

# Removal of Dyes by Using Low Cost Adsorbents Agricultural Wastes and Sand

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## Abstract

Dyes removal from wastewater has been a matter of concern, both in the aesthetic sense and health point of view. Dyes 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. The review evaluates different agricultural waste materials and different types of sands 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. Sand is mixed with cement and water to make concrete, used in the manufacture of brick, glass and other materials, and it can also be used as a medium for the filtration of water. Sand has been used as an adsorbent because of its enormous availability in the local environment. This review reveals that further research must be conducted to bring to the fore the expansive laboratory, industrial and environmental usage of sand materials as dye adsorbents. Consequently, the usage of different types of sand in the field of adsorption science represents a viable and powerful tool, resulting into the superior improvement in pollution control and environmental preservation.

**Keywords: Adsorption, Dyes, low-cost adsorbents, sand, Wastewater treatment.**

## 1. 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 7×100000 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 photo synthesis 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 nonionic (dispersive dyes). Many treatment processes have been applied for the removal of dye from wastewater such as: Fenton process. (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/TiO<sub>2</sub> (Sohrabi and Ghavami 2008), sonochemical 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- Grabowsk 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, regeneration 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). Organic dyes are an integral part of many industrial effluents which demand an appropriate method to dispose of them. Commonly suggested methods include biodegradation, photo-catalytic, photolytic and advanced oxidative degradation of these solutions. 3–7 Considerable interest has recently been focused on using the adsorption technique for the removal of some dyes from solutions on various adsorbent surfaces such as clays, 8–9 fly ash, 10–11 peat, 12 activated carbon, 13–14 polymers 15–16 and alumina. 17–18 The process is known to be simple and efficiently treat dyes in concentrated form. Adsorption is a major industrial separation technique for the purification of effluent media. It is a mass transfer operation through which a solid material can selectively remove dissolved components from an aqueous solution by attracting the dissolved solute to its surface. Therefore, it involves the interphase accumulation of concentration of substances at a surface or at the inter phase. This separation technique finds wide application in removal of dye from aqueous media. In particular, it finds application in textile, leather, dyeing, cosmetics, plastics, food and paper industries where water recovery is essential. In order to achieve and sustain this efficient recovery of desired water quality, a careful selection of adsorbent is paramount. 1, 29, 30 However, most adsorbent materials in Nigeria are imported from other countries despite of the abundance of raw materials in Nigeria for the production of the required quantity of adsorbents for local industries. 30 This

situation is a concern and calls for serious efforts to search for adsorbents sourced from local raw

## 2. Removal of dyes by low-cost sorbents

Low cost adsorbents Agricultural Wastes and various types of Sands are used for the Removal of dyes.

### 2.1. Agricultural Wastes (Adsorbents)

**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<sup>-1</sup> 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<sup>-1</sup>.

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

materials such as plantain peels, animal hairs, corn cobs, coal, and animal bones, etc.

Methylene blue on jack fruit peel was found to be 285.713 mg g<sup>-1</sup>.

**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<sup>-1</sup> 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 intraparticle 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<sup>-1</sup> 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  $ZnCl_2$ . 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  $0.5 \text{ g L}^{-1}$  and initial concentration of  $100 \text{ mg L}^{-1}$ , 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 adsorption capacity of these sorbents is listed in Table 1.

#### Reported adsorption capacities $q_m$ (mg/g) of different agricultural wastes:

| Adsorbent   | Dye        | Maximum adsorption capacity(mg/g) | Reference                      |
|-------------|------------|-----------------------------------|--------------------------------|
| Coir pith   | Congo red  | 2.6                               | Namasivayam and kavitha (2002) |
| Orange peel | Aid violet | 19.88                             | Rajeswari et al(2001)          |
| Banana      | Basic      | 20.8                              | Annadurai et                   |

|   |                |        |                               |
|---|----------------|--------|-------------------------------|
| peel  | blue9          |        | 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             | 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 EI-khaiary (2008b) |
| Peant hull                                  | Reactive dye   | 55.5   | Tanyildizi(2011)              |
| Citrullus lanatus rind                      | Crystal violet | 11.9   | Bharathi and Ramesh(2012)     |

## 2.2. Sand Materials (Adsorbents)

**2.2.1. Gypsum** Gypsum is a commonly available commodity used for treating industrial effluents. The abundance of gypsum in nature, besides its low cost, was the main factor in studying the potentials of this

material as an adsorbent. Moreover no pretreatment of this material is required as compared to other adsorbents such as activated coal or inorganic substances. Attention is focused on the use of gypsum as an alternative low-cost adsorbent for the removal of Methylene Blue (MB) from aqueous solutions due to the reason that many textile manufacturers use this and it releases aromatic amines (e.g. benzidine, methylene) and is a potential carcinogen.<sup>93</sup> Effluents containing dyes are difficult to treat because most of these chemicals are not prone to aerobic digestion.<sup>94</sup> There are several reported methods for the removal of pollutants from effluents; however, there is no single process which is capable of treating these effluents because of the complexity of the matrix. Practically, a combination of different processes is often used to achieve the desired water quality in the most economical way. Liquid-phase adsorption is one of the most studied methods for the removal of pollutants from wastewater since it generally will produce a high quality treated effluent. The treatment of wastewaters by the adsorption process is an excellent choice especially if the sorbent is inexpensive and does not require an additional pre-treatment step before its application. Few reports are available on the use of gypsum as adsorbent for dye removal. Commercially obtained gypsum powder (unbranded) was used as an adsorbent material because of its availability in huge quantities, its cheapness and its application without prior treatment. The surface area of the gypsum sample was found by the nitrogen adsorption method using the Quantasorb Autosorb Automated gas sorption system (Quantochrom corporation). After dye adsorption, a significant change is observed in the structure of this adsorbent. The adsorbent appears to have a rough surface and pores containing a new shiny and bulky particle.

**2.2.2 Bentonite Sand Mix** Bentonite is composed of 74% claysized (2 $\mu$ m), 9% sand (4.75 to 0.075mm) and 17% silt-sized (0.075 to 0.002mm) fractions. On treatment with HDPy<sup>+</sup> ions, the HDPy<sup>+</sup>B specimen coagulates to sandsized particles (sand content = 98%, silt content = 2%).<sup>107</sup> Gaomiaozi (GMZ) bentonite has been extracted from the northern Chinese Nei Mongolia autonomous region, 300 km northwest from Beijing. There are 160 million tons with 120 million tons Na bentonite reserves in the deposit and the mining area is about 72kms. In China, GMZ bentonite has been selected as one of the

candidate so f buffer/back fill material for the geological disposal of highly radioactive waste.<sup>108–110</sup> GMZ bentonite has attracted great interest in China because of its outstanding properties, such as its prominent high swelling and sealing abilities, cation exchange capacity and strong adsorption capacity.

**2.2.3. Ooid Sand** The utility of ooid sand, also called riverbed sand, lies in availability in ample amounts; it can be an economically viable alternative to costly adsorbents. Different thermodynamic parameters such as change in standard free energy ( $\Delta G^\circ$ ), enthalpy ( $\Delta H^\circ$ ) and entropy ( $\Delta S^\circ$ ) have been determined. The values of  $\Delta G^\circ$  were found to be negative at all temperatures which indicate that the adsorption process is spontaneous in nature. As the temperature increases, the values of  $\Delta G^\circ$  decrease, indicating less driving force<sup>127</sup> at elevated temperatures. The  $\Delta G^\circ$  addresses the possibility and feasibility of any reaction and more negative values of  $\Delta G^\circ$  reflect a more energetically favorable adsorption process. The value of the enthalpy change  $\Delta H^\circ$  was found to be negative for this system which confirms the exothermic nature of the process of adsorption. Equilibrium studies have demonstrated that the Langmuir model fits better than the Freundlich model for the adsorption equilibrium data in the examined concentration range. The value of the adsorption capacity of ooid sand was found to be significant, which indicates that it can be successfully used for the removal of Ni(II). Further as the adsorbent is naturally available, it incurs no extra financial burden on the users and hence it can always be recommended for the treatment of Ni(II) containing waters and wastewaters.

**2.2.4. Desert Sand** Desert sand contains active components that can strongly adsorb positively charged organic material from an aqueous solution. An example is sand in the present Sahara Desert (SaDeS) in Tozeur, Tunisia, the active component of which was related with kyanite, a negatively charged mineral that imparts electrostatic attraction towards cationic material. In recent years, Sahara Desert sand has become the subject of investigations related to its influence on the lower atmosphere and its effects on the oceanographic equilibrium. Many of these studies have reported that the capacity of adsorbing and carrying volatile organics. Although this fact is known, there are not many studies in the literature



treating adsorption itself, while there are no studies focusing on removal of industrial wastes by the use of SaDeS. In view of the limited supply of water in countries of northern Africa, where SaDeS is abundant, use of this natural material for cleaning waste waters may be of great value. It has been noted that washed SaDeS loses its active component and its original microstructure is lost. More than 90 % of methylene blue may be removed from a  $3.5 \times 10^{-5}$  M 25 mL solution with the use of 20 mg of adsorbent. The adsorption is found to be pseudo second order. The Pseudo first order and pseudo second order models have been widely used in understanding dye kinetics. These models were tested for the adsorption of MB on SaDeS and the best model was selected depending on the linear regression correlation coefficient. The pseudo first order model has been described by Lagergren, where as the pseudo second order model was also applied using Ho's pseudo second order model. The thermodynamic parameters, i.e. the Gibbs free energy, enthalpy change and entropy change, were calculated and found to be  $-6411 \text{ J mol}^{-1}$ ,  $-30360 \text{ J mol}^{-1}$  and  $-76.58 \text{ J mol}^{-1} \text{ K}$ , respectively. These values indicate that the adsorption of MB onto desert sand has a decreased randomness at the solid solution interface, and is an exothermic spontaneous process at low temperatures. It is therefore proposed that natural SaDeS is a good candidate as a low cost adsorbent to be used for the removal of dyes from water.

**2.2.5. Silica and Quartz Sand** these are natural sands, eroded from mountain rock, which is mined from where it was deposited. The host rock determines the exact mineral composition. Due to its chemical hardness, it is therefore found to be extremely resistant to weathering and breakdown. The sorbent was sediment obtained from Guanting Reservoir (Beijing, China), which contained 25% sand, 67 % silt, 8 % clay, and 2.06 % organic carbon. The neutral red (NR) dye in aqueous solution present as a pollutant material in textile wastewater<sup>6</sup> was removed by adsorption on sand. This removal of NR dye from the aqueous solution onto the sand surface was carried out at room temperature (298 K). It was noted that the local sand sample used as an adsorbent was initially characterized for its textural properties including surface area, mean pore radius and total pore volume. These properties were examined from the low temperature adsorption of nitrogen on sand samples at 77 K. The conditions of maximum

adsorption of the dye were optimized. It was seen that under optimized conditions, up to 85 % of the dye could be removed from the solution onto the sand surface. The experimental data were fitted to the Freundlich isotherm which showed that adsorption was monolayer in nature. The rate constant for adsorption of the NR dye was found to be  $3.85 \text{ min}^{-1}$  using the Lagergren equation. Furthermore, in order to determine the actual rate control step involved in the dye adsorption process, the adsorption data were further analyzed by using the kinetic expression given by Boyd et al. This equation revealed that the adsorption process was physical in nature and that the dye did not actually diffuse in the sand. This indicates that a particle diffusion mechanism is not operative and hence does not control the kinetics of NR dye adsorption on sand. The adsorption of the dye decreased in the presence of all the added ions; the effect was more pronounced in the presence of chloride, sodium and copper ions.

### 3. 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),

$$\text{Log}(q_{\text{eq}} - q) = \log q_{\text{eq}} - \frac{K_1}{2.303} t$$

Where  $q_{\text{eq}}$  and  $q$  are the adsorption capacity at equilibrium and at time  $t$ , respectively ( $\text{mg g}^{-1}$ ),  $K_1$  is the rate constant of pseudo-first-order adsorption ( $\text{L min}^{-1}$ ). The values of  $\log(q_{\text{eq}} - q)$  were linearly correlated with  $t$ . The plot of  $\log(q_{\text{eq}} - q)$  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

$$\frac{t}{q} = \frac{1}{K_{II} q_{\text{eq}}^2} + \frac{1}{q_{\text{eq}}} t$$

Where  $K_{II}$  is the rate constant of pseudo-second-order adsorption ( $\text{g mg}^{-1} \text{min}^{-1}$ ). The plot of  $(t/q)$  and  $t$  should give a linear relationship from which  $q_{\text{eq}}$  and  $K_{II}$  can be determined from the slope and intercept of the plot, respectively. In 1934, the kinetic law of chemisorptions was established through 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 :

$$dq/dt = \alpha \cdot e^{-\beta q}$$

Where  $\alpha$  is the initial adsorption rate ( $\text{mg g min}^{-1}$ ) and  $\beta$  is the desorption constant ( $\text{mg g}^{-1} \text{min}$ ) during any experiment. To simplify the Elovich equation, Chien and Clayton (1980) assumed  $\alpha\beta \gg t$  and by applying the boundary conditions  $q = 0$  at  $t = 0$  and  $q = q$  at  $t = t$  Equation becomes

$$q_t = 1/\beta \ln(\alpha\beta) + 1/\beta \ln(t)$$

If the adsorption fits the Elovich model, a plot of  $qt$  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

$$\log(c_0/c_t) = k/2.303 \times (t),$$

where  $C_0$  and  $C_t$  are the concentrations of dye solution (in  $\text{mg L}^{-1}$ ) 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

$$\log[1-U(T)] = -k_B/2.303 \times (t)$$

$$U(T) = C_0 - C_t / C_0 - C_e \times (t),$$

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

$$\log q_t = \log a + b \log t.$$

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

$$q_t = k_{id}t^{1/2} + C,$$

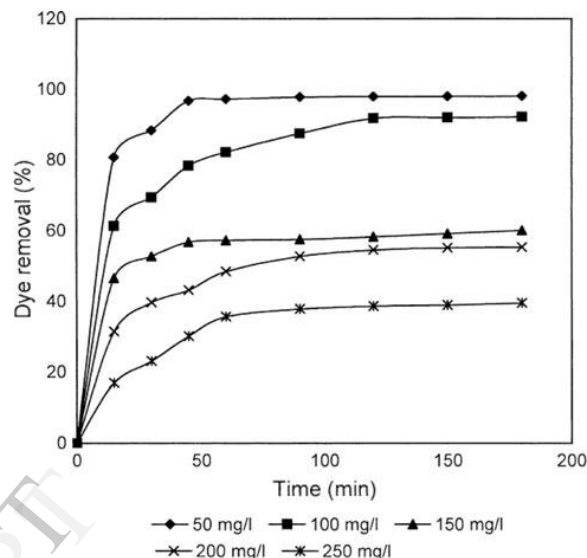
Where  $C$  is the intercept and  $k_{id}$  is the intraparticle diffusion rate constant ( $\text{mg g}^{-1} \text{min}^{0.5}$ ), which can be evaluated from the slope of the linear plot of  $q_t$  versus  $t^{1/2}$ .

## 5. Factors affecting adsorption

### 5.1. 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. 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  $\text{mg g}^{-1}$  with an increase in the initial dye concentration from 100 to 500  $\text{mg L}^{-1}$ . 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. 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 concentration.



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

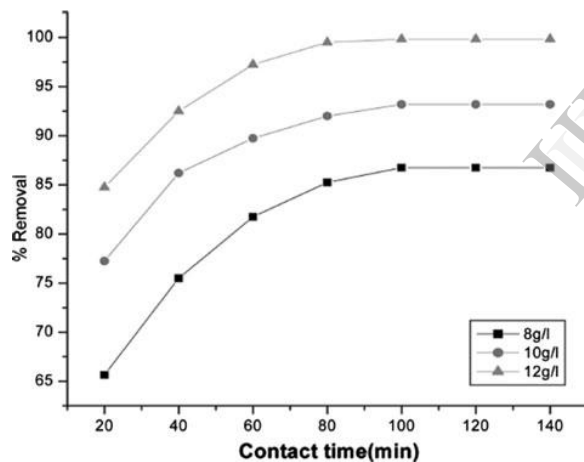
This may be probably as a result of the fact that for a fixed adsorbent dose, the total available adsorption sites remain invariable for all the concentrations checked. With increasing concentration the available adsorption sites become fewer and hence the percent removal of dye is dependent upon the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

### 5.2. 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 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.



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

#### 5.4. 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).

#### 5.5. 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 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. 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 is probably due to the presence of excess  $\text{H}^+$  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 (pHIEP) of adsorbents that prepared from agricultural solid wastes in order to better understand of adsorption mechanism. Cationic dye adsorption is favored at  $\text{pH} < \text{pH}_{\text{pzc}}$ , due to the presence of functional groups such as OH,  $\text{COO}^-$  groups. Anionic dye adsorption is favored at  $\text{pH} < \text{pH}_{\text{pzc}}$  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 (Ozcan 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<sup>-1</sup>, 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).

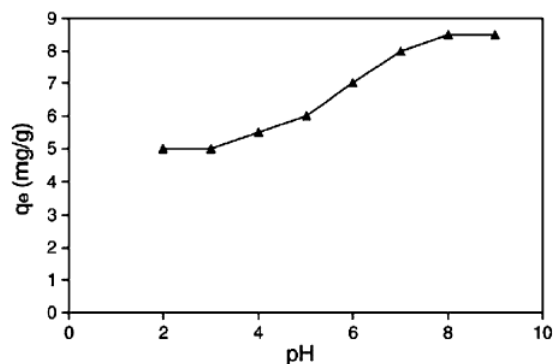


Fig. 3. Effect of pH onto crystal violet biosorption (Kumar and Ahmad 2011)

### 5.6. 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.

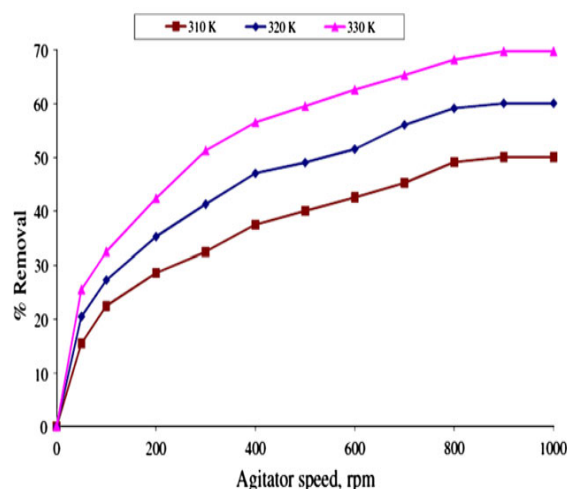


Fig. 4 Effect of agitation speed with various temperatures (Patel and Vashi 2010)

### 5.7. 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. 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,  $\Delta G$  contributes to the total free energy change of adsorption,  $\Delta G$  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.

### 5.8. Effect of temperature

A study of the temperature dependence of adsorption reactions gives valuable knowledge about the enthalpy and entropy changes during adsorption. 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 (Senthilkumar et al. 2006). Senthil kumar et al. (2006) reported that the enhancement of adsorption.

Effect of agitation speed with various temperatures (Patel and Vashi 2010) Appl Water Sci (2013) 3:773–790 783 123 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).

## 6. 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 & 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.

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

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

$$B = \frac{\pi^2 D_i}{r_0^2}$$

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  $B_t$  values were obtained for each observed value of F, from Reichenberg's table (1953). The linearity test of  $B_t$  versus time plots was employed to distinguish between the film diffusion and particle diffusion-controlled adsorption. If the plot of  $B_t$  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 ( $\leq 5 \times 10^{-5}M$ ) concentrations, respectively. Kumar and Ahmad (2011) reported the removal mechanism of  $C_V$  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, Vander Waals forces, etc. The structure of the  $C_V$  molecule was a prominent factor for its biosorption. The complexation between  $C_V$  and TGW can take place through the weak and strong forces. The weak interactions occur due to the Vander Waals forces while the strong interactions occur due to (1) hydrogen bonding interaction between the nitrogen containing amine groups of  $C_V$  and TGW surface (2) hydrophobic-hydrophobic interactions between the hydrophobic parts of  $C_V$  and TGW (3) electrostatic interaction between the cationic dye [due to the presence of  $N^+$  (CH<sub>3</sub>)<sub>2</sub> group] and negatively charged TGW surface in basic medium. A proposed mechanism for the biosorption of the  $C_V$  onto TGW. 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.

## 7. Conclusion

In this review, a wide range of agricultural waste materials and various sand materials has been presented as low cost adsorbents. 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. However the applications of these materials are limited practically because the adsorbents are not available in large amounts. This shows that, despite having a significant capacity for dye adsorption, most of these materials are not produced in large quantities. Consequently, they are not available in sufficient bulk to be commercialized for full-scale application. 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.

## 8. References

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