Desalination and Water Treatment
www.deswater.com

doi: 10.1080/19443994.2015.1093551

57 (2016) 18851–18860
August

Taylor & Francis
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A comparative study on the adsorptive efficiency of low-cost adsorbents for the removal of methylene blue from its aqueous solution

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Received 12 March 2015; Accepted 4 September 2015

ABSTRACT

Water pollution has become the greatest menace due to the discharge of effluent water from industries like dyeing, sugar, chemical processing, etc. The release of colored water containing dyes and heavy metals into the fresh water streams pollutes the water bodies and also penetrates deep into the soil making it unfit for use by human beings. In order to bring a solution to the water pollution problem, raw shot blasting dust (SBD) and phosphoric acid-treated activated carbon (PAC) prepared from putrescible vegetable waste (PVW) were selected as adsorbents. To evaluate the efficiency of both the adsorbents, Methylene blue (MB) was selected as the model compound. The composition and physico-chemical properties of both SBD and PAC were analyzed. Surface morphology was studied through scanning electron microscopy. FTIR studies were used in evaluating the presence of functional groups on the surface of the adsorbents. XRD analysis revealed that PAC is amorphous with few crystallite formations and SBD is crystalline in nature. The BET surface area, total pore volume, and pore widths were higher for PAC than SBD. The effect of pH, initial dye concentration, adsorbent dosage, and contact time were evaluated and optimum experimental conditions were verified. The adsorption of MB onto SBD and PAC follows pseudo-second-order kinetics. Langmuir and Freundlich isotherm models were applied to the equilibrium data and for both the adsorbents, Langmuir model fitted well. Economical evaluation and adsorption efficiency was done for both the adsorbents. From the present study, it could be concluded that the adsorption efficiency of PAC is better and SBD is more cost effective.

Keywords: Shot blasting dust; Putrescible vegetable waste; Methylene blue; Langmuir isotherm; Freundlich isotherm; Adsorption efficiency

1. Introduction

Contamination of surface and groundwater with the textile industry effluents is a major concern to public health. Synthetic dyes, suspended solids, and dissolved organics are the chief hazardous materials found in textile effluents [1]. These materials can affect the physical and chemical properties of fresh water. In addition to the undesirable colors of textile effluents, some dyes may degrade to produce carcinogens and

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toxic products [2]. Furthermore, the colored effluents reduce light penetration and potentially prevent photosynthesis [3,4]. Thus, it is necessary to treat the dyeing effluents prior to their discharge into fresh water bodies.

The overall generation rate of solid waste for the entire community requires a proper design of solid waste management system. Throughout human history, water has been a source of life as well as death. At present, most of the municipal solid waste in the country is disposed off unscientifically. This has adverse impacts not only on the ecosystem, but also on the human environment. Unscientific disposal practices leave waste unattended at the disposal sites, which attract birds, rodents, and flies, creating unhygienic conditions like odor, release of airborne pathogens, etc. [5].

Various studies on effluent adsorption have been conducted using low-cost adsorbents [6–12] solid waste, groundnut shell, vegetable peels, jackfruit peel, palm nut, industrial wastes, etc. Many treatment methods are available for effluent water, like coagulation, flocculation, photocatalytic degradation, membrane filtration, microbiological decomposition, electrochemical oxidation, fungus bio-sorbent, and adsorption. Among these methods, adsorption is considered to be an economical and efficient process for the removal of dyes, heavy metals, and hazardous impurities from liquid effluents.

The present study focuses on the solid waste disposal problem and dye effluent treatment by using novel low-cost adsorbents. Thus, a comparative analysis has been carried out to investigate the adsorption efficiency of two different adsorbents, one being silica based and the other an activated carbon for the removal of a basic dye, Methylene blue (MB) from its aqueous solution.

2. Materials and methods

2.1. Preparation of adsorbent materials

Shot blasting dust (SBD) is a solid waste generated from foundries to remove excess sand from the casting. It is a blend of sand, iron in oxide form, and bentonite clay as a binder. In order to remove the oily substances which are present in SBD, it was stirred with double-distilled water in a magnetic stirrer for 10–12 h. The resultant supernatant liquid containing oily substances was filtered off. Oily substances in SBD were completely removed by washing it several times with double-distilled water. It was then dried in a hot air oven for 5 h at 110˚C [13].

Putrescible vegetable waste (PVW) was collected from market places, kitchens of college hostels, and marriage halls in and around Coimbatore city, Tamilnadu, India. During the one-year period, all types of vegetable wastes and their peel off were collected. PVW was dried in sunlight to remove the moisture content. It was then dried in a hot air oven at 110˚C for 4–6 h. The dried PVW to be carbonized was impregnated with a boiling solution of 30% H_3PO_4 for 2 h and was soaked in the same solution for 24 h [14]. At the end of 24 h, the excess solution was decanted off and air dried and was carbonized in muffle furnace at 400˚C. The dried material was powdered and activated in a muffle furnace at 800˚C for a period of 10 min. Finally, the activated carbon was washed with plenty of water to remove residual acid, dried, and powdered. Using a mechanical sieve, particles of size in the range 70–105 μ were separated and used for the study.

2.2. Preparation of adsorbate

The molecular formula and molecular weight of MB dye are $C_{16}H_{18}N_3SCl$ and 319.85 g mol^{-1}, respectively. Stock solutions of the dyes were prepared by dissolving 1 g of the dye in 1,000 ml of double-distilled water. Different initial concentrations were prepared by diluting the stock solution. Double-distilled water was employed throughout the study as solvent. The pH measurements were made using pH meter. The pH adjustments of the solution were made by 0.1 M HCl or 0.1 M NaOH. The chemicals were of analar grade and all the adsorption experiments were carried out at room temperature (27 ± 2˚C).

2.3. Batch adsorption studies

The adsorption of MB was performed by batch experiments. The batch technique was selected because of its simplicity. The experiments were carried out in a mechanical shaker at 150 rpm using 250-ml shaking flasks containing 50 ml of the dye solutions of desired concentrations and initial pH values. The effect of each parameter like adsorbent dose, adsorbent particle size, different dye concentrations, agitation time, were studied by fixing the values of other parameters. To correct any adsorption of dye on containers, control experiments were carried out in duplicate. It was noted that there was no adsorption by the container walls.

The percentage of dye adsorbed by the adsorbents was calculated using the following equation:

$$\text{Removal}\,\% = \frac{C_0 - C_t}{C_0} \times 100 \quad (1)$$

where C_0 and C_t (mg/L) are the initial and final concentration of dye solutions.

3. Results and discussion

3.1. Physico-chemical parameters of the adsorbent

Composition in SBD is given in Table 1. From the table, it is clear that silica is the major constituent in SBD. Through scanning electron microscopy (SEM), EDAX analysis the composition of PAC was derived and is presented in Table 2. In PAC, carbon is the major constituent. Physico-chemical parameters of PAC and SBD are as shown in Table 3. From Table 3, it is evident that moisture content, water soluble content, and acid soluble content are lower in SBD than in PAC. The important adsorption parameters like Iodine number and MB number are high in PAC. pH value indicates that SBD is more acidic in nature than PAC. Surface area parameters clearly indicate that the surface properties of PAC are better than SBD. As shown in Table 3, the BET surface area for PAC is much higher than SBD. Comparing the total pore volume and pore diameter of PAC and SBD, it is found that all the surface parameters are higher in PAC than in SBD.

SEM analysis (Fig. 1) shows that the surface of both the adsorbents are highly porous in nature. To explore the surface characteristics of SBD, an FT-IR analysis was performed in the range 400–4,000 cm^{-1}. IR spectrum for PAC and SBD is as shown in Fig. 2. In the spectrum for SBD, the peak positions showing major adsorption bands were observed at 1,082, 796, 695, 470, 550, 2,360, and 462 cm^{-1}. A peak at 1,082 cm^{-1} reflects the siloxane (Si–O–Si) group stretching vibration [13]. Peaks at 796 and 695 cm^{-1} correspond to Si–O–H vibration. Peaks at 550 and 470 cm^{-1} are characteristic of Si–O–Si bending vibration [13]. A peak at 2,360 cm^{-1} may be due to traces of ammonia ions because the SBD is collected at very high temperature and also because of the existence of nitrogen in air. The peak at 452 cm^{-1} represents the presence of Iron oxide in Hematite form [13].

PAC displayed a broad band at 3,429 cm^{-1} which is attributed to O–H stretching in hydroxyl functional groups [15]. Two peaks at 2,357 and 2,337 cm^{-1} correspond to N–H stretching absorption bands [16]. A peak at 1,172 cm^{-1} is broad and intense which could be assigned to C–P bond which is formed during the impregnation process. The broad peak at 1,109 cm^{-1} in PAC can be assigned to the stretching vibrations of acidic HPO_4^{2-} groups and 1,393 cm^{-1} due to deformation vibration of P–OH group [17] and 669 cm^{-1} due to C–P bonding [18].

XRD analysis was done for both the adsorbents to find out whether they are crystalline or amorphous in nature and it is presented in Fig. 3. It confirms that PAC is amorphous [19] with few crystallite formations and SBD is crystalline [20] in nature.

Table 1
Composition of SBD

Composition	Weight percentage
SiO_2	64.95
Fe_2O_3	44.5
Clay	0.55
Carbon	NiL

Table 2
Composition of PAC

Composition	Weight percentage
Carbon	49.76
Oxygen	36.5
Phosphorus	11.08
Sulfur	0.15
Calcium	0.5
Silicon	2.01

Table 3
Physico-Chemical characteristics of PAC and SBD

Parameters	PAC	SBD
Moisture content (%)	4.5	0.59
Ash content (%)	8.37	NIL
Water soluble content (%)	19.26	28.94
Acid soluble content (%)	1.63	11.08
Volatile matter (%)	20.5	NIL
Iodine number (mg/g)	1,101.9	10.5
Methylene blue number	525	45.2
pH	6.65	6.17
Yield (%)	76.48	96
BET Surface area (m^2/g)	603.7	4.0616
Total pore volume (cm^3/g)	0.7053	0.001766
Average pore diameter (Å)	46.74	11.79

3.2. Effect of adsorbent dosage

Due to the greater availability of the adsorbent sites at the higher concentrations of the adsorbent, the percentage removal of the dye increases with increase in the adsorbent dosage [8]. It is observed from Fig. 4,

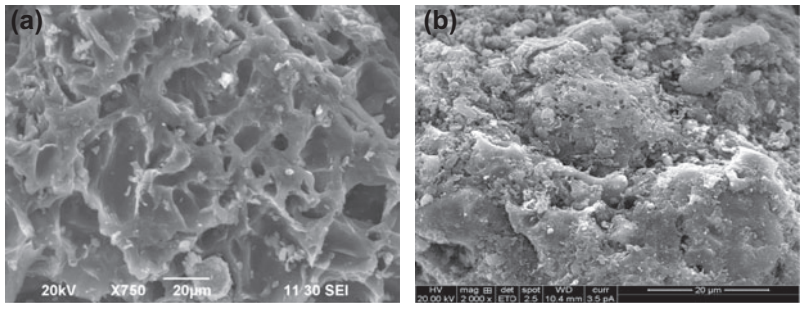

Fig. 1. SEM images of (a) PAC and (b) SBD.

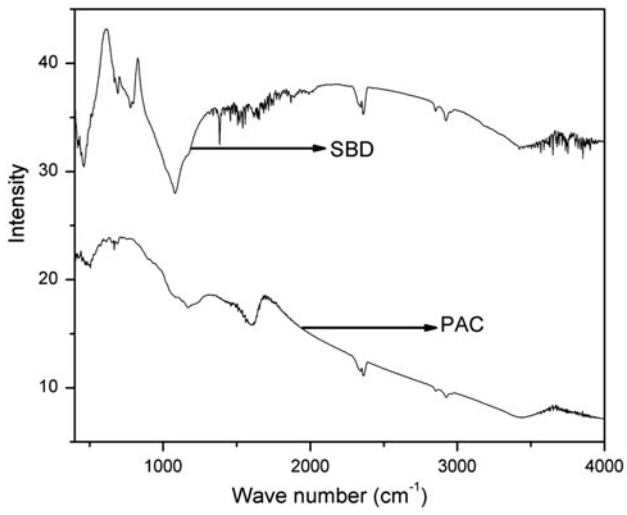

Fig. 2. IR spectra for PAC and SBD.

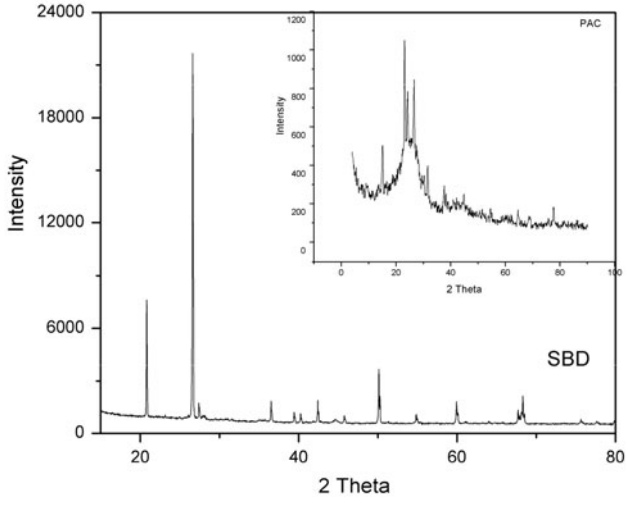

Fig. 3. XRD spectra for PAC and SBD.

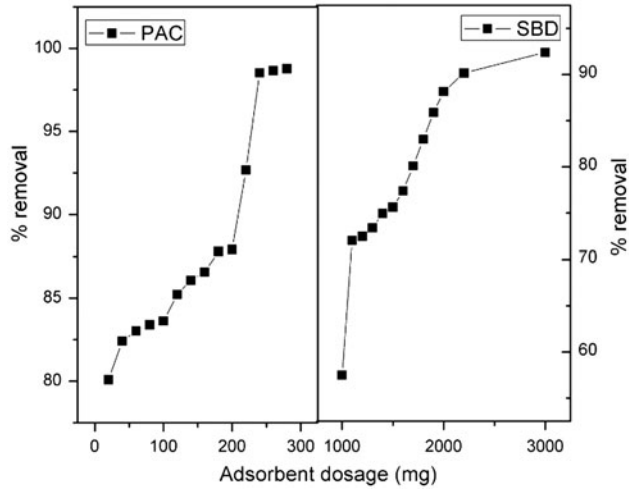

Fig. 4. Effect of adsorbent dosage for the adsorption of MB onto PAC and SBD.

that as the dosage increased, for both the adsorbents, the percentage removal of MB also increased. More than 90% of dye removal was achieved at 250 mg and 3 g for PAC and SBD, respectively. This is due to the reason that the surface area for PAC is higher than SBD.

3.3. Effect of pH

The pH of dye solution plays an important role in the adsorption process. To determine the effect of pH on the removal of dye, its adsorption was studied at varied pH range of 2–10 which is shown in Fig. 5. It is known that ionic dye molecules upon dissolution release colored dye anions/cations into solution. The adsorption of these charged dye groups onto the adsorbent surface is primarily influenced by the surface charge on the adsorbent which is in turn influenced by

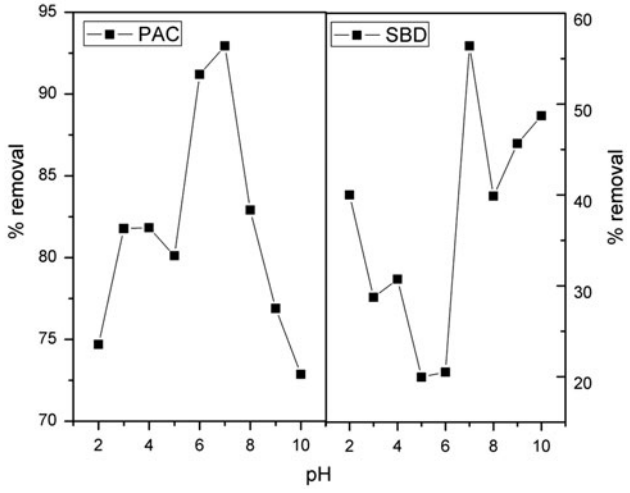

Fig. 5. Effect of pH for the adsorption of MB onto PAC and SBD.

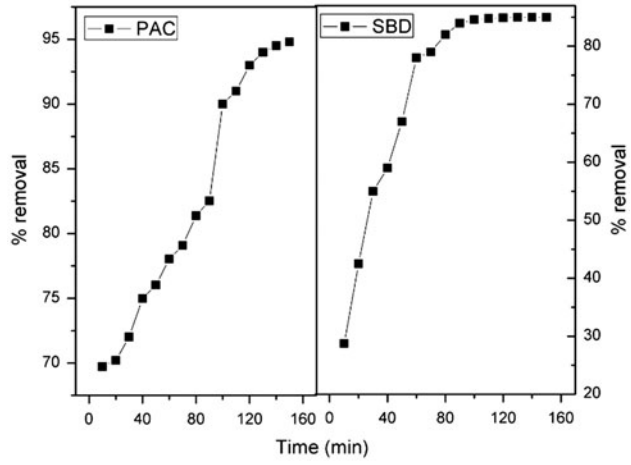

Fig. 6. Effect of time for the adsorption of MB onto PAC and SBD.

the solution pH [21]. In water, MB produces cations and reduced ions. As the pH increases, the negative charge density on the adsorbents (PAC and SBD) increases leading to more electrostatic attraction of positively charged dye molecules. Due to this reason, at pH 7 maximum adsorption of MB onto PAC and SBD took place. At lower pH, due to the accumulation of H^+ ions on the surface of SBD, it became more positively charged leading to lower adsorption of dye molecules. Similar studies were reported in the adsorption of MB by fly ash [22], tuncbilek lignite [23].

3.4. Effect of contact time and initial dye concentration

To evaluate the equilibrium time for the adsorption of MB by PAC and SBD, effect of time experiment was carried out. From Figs. 6 and 7, it is evident that after 10 min of adsorption, PAC and SBD could remove 70 and 25% of the dye, respectively. PAC attained equilibrium at 130 min and SBD at 80 min with the maximum removal percentage of 92. The effect of dye concentration was carried out by fixing the equilibrium time as 120 min. As the concentration increased, the removal percentage of MB decreased gradually and at 100 mg/L it was 55 and 15% for PAC and SBD, respectively. When the concentration of dye increased, the limited capacity of the adsorbent checks any further adsorption of dye. Hence, the overall removal percentage decreased [24]. Above results clearly indicate that the adsorbent PAC having more surface area adsorbs more dye molecules than SBD.

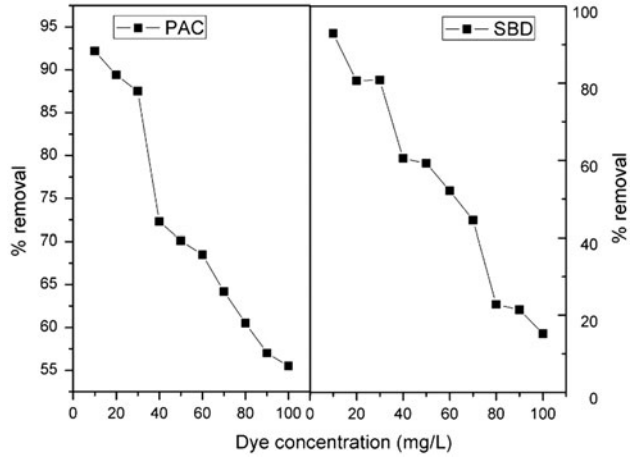

Fig. 7. Effect of dye concentration for the adsorption of MB onto PAC and SBD.

3.5. Adsorption kinetics

Kinetic models are useful in sorting out a solution for treatment process and also to find out the physical and chemical properties of an adsorbent. Various kinetic studies like pseudo-first-order and pseudo-second-order kinetic models were analyzed in this study.

3.5.1. Pseudo-first-order kinetic model

The pseudo-first-order model of Lagergren [25] is based on the assumption that the rate of change of adsorbed solute with time is proportional to the difference in equilibrium adsorption capacity and the adsorbed amount. The pseudo-first-order equation is expressed as in Eq. (2):

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \quad (2)$$

When the boundary conditions $q_t = 0$ at $t = 0$, Eq. (2) can be integrated into the following equation:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303}t \quad (3)$$

where q_e (mg/g), and q_t (mg/g), are the adsorption capacity per unit weight of adsorbent at equilibrium and at time t (min), respectively. The pseudo-first-order rate constant is k_1 (min^{-1}). Linear plot of $\log(q_e - q_t)$ vs. t gives the value for rate constant k_1 (Fig. 8). From the figure, it is visible that all the points do not fall on the straight line for both the adsorbents. There is a vast deviation between $q_{e(exp)}$ and $q_{e(cal)}$ as shown in Table 4. Also, the correlation coefficient values are low for both PAC and SBD. From all the above data, it is clear that the adsorption of MB onto PAC and SBD do not follow first-order kinetics. Similar results were observed for the adsorption of MB by the activated carbon prepared from coir pith [26].

3.5.2. Pseudo-second-order kinetic model

The pseudo-second-order model [27] is based on the assumption that the rate-limiting step involves chemisorption. The equation is represented as in Eq. (4):

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \quad (4)$$

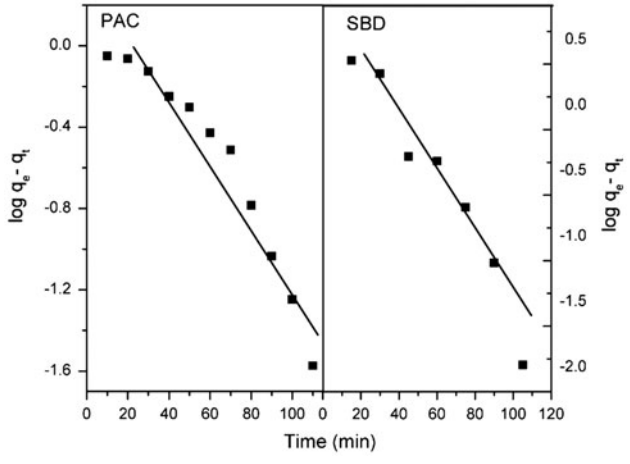

Fig. 8. Pseudo-first-order kinetics for the adsorption of MB onto PAC and SBD.

Table 4
Calculated Kinetic parameters for the adsorption of MB onto PAC and SBD

Kinetic parameters	PAC	SBD
$q_{e(exp)}$ (mg/g)	5.25	4.808
Pseudo-first-order kinetics		
$q_{e(cal)}$ (mg/g)	0.6725	0.4097
$k_1 \times 10^{-2}$ (min^{-1})	3.245	5.62
R^2	0.9585	0.9074
Pseudo-second-order kinetics		
$q_{e(cal)}$ (mg/g)	5.456	4.882
$k_2 \times 10^{-3}$ (g/mg/min)	3.257	1.75
h	0.9696	0.1231
R^2	0.9996	0.9915

When the initial conditions $q_t = 0$ at $t = 0$, after integration, the linear form of the pseudo-second-order equation is given in Eq. (5):

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}(t) \quad (5)$$

where k_2 is the pseudo-second-order rate constant (g/mg/min). The initial adsorption rate h (mg/g/min) at $t = 0$ is defined as follows:

$$h = k_2 q_e^2 \quad (6)$$

The straight line plot of t/q_t vs. t, for the adsorption of MB by both the adsorbents is shown in Fig. 9. From the linear plot, the values of h, q_e, and k_2 are calculated (Table 4). Considering the closer $q_{e(exp)}$ and $q_{e(cal)}$ values and high correlation coefficient values obtained for pseudo-second-order reaction, it can be concluded that the adsorption of MB onto PAC and SBD follows second-order kinetics [26].

3.6. Adsorption isotherm models

Adsorption equilibrium data which expresses the relationship between mass of adsorbate adsorbed per unit weight of adsorbent and liquid-phase equilibrium concentration of adsorbate are represented by adsorption isotherms and provide important design data for adsorption system. The equilibrium data for the removal of MB by PAC and SBD were analyzed by Langmuir and Freundlich adsorption isotherms.

3.6.1. Langmuir isotherm model

The Langmuir isotherm theory assumes monolayer coverage of adsorbate over a homogenous adsorbent

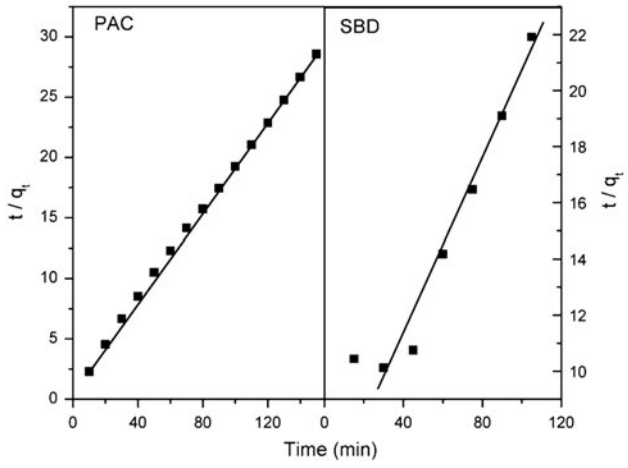

Fig. 9. Pseudo-second-order kinetics for the adsorption of MB onto PAC and SBD.

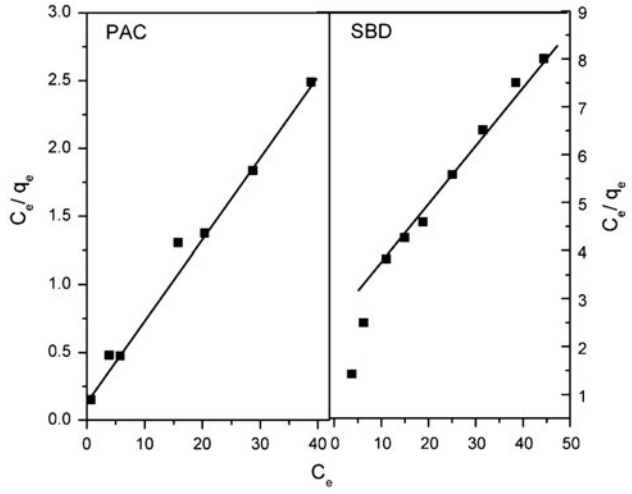

Fig. 10. Langmuir isotherm model for the adsorption of MB onto PAC and SBD.

surface [28]. A basic assumption is that sorption takes place at specific homogeneous sites. The form of Langmuir isotherm equation is expressed as follows:

$$q_e = \frac{Q_m K_a C_e}{1 + K_a C_e} \tag{7}$$

where Q_m is the theoretical maximum adsorption capacity per unit weight adsorbent (mg/g), K_a is Langmuir adsorption constant (L/mg), $C_{e,}$ and q_e are the concentration and amount of dye adsorbed at equilibrium, respectively. The Langmuir isotherm Eq. (7) can be linearized into the following form:

$$\frac{C_e}{q_e} = \frac{1}{K_a Q_m} + \frac{1}{Q_m} \times C_e \tag{8}$$

A graph was plotted between C_e/q_e and C_e (Fig. 10) for PAC and SBD. The Langmuir plot for the adsorption of MB onto PAC and SBD was found to be linear. The Langmuir parameters are given in Table 5. The monolayer adsorption capacity was found to be higher for PAC than SBD. The fact that Langmuir isotherm fits the experimental data very well confirms monolayer coverage of dye onto adsorbent particles and also the homogeneous distribution of active sites on the material, since the Langmuir equation assumes that the surface is homogeneous [29].

Langmuir adsorption capacity for PAC is 8.247 mg/g and for SBD is 4.5901 mg/g. High adsorption capacity of PAC is due to high surface area and more porous structure. A comparison of Q_m values for various adsorbents is shown in the Table 6. A good fit of experimental data and correlation coefficient is observed in the adsorption of MB onto PAC with a value of 0.9703. Even though there is a linear fit for SBD, the correlation coefficient is lesser with a value of 0.8932. It is thus inferred that Langmuir monolayer

Table 5
Calculated Isotherm parameters for the adsorption of MB onto PAC and SBD

Isotherm parameters	PAC	SBD
Langmuir Isotherm		
Q_m (mg/g)	8.247	4.5901
b_L (L/mg)	0.0579	0.3184
R^2	0.9703	0.8932
Freundlich Isotherm		
$1/n$	0.1212	0.4049
K_f ($mg^{(1-1/n)}\ L^{1/n}\ g^{-1}$)	7.3198	1.1178
R^2	0.9708	0.8752

Table 6
Comparison of Q_m values for various adsorbents

Adsorbent	Dyes	Q_m (mg/g)	Refs.
Neem leaf powder	Methylene blue	3.67–19.61	[30]
Spent coffee grounds	Methylene blue	18.73	[31]
Tripoli	Methylene blue	16.62	[32]
Coir pith carbon	Methylene blue	5.87	[33]
Fly ash	Methylene blue	2.94	[34]
Neem saw dust	Basic violet 3	3.78	[35]
Coir pith	Basic violet 10	2.56	[36]
Red mud	Direct red 28	4.05	[37]

adsorption is best suited for the adsorption of PAC than SBD.

3.6.2. Freundlich isotherm model

The Freundlich isotherm [38] model is the earliest known equation describing the adsorption process. It is an empirical equation which can be used for non-ideal sorption that involves heterogeneous sorption. The Freundlich isotherm can be derived assuming a logarithmic decrease in the enthalpy of sorption with the increase in the fraction of occupied sites and is commonly given by the following non-linear equation:

$$q_e = K_f C_e^{1/n} \tag{9}$$

where K_f can be defined as the adsorption or distribution coefficient and represents the quantity of dye adsorbed onto adsorbent for unit equilibrium concentration. $1/n$ indicates the adsorption intensity of dye onto the adsorbent or surface heterogeneity, thus becoming more heterogeneous as its value gets closer to zero. A value for $1/n$ below 1 indicates a normal Freundlich isotherm, while $1/n$ above 1 is indicative of cooperative adsorption. The linear form of the equation is:

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \tag{10}$$

The applicability of the Freundlich adsorption isotherm was also analyzed, using the same set of experimental data, by plotting $\log q_e$ vs. $\log C_e$ (Fig. 11). In the present study, for both the adsorbents $1/n$ values are between 0 and 1 (Table 5) indicating that the adsorption of MB onto them is favorable [39]. The Freundlich model suggested that the adsorbent surfaces are more heterogeneous and the Langmuir model confirmed a better monolayer adsorption capacity for both the adsorbents. On comparison, both the models are suitable to explain the adsorption process completely.

4. Economical evaluation of PAC and SBD

PAC is available in abundance as a solid waste from market places, kitchens of marriage halls, hostels, and hotels at no cost. Cost involved was for handling, segregation, collection, transportation of the waste, and phosphoric acid used for the conversion of PVW into PAC. Consumption charges for drying in hot air oven and activation in muffle furnace were also taken into account. Table 7 clearly shows the cost involved for production of both the adsorbents. Considering all the above, production cost for 1 kg of PAC would be approximately Rs. 760.7. For SBD, transporting, washing with water, and drying in hot air oven were done. The cost involved for 1 kg of SBD is approximately Rs. 115. On comparing PAC and SBD, SBD is available at a cheaper cost.

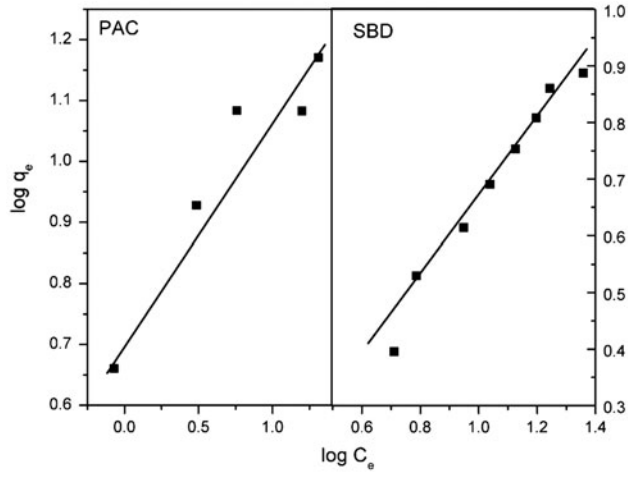

Fig. 11. Freundlich isotherm model for the adsorption of MB onto PAC and SBD.

Table 7
Cost analysis for the production of PAC and SBD

Procedure involved	PAC Cost per kg (in Rs.)	SBD
Transportation of raw material	125.3	50.5
Segregation of PVW	77.4	–
Sieving of adsorbents	18.5	24.0
Electrical charges	138.8	40.5
Chemical charges	400.7	–
Total cost	760.7	115

5. Conclusion

Waste biomass is getting increasing attention all over the world as it is a kind of renewable, widely available, cheap, and environmentally friendly resource. Also, the presence of dye molecules in water is highly toxic to all types of flora and fauna. This study highlights the comparative study on the adsorption of MB by activated carbon and the foundry solid

waste (SBD). In PAC, higher percentage of carbon is present and in SBD more silica content is found. Moisture content, water soluble content, and acid soluble content are lower in SBD than in PAC. Iodine number, MB number, and surface area are higher in PAC than SBD. pH value indicates that SBD is more acidic in nature than PAC. The IR spectra for PAC confirm the presence of surface functional groups like –OH, –NH, C–P, P–OH, and HPO_4^{2-} groups. SBD shows major IR peaks for Si–O–Si, Si–OH, and iron oxide in Hematite form. XRD spectra prove that PAC is amorphous and SBD is crystalline. Due to greater surface area in PAC, more than 90% of dye removal could be achieved at 250 mg and for SBD it is achieved at 3 g. PAC attained equilibrium at 130 min and SBD at 80 min with the maximum removal percentage of 92. Adsorption of MB onto PAC and SBD follows second-order kinetics. On comparing the Langmuir and Freundlich models, both the models are suitable to explain the adsorption process completely. Maximum monolayer adsorption capacity for PAC is 8.247 mg/g and for SBD it is 4.5901 mg/g. Economical evaluation shows that SBD is cheaper than PAC. From the present study, it could be concluded that PAC is the best adsorbent for the adsorption of MB from its aqueous solution.

List of symbols

C_0 — initial dye concentration (mg/L)
C_t — final dye concentration (mg/L)
C_e — equilibrium liquid phase concentration of dye solutions (mg/L)
K_F — Freundlich adsorption constant (mg/g)
q_t — amount of dye adsorbed per gram of adsorbent at any time
q_e — amount of dye adsorbed per gram of adsorbent at equilibrium
T — time
R^2 — correlation coefficient
n — Freundlich adsorption constant

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