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Removal of a basic dye from aqueous solution by adsorption using *Parthenium hysterophorus*: An agricultural waste

Hem Lata [a], V.K. Garg [b], R.K. Gupta [a,*]

[a] *Department of Chemistry, Guru Jambheshwar University, Hisar 125001, Haryana, India*
[b] *Department of Environmental Science and Engineering, Guru Jambheshwar University, Hisar 125001, Haryana, India*

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Abstract

Adsorbents prepared from *Parthenium hysterophorus* – unwanted weed – were successfully used to remove methylene blue from an aqueous solution in a batch reactor. The adsorbents included sulphuric acid treated Parthenium (SWC) and phosphoric acid treated Parthenium (PWC). Aqueous solutions of various concentrations (50–250 mg/L) were shaken with certain amount of adsorbent to determine the adsorption capacity on SWC and PWC for methylene blue. The effects of adsorbent surface change, initial pH, initial dye concentration, adsorbent dose and contact time on dye removal have been determined. Similar experiments were carried out with commercially available activated carbon (AC) for comparison. Initial pH of aqueous solution had negligible effect on the adsorption capacity of all the studied adsorbents. Maximum dye was sequestered from the solution within 60–90 min after the beginning of every experiment. At 500 mg/L methylene blue concentration, AC had 1.93 and 3.4 times more adsorption capacity than PWC and SWC, respectively. The adsorption capacity of the studied adsorbents was in the order AC > PWC > SWC. Adsorption follows both Langmuir and Freundlich isotherm models. The results showed that SWC and PWC can be considered as potential adsorbents for methylene blue removal from dilute aqueous solutions.

Keywords: Adsorption; Methylene blue; Sulphuric acid; Phosphoric acid; Parthenium; Sorption isotherm

1. Introduction

Almost every industry uses dyes to color their products and the residual and unspent dyes are discharged into the environment, particularly aquatic environment [1]. Color is the most obvious indicator of water pollution. Effluents from dye manufacturing industry, textile industry and pulp and paper industry are highly colored [2]. Pollution of water bodies due to release of dye laden industrial wastewater is a challenge to environmental engineers in developing countries. The discharge of colored waste into streams not only affects their aesthetic nature but also interferes with the transmission of sunlight into streams and therefore reduces photosynthetic action. They may also be toxic to some aquatic life because they contain metals, chlorides, etc. [3]. Over 90% of some 4000 dyes tested in an ETAD [Ecological and Toxicological Association of the dyestuff] survey had LD_{50} values greater than 200 mg/kg. The highest rates of toxicity were found amongst basic and diazo direct dyes [4]. The textile industry alone accounts for two thirds of the total dyestuff production, about 10–15% of the dyes used come out through the effluent [5]. Thus, the removal of dyes from colored effluents, particularly from textile industries, is one of the major environmental concerns these days [6,7].

Current methods for removing dyes from wastewater include flocculation, electroflotation, precipitation, electrokinetic coagulation, ion exchange, membrane filtration, electrochemical destruction, irradiation and ozonation. However, these processes are costly and cannot effectively be used to treat wide range of such wastewaters. The alum coagulation process is ineffective for the treatment of azoic, reactive, acidic and basic dyes [8]. Liquid-phase adsorption has been

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* Corresponding author. Tel.: +91 1662 263152; fax: +91 1662 276240.
E-mail addresses: rkgic@yahoo.com, vinodkgarg@yahoo.com (R.K. Gupta).

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shown to be an effective way for removing suspended solids, odors, organic matter and oil from aqueous solution in terms of initial cost, simplicity of design, ease of operation and insensitivity to toxic substances [9]. Although activated carbon is the most effective adsorbent for adsorption of dye, it is quite expensive and hence there is an increasing need for equally effective but cheaper adsorbents [6]. Recently, there have been several reports on the economic removal of dyes using adsorbents such as rice husk [1], sewage sludge based activated carbon [10], cassava peel [11], waste coir pith [12], mahogany sawdust and rice husk [13] orange peel [14], Indian rosewood [15], bagasse pith [16], neem leaf powder [17], barley husk [18], wood [19], banana pith [2], red mud [20], etc. New economical, easily available and highly effective adsorbents are still needed. Parthenium (*Parthenium hysterophorus* L.) also known as white top or carrot weed, an annual herbaceous weed − a native of North-east Mexico, has now widely spread in India, China, Australia, Pacific Islands, etc. The biomass of this plant is not put to any use and disposed along the roadsides, agricultural fields, railway tracts after uprooting. The biomass of this plant is available round the year at zero price.

In our laboratory, the work is in progress to look into the possibility of the use of waste biomass for industrial pollution control. The aim of the present work was to study the adsorption capacity of differently treated white top Parthenium plant for dye removal, methylene blue, from aqueous solution under different experimental conditions and their performance was evaluated against commercially available activated carbon (AC).

2. Experimental

2.1. Adsorbents

2.1.1. Commercially available activated carbon (AC)

Commercially available activated carbon (AC) used in the present was supplied by S.D fine chemicals, Mumbai, India. It was used as such without further grinding and sieving. The general characteristics of AC (as provided by the supplier) were: particle size = <300 mesh, surface area = 88 $m^2\ g^{-1}$, pH = 6.5−7.5, acid soluble = 3%; water soluble = 1%; loss on ignition at 120 °C = 5%.

2.1.2. Preparation of sulphuric acid treated Parthenium carbon (SWC)

Fully grown plants of Parthenium were collected in and around Hisar city (India), cut into small pieces of 2−3 cm and dried in sunlight. The dried Parthenium was used for carbon preparation by mixing one part of Parthenium and 1.5 parts of concentrated sulphuric acid and keeping it at 120 °C for 24 h. The carbonized material was then washed with distilled water several times to remove the free acid and soaked in 1% sodium bicarbonate solution overnight to remove any residual acid. This material was then washed with distilled water and dried at 105 °C in a hot air oven for 24 h. It was ground and sieved in the size range of 0.3−1.0 mm. The various physico-chemical characteristics of PWC were: particle size = 0.3−1.0 mm; bulk density = 0.57 g/mL; pH = 7.2; moisture content (%) = 0.15; water solubility (%) = 2.86; acid solubility (%) = 4.0. The material was placed in airtight plastic containers for further use.

2.1.3. Preparation of phosphoric acid treated Parthenium carbon (PWC)

The dried biomass of Parthenium (as given in Section 2.1.2) was impregnated with H_3PO_4 (50%) in a ratio of 2:1 (acid volume:weight of Parthenium) and allowed to get carbonized at 300 °C in a muffle furnace. The carbon so obtained was washed with distilled water till all the free acid was removed and dried in hot air oven at 105 °C. Finally it was ground and sieved in the size range of 0.3−1 mm.

2.2. Dye solution preparation

The basic dye, methylene blue (C.I. 52015, S.D. Fine Chemicals, 85% dye content, chemical formula = $C_{16}H_{18}N_3SCl$, FW = 319.86, nature = basic blue, and $\lambda_{max} = 665$ nm) has been used in this study. An accurately weighed quantity of the dye was dissolved in double distilled water to prepare the stock solution (1000 mg/L). Experimental solutions of desired concentration were obtained by successive dilution.

2.3. Methods

In each adsorption experiment, 100 mL of dye solution of known concentration and pH was added to 0.4 g of AC or SWC or PWC in a 250 mL glass-stoppered flask at room temperature, 26 ± 1 °C, and the mixture was stirred on a rotary shaker at 180 rpm. The samples were withdrawn from the shaker at predetermined time intervals. The absorbance of supernatant solution was estimated to determine the residual concentration. Residual dye concentration was determined using absorbance values before and after the treatment at 663 nm with an ELICO spectrophotometer (Model SL-177) using silica cells of path length 1 cm. Initial pH was controlled by the addition of dilute 0.1 N HCl or 0.1 N NaOH solution; concentration of dye solution (50−250 mg/L) at different time intervals; and by varying the amount of adsorbents (0.2−1.0 g/100 mL). The experiments were carried out at initial pH values ranging from 3 to 10. Three main system variables, pH, initial dye concentration, and adsorbent dosage, were varied to investigate their effect on adsorption kinetics. Samples were diluted with double distilled water if absorbance values exceeded 0.900. Each experiment result was an average of three independent adsorption tests. Blank runs with only the adsorbents in 100 mL of double distilled water and 100 mL of dye solution without any adsorbent, were conducted simultaneously at similar conditions to account for any color leached by the adsorbent and adsorbed by the glass containers. Each experimental point is the average of three independent runs and all the results were reproducible with ±3% error limit.

3. Results and discussion

Neither changes appeared in the absorption spectrum nor additional peaks formed for the dye solution after shaking it with the adsorbent. This indicated that there were no breakdown product(s) of the dye and also supported the fact that the dye removal from the solution in this study was through the mechanism of adsorption [8].

3.1. Effect of adsorbent surface modification

Experiments were conducted with AC, SWC or PWC at constant adsorbent dosage (0.2 g/50 mL), pH (neutral), and temperature (26 ± 1 °C) for 120 min by varying methylene blue concentration (50–500 mg/L). It is evident from Fig. 1 that AC has more adsorption efficiency in comparison to SWC and PWC at higher initial dye concentration studied. Decolourization of wastewater was 97%, 97% and 96% by AC, PWC and SWC, respectively, at 50 mg/L dye concentration. But at higher dye concentrations adsorption efficiency was in the order AC > PWC > SWC. At 500 mg/L concentration, AC was 1.93 and 3.4 times more effective than PWC and SWC, respectively. The difference in adsorption capacity can be attributed to better physical structure and surface area of AC than PWC and SWC [8].

3.2. Effect of pH

The pH value of the solution is an important process controlling parameter in adsorption, and the initial pH value of the solution has more influence than the final pH [21]. To study the effect of pH on methylene blue adsorption onto AC, SWC and PWC, the experiments were carried out at 100 mg/L initial dye concentration with 0.4 g/100 mL adsorbent dosage at 26 ± 1 °C for 120 min equilibrium time. The dye adsorption by AC was 98.4% in the studied pH range followed by PWC (98.5–98.9%) and SWC (66.2–72.1%) (Fig. 2). The dye adsorption efficiency was not effected by pH expect minor variations in the pH range of 3–10. Similar observations have been reported for the adsorption of methylene blue by giant Duckweed [21] and sawdust [15]. The percentage sorption of dye was not significantly altered ($P > 0.05$) when the initial pH was increased from 3 to 10. Hence neutral pH was chosen while studying the effect of other system variables on adsorption process. Final pH of solution was higher than initial pH. This increase in pH was more at 5–7 pH values. Basic dye upon dissolution released colored dye cation in solution. The adsorption of these charged dye groups onto the adsorbent surface was primarily influenced by the surface charge on the adsorbent which in turn was influenced by pH of the solution. The parent material used to prepare the adsorbents was composed of many constituents including polar functional groups which may have provided negative charge to the adsorbents. Hence, the adsorbent surfaces had a high adsorption capacity for cationic (basic) dyes.

3.3. Effect of initial dye concentration on dye removal

The effect of initial dye concentration in the solution on the rate of adsorption onto AC, SWC and PWC was studied. The experiments were carried out at fixed adsorbent dose (0.2 g/50 mL) in the test solution, temperature (26 ± 1 °C), pH (neutral) and at different initial concentrations of methylene blue (50 mg/L, 100 mg/L, 150 mg/L, 200 mg/L and 250 mg/L) for different time intervals (15, 30, 45, 60, 90 and 120 min). Dye removal by AC was in the range of 95–97% at all studied concentrations. The percent dye removal versus time curves are single, smooth and continuous leading to saturation, suggesting the possibility of monolayer coverage of methylene blue on the outer surface of the adsorbent (Figs. 3 and 4)

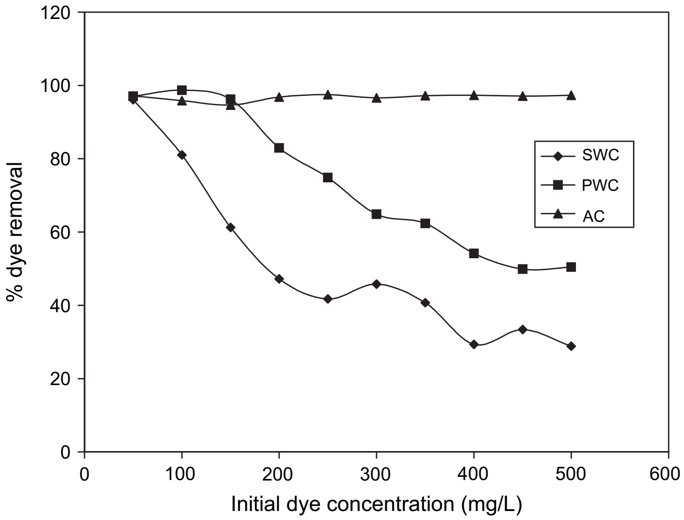

Fig. 1. Effect of adsorbent surface change on dye removal (pH = constant, adsorbent dose = 0.2 g/50 mL, and equilibrium time = 2 h).

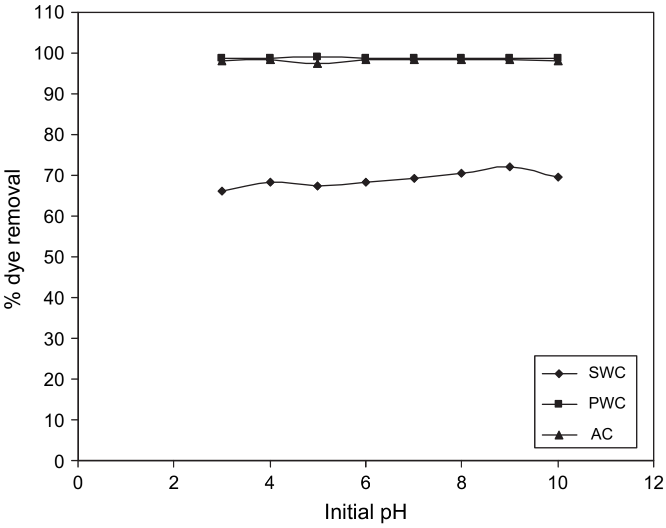

Fig. 2. Effect of pH on methylene blue adsorption (dye concentration = 100 mg/L, adsorbent dose = 0.4 g/100 mL, and equilibrium time = 2 h).

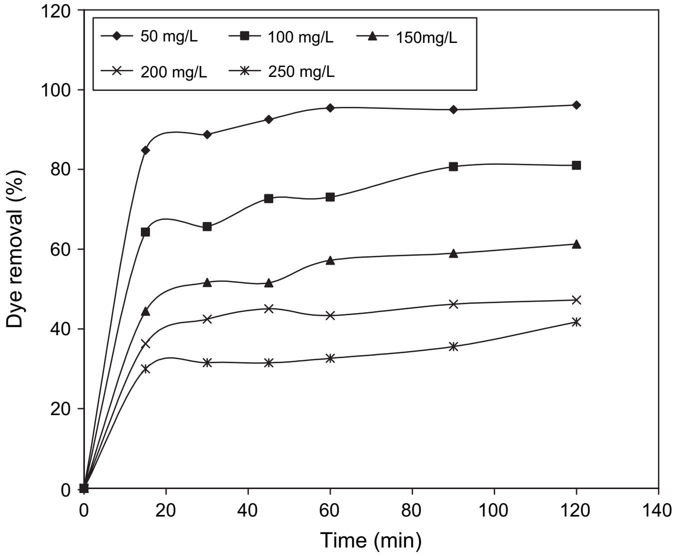

Fig. 3. Effect of initial dye concentration on the adsorption of methylene blue onto SWC (adsorbent dose = 0.2 g/50 mL, and pH = constant (neutral)).

[22]. Percent adsorption efficiency of SWC and PWC decreased with increase in initial dye concentration in solution (Figs. 3 and 4). Though the percent adsorption decreased with increase in initial dye concentration, the actual amount of dye adsorbed per unit mass of adsorbent increased with increase in dye concentration in test solution. The unit adsorption for SWC was increased from 12.1 mg/g to 26.1 mg/g as the methylene blue concentration in the test solution was increased from 50 mg/L to 250 mg/L. Similarly, unit adsorption for PWC was increased from 12.2 mg/g to 47.1 mg/g as the dye concentration in the test solution was increased from 50 mg/L to 250 mg/L. Maximum dye was sequestered from the solution within 15 min after the start of every experiment. After that, the concentration of methylene blue in liquid phase remained almost constant. The equilibrium was established quickly within 15 min at all studied concentrations by AC. However, SWC, PWC took about 60 and 90 min, for equilibrium attainment. This may be due to the fact that SWC and PWC have macro- and micropores. In the process of dye adsorption initially dye molecules have to first encounter the boundary layer effect and then they have to diffuse from boundary layer film onto adsorbent surface and then finally, they have to diffuse into the porous structure of the adsorbent. These observations are consistent with the observations of other co-workers [15,20,22] for the biosorption of basic dyes by water hyacinth, duckweed and sawdust. This phenomenon will take relatively longer contact time [13]. The time profile of dye uptake is a single, smooth and continuous curve leading to saturation, suggesting the possible monolayer coverage of dye on the surface of the adsorbent [13].

3.4. Effect of adsorbent dosage on dye removal

The adsorption of methylene blue onto SWC, PWC and AC was studied by varying the adsorbent quantity (0.2, 0.4, 0.6, 0.8, 1.0 g/100 mL) in the test solution while keeping the initial dye concentration (100 mg/L), temperature (26 ± 1 °C) and pH (neutral) constant at all different time intervals. The percent adsorption was increased and equilibrium time was decreased with adsorbent dosage (Figs. 5 and 6). The adsorption was 97% by AC even at the minimum studied adsorbent dosage (0.2 g/100 mL) within 15 min. The adsorption increased from 52.8% to 97.2%, as the SWC dosage was increased from 0.2 to 1.0 g/100 mL under the optimized conditions (Fig. 5). For PWC, adsorption increased from 76.3% to 99.1%, as the dosage was increased from 0.2 to 1.0 g/100 mL (Fig. 6). Maximum dye removal was achieved within 60–90 min after which methylene blue concentration in the test solution was almost constant. Increase in adsorption with adsorbent dose can be attributed to increased adsorbent surface area and availability of more adsorption sites. But

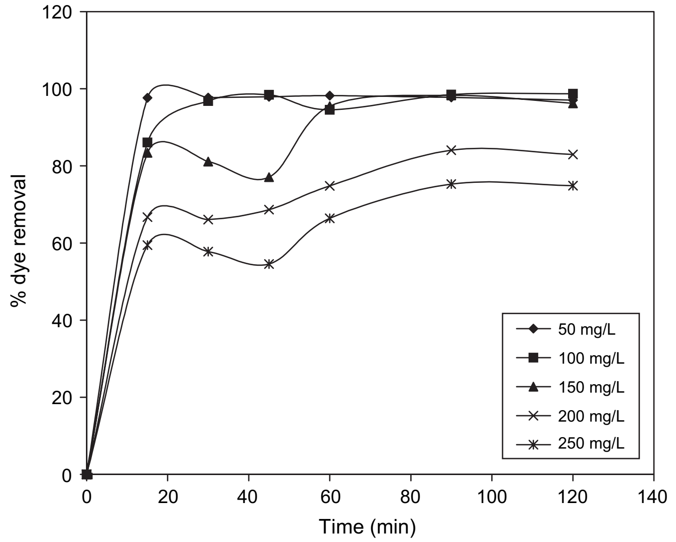

Fig. 4. Effect of initial dye concentration on the adsorption of methylene blue onto PWC (adsorbent dose = 0.2 g/50 mL, pH = constant (neutral)).

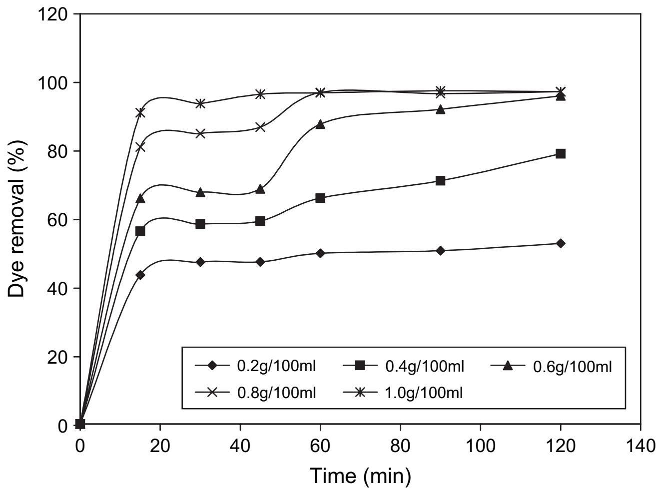

Fig. 5. Effect of adsorbent mass on adsorption of methylene blue onto SWC (dye concentration = 100 mg/L, volume of sample = 100 mL, and pH = constant (neutral)).

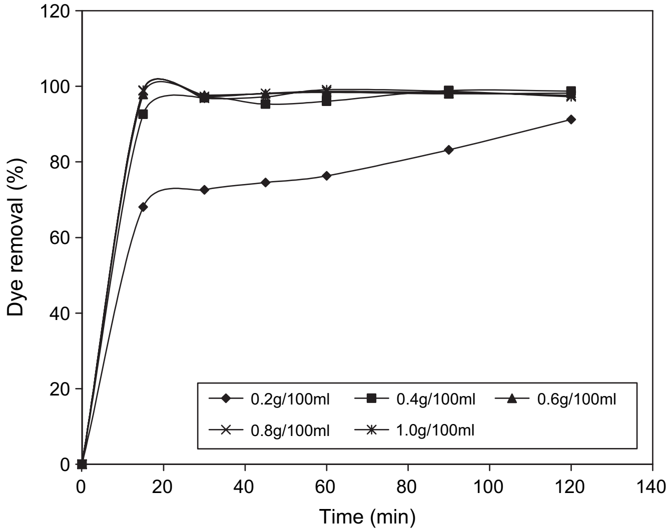

Fig. 6. Effect of adsorbent mass on adsorption of methylene blue onto PWC (dye concentration = 100 mg/L, volume of sample = 100 mL, and pH = constant (neutral)).

unit adsorption decreased with increase in adsorbent dose. For SWC, unit adsorption was decreased from 26.4 mg/g to 9.7 mg/g as the adsorbent dose increased from 0.2 to 1.0 g/100 mL in the test solution. For PWC, unit adsorption was decreased from 41.6 mg/g to 9.9 mg/g as the PWC dose increased from 0.2 to 1.0 g/100 mL in the test solution. This may be attributed to overlapping or aggregation of adsorbent surface area available to methylene blue and an increase in diffusion path length. Equilibrium time was lesser at higher adsorbent doses [15].

3.5. Adsorption isotherm

Adsorption equilibrium data which express 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 removal of methylene blue in the present investigations were analysed using Langmuir adsorption model:

$$\frac{C_e}{q_e} = \frac{1}{Q_0 b} + \frac{C_e}{Q_0} \tag{1}$$

where, C_e (mg/L) is the equilibrium concentration of dye, q_e is the amount of dye adsorbed at equilibrium time (mg/g) and Q_0 and b are Langmuir constants related to adsorption capacity and energy of adsorption, respectively. The linear plots of C_e/q_e versus C_e (Fig. 7) suggest the applicability of the above model for the present system, showing formation of monolayer coverage of the adsorbate at the outer surface of adsorbent. The values of Q_0 and b were determined from the slope and intercept of the plots, respectively, and are given in Table 1. The essential characteristics of Langmuir isotherm can be expressed in terms of dimensionless constant separation factor for equilibrium parameter, R_L [23] which is defined as given below:

$$R_L = \frac{1}{(1 + bC_0)} \tag{2}$$

where C_0 is the initial dye concentration (mg/L) and b is the Langmuir constant (L/mg). The values of R_L for the studied system at different initial concentrations were found to be in between 0 and 1 (Table 1) which indicate favourable adsorption of dye onto the adsorbent. Freundlich isotherm was also applied for the adsorption of dye [24]:

$$\log_{10}(x/m) = \log_{10}(K_f) + (1/n)\log_{10}(C_e) \tag{3}$$

where, x is the amount of dye adsorbed (mg), m is the weight of adsorbent used (g), and C_e is the equilibrium concentration of dye in solution (mg/L). K_f and n are the constants incorporating all factors affecting the adsorption process (adsorption capacity and intensity). Linear plots of $\log_{10}$ (x/m) versus $\log_{10} C_e$ shows that adsorption also follows Freundlich isotherm well (Fig. 8). Values of K_f and n were calculated from the intercept and slope of the plot and are given in Table 1. Mckay et al. [25] have reported that an 'n' value in the range 2–10 indicates favourable adsorption. Determination coefficient, R^2 of both Langmuir and Freundlich equation, is near to unity, indicating the good agreement data with both the isotherm models.

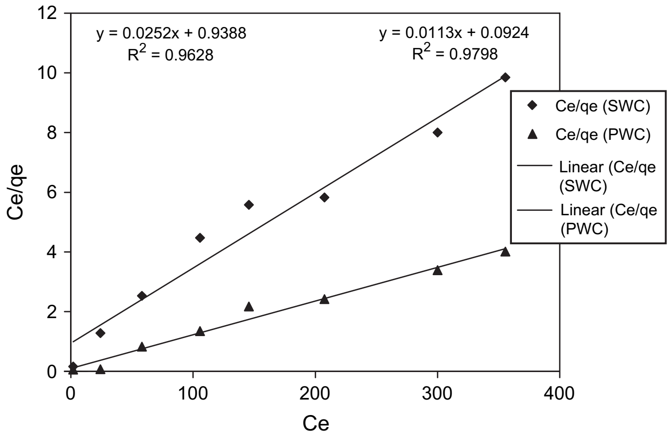

Fig. 7. Langmuir plot of C_e/q_e versus C_e for dye adsorption.

Table 1
Values of Langmuir and Freundlich parameters obtained for the studied systems

Adsorbent	Methylene blue dye					
	Langmuir parameters			Freundlich parameters		
	Q_0	b	R^2	K_f	n	R^2
SWC	39.68	0.027	0.9628	10.46	4.75	0.9258
PWC	88.49	0.071	0.9798	21.85	6.55	0.9559

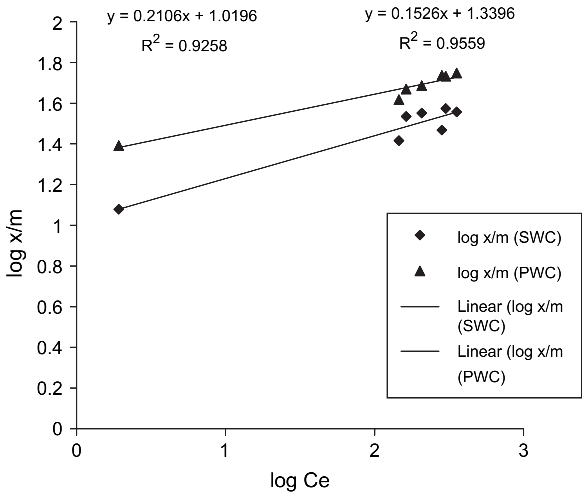

Fig. 8. Freundlich plot of log *x*/*m* versus log C_e for dye adsorption.

4. Conclusion

The removal of methylene blue from wastewater using AC, SWC and PWC has been investigated under different experimental conditions in batch mode. The adsorption of methylene blue was dependent on adsorbent surface characteristics, adsorbent dose and methylene blue concentration in wastewater. Initial pH of solution had no marked effect on the adsorption for this dye. Higher dye removal by SWC and PWC was possible provided the initial dye concentration was low in solution. The adsorption follows both Langmuir and Freundlich isotherm models. The fitness of Langmuir model in the present system shows the formation of monolayer coverage of the adsorbate at the outer surface of the adsorbent. AC is an expensive material and regeneration is essential, whereas SWC and PWC are economically cheap and so regeneration is not necessary. Parthenium is an unwanted weed, growing throughout the country without any input and effort. The data may be useful for designing and fabricating an economically cheap treatment process using batched or stirred tank flow reactors for the removal of methylene blue from dilute industrial wastewaters.

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