The authors reported that

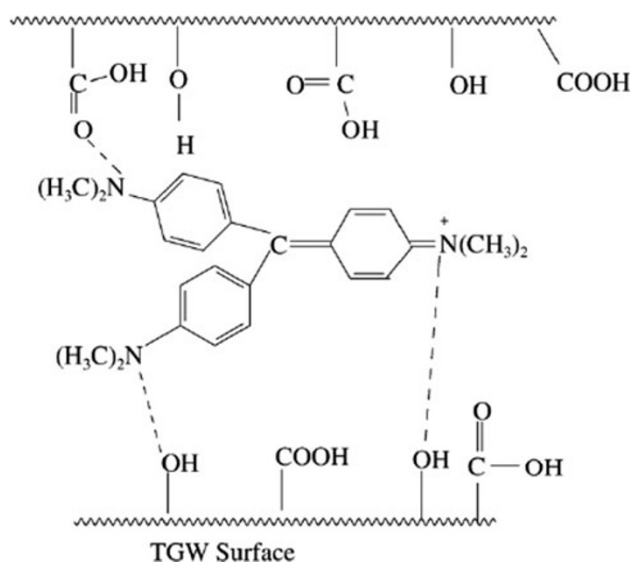
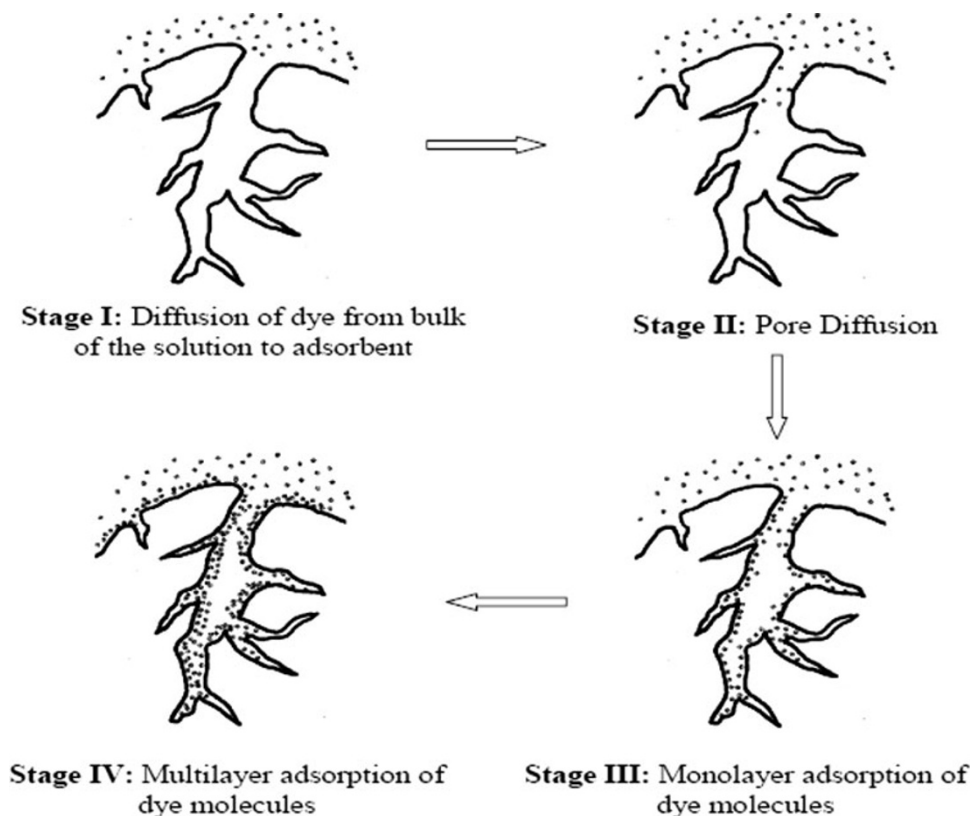


Fig. 5 Proposed mechanism for the biosorption of CV onto TGW (Kumar and Ahmad 2011)

Fig. 6 Proposed four-stage mechanism of dye adsorption (Sivakumar and Palanisamy 2010)

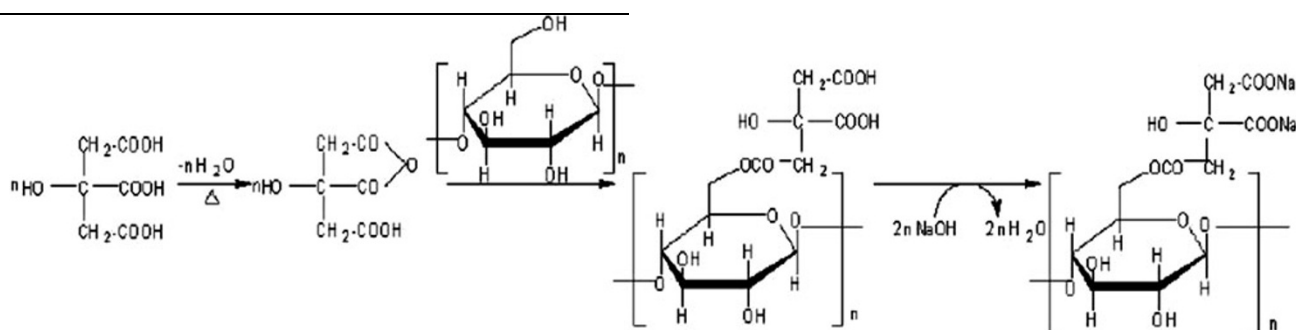


the activated rice husk possesses the highest sorption capacity, especially for 2.5 and 5 g L⁻¹ of sorbent. The removal curves are single, smooth and continuous leading to saturation. Activated rice husk is observed to have higher adsorption capacity than the untreated rice husk in the removal of Direct Red-23. Formaldehyde-treated sawdust was used by Bello et al. (2010) for removing Methylene blue from aqueous solution. Garg et al. (2004) treated *Prosopis cineraria* tree saw dust with formaldehyde and sulphuric acid for removing Malachite green. The authors reported that the optimum pH for dye removal by formaldehyde-treated *Prosopis cineraria* sawdust and sulphuric acid-treated *Prosopis cineraria* sawdust was 6–10. Higher dye removal by sulphuric acid-treated *Prosopis cineraria* sawdust and formaldehyde-treated *Prosopis cineraria* sawdust was possible provided the initial dye concentration was low in solution. The adsorption capacity of formaldehyde-treated *Prosopis cineraria* sawdust is less than that of sulphuric acid-treated *P. cineraria* sawdust. Low and Lee (1990) treated coconut husk with a mixture of formaldehyde/HCl for removing Methylene blue from aqueous solution. Sharma and Uma (2010) prepared activated carbon by pyrolyzing rice husk, in the presence of ZnCl₂. They reported that the activated carbon displayed both microporous and mesoporous nature with a significant surface area of 180.50 m² g⁻¹. Water hyacinth roots were treated with 2 N HCl by Rajamohan (2009) for removing

Congo red. Kumar and Ahmad (2011) TGW with H_2SO_4 and $ZnCl_2$ for removing crystal violet from aqueous solution. Wood sawdust obtained from walnut and its polypyrrole coated form for the removal of Methylene blue from aqueous solutions was used by Ansari and Mosayezadeh (2010). They reported that sawdust and its polypyrrole coated form have maximum monolayer adsorption capacity of 19.41 and 34.36 mg g^{-1} , respectively. Hema and Arivoli (2007) used carbonized leaves of *Pandanus* with concentrated sulphuric acid in the weight ratio of 1:1 (W/V) for removing Congo red, Malachite green and Rhodamine B.

Ferric chloride orthophosphoric acid treated > raw > trioxonitrate acid treated > potassium carbonate treated

Arivoli et al. (2009) prepared activated carbon from *Borassus* bark by sulphuric acid activation to remove Malachite green in aqueous solution. The kinetic and thermodynamic behaviors of cationic dyes (Methylene blue and crystal violet) adsorption onto citric acid esterifying wheat straw from aqueous solution were investigated by Gong et al. (2005). The thermochemical esterification of wheat straw can be schematically expressed as:



Ong et al. (2010) compared the efficiency of base-treated rice hull, hydrochloric acid-treated rice hull, quaternized rice hull, citric acid-treated rice hull, nitrilotriacetic acid-treated rice hull and ethylenediamine-modified rice hull for removing cationic dye BB3 and anionic dye RO16 from aqueous solution. Activated carbons were prepared from coconut shell, coir pith and rice husk using 1 M ferric chloride, 1 M trioxonitrate (V) acid, 1 M orthophosphoric acid and 1 M potassium carbonate as the chemical activating reagents for removing blue dye by Adekola and Adegoke (2005). They reported that ferric chloride-activated carbons produced from coconut coir pith are better adsorbents for blue dye than those prepared from rice husk. For coconut coir pith; the trend of their adsorption capacity follows the order:

Ferric chloride orthophosphoric acid treated > potassium carbonate treated > raw coir pith.

For rice husk, the sample activated with ferric chloride solution gave the highest adsorption capacity while the purified carbon gave the lowest value as below:

Ferric chloride orthophosphoric acid treated > potassium carbonate treated = trioxonitrate acid treated > raw

For coconut shell; the trend of their adsorption capacity is:

Desorption study

Desorption studies help to elucidate the nature of adsorption and recycling of the spent adsorbent and the dye. If the adsorbed dyes can be desorbed using neutral pH water, then the attachment of the dye by the adsorbent will be weak bonds. If sulphuric acid or alkaline water desorbs the dye then the adsorption will be through ion-exchange. If an organic acid, such as acetic acid can desorb the dye, then the dye has been held by the adsorbent through chemisorption (Arivoli et al. 2009). Desorption process usually done by mixing a suitable solvent with the dye-saturated substrate and shaken together for fixed time, until the dye extract on the solvent and then using filtration to separate the adsorbent. The dye-solvent mixture dried at high temperature to evaporate the solvent. The desorbed dye then determine in spectrophotometer (Robinson et al. 2002a). Mahmoodi et al. (2011) studied the desorption of three textile dyes from pinecone and they concluded that the maximum desorption for Acid black 26, Acid green 25 and Acid blue 7 was 93.16, 26.97 and 98 %, respectively. Bello et al. (2010) reported that effect of various reagents used for desorption studies shows that hydrochloric acid is a better reagent for desorption, because we could get more than 90 % removal of adsorbed dyes. Also, the adsorbent exhibits a stable structure towards this reagent.

The desorption of dyes by mineral acids indicates that the dyes are adsorbed onto treated sawdust by physisorption. Similar results were reported by Arivoli et al. (2009). Somasekhara Reddy (2006) reported that percent desorption of Congo red dye from tamarind fruit shell increases with increase in pH of solution. Robinson et al. (2002a) studied desorption of Cibacron red from corncob using mixture of methanol, chloroform and water. They found that the maximum value of desorption was 93 %. Kumar and Ahmad (2011) studied the desorption of crystal violet dye from ginger waste and they found that NaOH and H₂O did not showed any desorption while acetic acid desorbed about 35–50 % of dye. Ansari and Mosayebzadeh (2010) used different chemicals for the recovery of Methylene blue.

Conclusion

In this review, a wide range of agricultural waste materials, as low-cost adsorbent has been presented. The use of these low-cost biosorbents is recommended since they are relatively cheap or of no cost, easily available, renewable and show highly affinity for dyes. The process of biosorption requires further investigation in the direction of modeling, regeneration of biosorbent and immobilization of the waste material for enhanced efficiency and recovery. Further more interest should be concentrated by the researchers to predict the performance of the adsorption process for dye removal from real industrial effluents.

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