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Removal of malachite green dye from aqueous solution by adsorption using agro-industry waste: a case study of *Prosopis cineraria*

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Abstract

Adsorbents prepared from *Prosopis Cineraria* sawdust—an agro-industry waste—were successfully used to remove the malachite green from an aqueous solution in a batch reactor. The adsorbents included formaldehyde-treated sawdust (PCSD) and sulphuric acid-treated sawdust (PCSDC). The effects of adsorbent surface change, initial pH, initial dye concentration, adsorbent mass and contact time on dye removal have been determined. Similar experiments were carried out with commercially available coconut based carbon (GAC) to evaluate the performance of PCSD and PCSDC. The adsorption efficiency of different adsorbents was in the order GAC > PCSDC > PCSD. Kinetic parameters of adsorption such as the Lagergren pseudo-first-order constant and the intra particle diffusion were determined. An initial pH of the solution in the range 6–10 was favourable for the malachite green removal for both the adsorbents. These experimental studies have indicated that PCSD and PCSDC could be employed as low-cost alternatives in wastewater treatment for the removal of dyes.

Keywords: Sawdust; Adsorption; Batch mode; Malachite green; Kinetics

1. Introduction

Dyes are used in large quantities in many industries including textile, leather, cosmetics, paper, printing, plastic, pharmaceuticals, food, etc. to colour their products. Presently more than 9000 dyes are incorporated in colour index belonging to various chemical application classes. The textile industry alone accounts for two thirds of the total dye stuff production, about 10–15% of the dyes used come out through the effluent [1]. The effluents from dye manufacturing and consuming industries are highly colored coupled with high chemical and biological demands (COD and BOD) and suspended solids. Discharge of such effluents imparts colour to receiving streams and affects its aesthetic value. Colour interferes with penetration of sunlight into waters, retards photosynthesis, inhibits the growth of aquatic biota and interfere with gas solubility in water bodies [2]. Direct discharge of these effluents into municipal wastewater plants and/or environment may cause the formation of toxic carcinogenic breakdown

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products. Over 90% of some 4000 dyes tested in an ETDA (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 [3].

Recently the Minimum National Standards (MINAS) have been developed for different industries by Central Pollution Control Board, New Delhi (India). Accordingly, industries have been required to reduce the pollution load including decolourization of their effluents before disposal into surface waters, municipal sewage system or on land.

Dyes laden wastewater is usually treated by physical or chemical processes. These include flocculation, electro-floatation, precipitation, electro-kinetic coagulation, ion exchange, membrane filtration, electrochemical destruction, irradiation, ozonation and Katox treatment method involving the use of activated carbon and air mixtures [2]. However, these processes are costly and cannot effectively be used to treat the wide range of dye wastewater. Adsorption has been found to be superior to other techniques for wastewater treatment in terms of initial cost, simplicity of design, ease of operation and insensitivity to toxic substances. Activated carbon (granular or powder) is the most widely used adsorbent with great success because of its large surface area, microporous structure, high adsorption capacity, etc. [4]. But its use is limited due to its high cost [5].

This has lead to search for cheaper substitutes. Several agro-industrial wastes/ residues have been investigated for the adsorption of dyes with varying success. These include hard wood [6], banana pith [7], Indian rosewood [8], waste coir pith [9], bagasse pith [10], neem leaf powder [11], banana and orange peels [12], barley husk [13], cassava peel [14], rice husk and Mahogany sawdust [15], etc. New economical, easily available and highly effective adsorbents are still needed. *Prosopis cineraria* (family: leguminosae, sub-family: minuscule) is a commonly grown perennial tree in dry-land agroforestry in dry and arid regions of Northern Western India. The wood of this tree is used for parquet floors, furniture, and turnery items, fence post, piling etc. Sawdust of *Prosopis cineraria* is a waste by-product of timber industry that is either used as domestic fuel or a packing material.

In our laboratory, the work is in progress on the possibility of the use of agroindustry wastes for industrial pollution control. The aim of the present work was to study the adsorption capacity of differently treated sawdust of *Prosopis cineraria* for a dye removal, malachite green, from aqueous solution under different experimental conditions and their performance was evaluated against commercially available granular carbon (GAC).

2. Experimental

2.1. Adsorbents

2.1.1. Granular activated carbon (GAC)

GAC used in the present study was coconut shell based and was supplied by S.D. Fine Chemicals, Mumbai, India.

Fine Chemicals, Mumbai, India. It was used as such without further grinding and sieving. The general characteristics of GAC (as provided by the supplier) were: Particle size $= <300$ mesh; surface area = 800 m^2/g; moisture = 3% (maximum); ash content = 2.5% (maximum); acid soluble = 2.5% (maximum); water soluble = 1.5% (maximum), pH value = 6.5–7.5; methylene blue adsorption = 270 mg/g.

2.1.2. Formaldehyde-treated Prosopis cineraria sawdust (PCSD)

Prosopis cineraria (Vernacular name *Khejri*) tree saw dust collected from a local sawmill was washed with hot distilled water and then dried in sunlight until all the moisture was evaporated. The material was ground to a fine powder in still mill. To immobilize the colour and water-soluble substances the ground powder was treated with 1% formaldehyde in the ratio of 1:5 (sawdust: formaldehyde, w/v) at 50 °C for 4 h. The sawdust was filtered out, washed with distilled water to remove free formaldehyde and activated at 80 °C in a hot air oven for 24 h. The resulting material was sieved in the size range of 20–50 mesh ASTM. The material was placed in an airtight container for further use.

2.1.3. Sulphuric acid treated Prosopis cineraria sawdust (PCSDC)

One part of dried PCSD was mixed with one part of concentrated sulphuric acid and heated in a muffle furnace for 24 h at 150 °C. The heated material was washed with distilled water and soaked in 1% sodium bicarbonate solution overnight to remove residual acid. The material was dried in an oven at 105 °C for 24 h and sieved in the size range of 20–50 mesh ASTM and used for the further study. PCSDC was characterized by adopting the standard procedures [16]. The various physico-chemical characteristics of PCSDC were: particle size = 20–50 mesh ASTM; surface area = 376 m^2/g; apparent density = 1.64 g/ml; bulk density = 0.69 g/ml; ash content = 3.45%; moisture content = 0.72%; CEC = 0.84 meq/g; water-soluble matter = 1.38%; acid soluble matter (4 N HCl) = 2.8%; 2 N NaOH soluble matter = 1.83%; and EC = 0.10 mS/cm. All adsorbents were dried at 110 °C overnight before the adsorption experiments.

2.2. Dye solution

Malachite green dye is widely used in textile, paper and carpet industries. Malachite green dye [C.I. = 42,000B, chemical formula = $C_{23}H_{26}0N_2$ FW = 346; nature = basic green; mp = 112–114 °C and λ_{max} = 615 nm (reported) and 617 nm (experimentally obtained by us)] was supplied by S.D. Fine Chemicals, Mumbai, India. An accurately weighed quantity of the dye was dissolved in double-distilled water to prepare stock solution (500 mg/l). Experimental solutions of the desired concentration were obtained by successive dilutions.

2.3. Methods

In each adsorption experiment, 100 ml of dye solution of known concentration and pH was added to 0.4 g of GAC, PCSD or PCSDC in a 250-ml round bottom flask at 27 ± 1 °C and the mixture was stirred on a rotary orbital shaker at

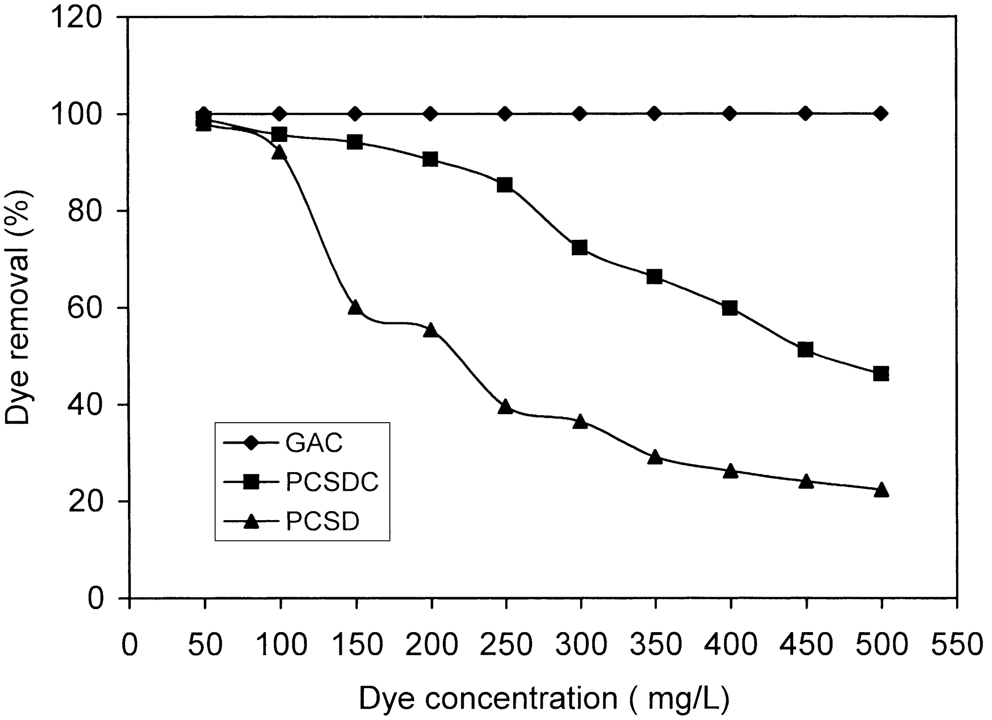

Fig. 1. Effect of adsorbent surface change on malachite green adsorption (adsorbent dose = 0.4 g/100 ml, equilibrium time = 3 h).

160 rpm. The samples were withdrawn from the shaker at the predetermined time intervals, and adsorbent was separated from the solution by centrifugation at 4500 rpm for 5 mm. The absorbance of the supernatant solution was estimated to determine the residual concentration. Residual dye concentration was determined using absorbance values measured before and after the treatment, at 617 nm with an Elico spectrophotometer (model SL-150) using silica cells of path length 1 cm. Experiments were carried out at initial pH values ranging from 2 to 10; initial pH was controlled by the addition of dilute HCI or NaOH solutions. Kinetics of adsorption was determined by analyzing adsorptive uptake of the dye from aqueous solution at different time intervals. Two main system variables, initial dye concentration in the test solution and adsorbent dosage, were varied to investigate their effect on the adsorption kinetics. Blank runs, with only the adsorbents in 100 ml of double-distilled water, were conducted simultaneously at similar conditions to account for any colour leached by the adsorbents and adsorbed by glass containers. Samples were diluted with double-distilled water if absorbance values exceeded 0.900. Each experiment result was an average of three independent adsorption tests.

3. Results and discussion

3.1. Effect of adsorbent surface modifications

Experiments were conducted with GAC, PCSD and PCSDC as adsorbents at different dye concentrations (50–500 mg/l) whilst maintaining the temperature (27±1 °C) and equilibrium time constant (3 h). Dye removal was 99±1% at 50 mg/l dye concentration by all the adsorbents. But at higher dye concentrations, adsorption capacity

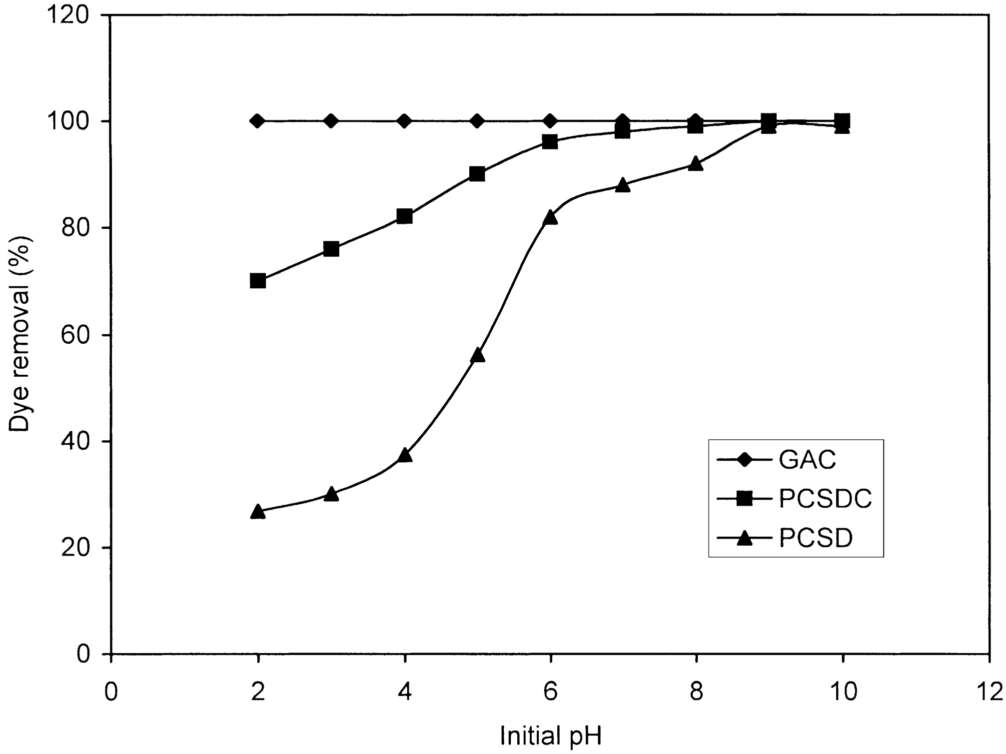

Fig. 2. Effect of pH on malachite green adsorption (dye concentration = 250 mg/l, adsorbent dose = 0.4 g/100 ml equilibrium time = 3 h).

was in the order GAC > PCSDC > PCSD (Fig. 1). At 500 mg/l dye concentration, GAC had 2.1 and 4.3 times more adsorption capacity than PCSDC and PCSD, respectively. The difference in adsorption capacity can be attributed to better physical structure and surface area of GAC than PCSDC and PCSD.

3.2. Effect of pH

To study the effect of pH on malachite green adsorption on GAC, PCSDC and PCSD, the experiments were carried out at 250 mg/l initial dye concentration with 0.4 g/100 ml adsorbent mass at 27 ± 1 °C for 3 h equilibrium time. The dye adsorption by GAC was unaffected by pH changes in the range of 2–10. PCSDC had maximum dye adsorption (96%) over the pH range of 6–10 which decreased to 70% at pH of 2.0. By PCSD, dye removal was minimum (26.8%) at the pH of 2.0, which increased to 99% at pH 10 (Fig. 2). Low pH (2–5) was unfavourable for malachite green adsorption by PCSDC and PCSD. As initial pH of the test solution decreased, the number of negatively charged adsorbent sites decreased and positively charged sites increased which did not favour the adsorption of positively charged dye cations [9] due to electrostatic repulsion. Also, lower adsorption of malachite green at acidic pH is due to the presence of excess H^+ ions competing with dye cations for the adsorption. This, however, did not explain the constant removal by GAC at all the studied pH values. There might be another mode of adsorption, for example ion exchange.

3.3. Effect of initial dye concentration

The influence of the initial concentration of malachite green in the solutions on the rate of adsorption on GAC, PCSDC and PCSD was studied. The experiments were carried out at fixed adsorbent dose (0.4 g/100 ml) in the test solution, 27 ± 1 °C

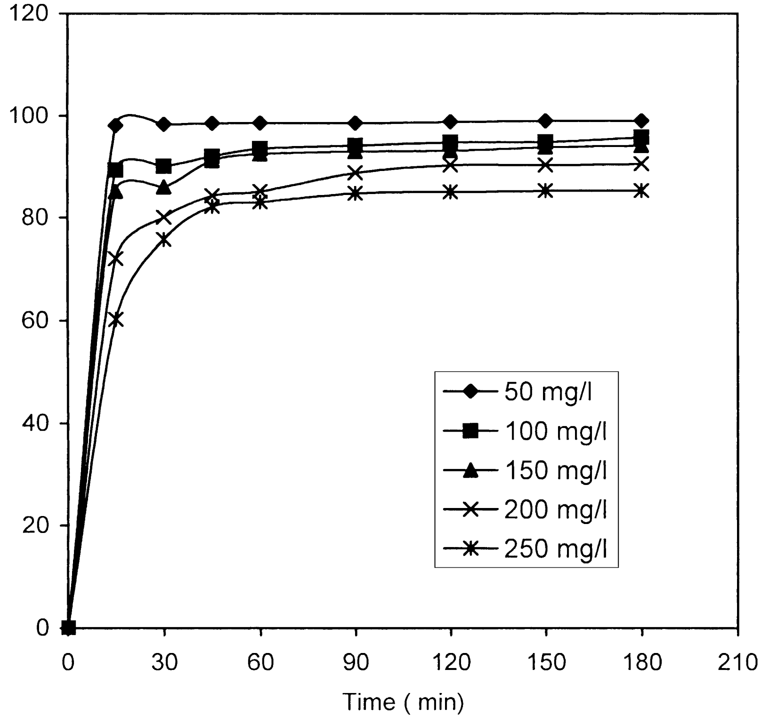

Fig. 3. Effect of initial dye concentration on the adsorption of malachite green on PCSDC (adsorbent dose = 0.4 g/100 ml, pH = natural).

temperature, natural pH and at different initial concentrations of malachite green (50, 100, 150, 200 and 250 mg/l) for different time intervals up to equilibrium time (3 h). Dye removal by GAC was 100% at all the studied dye concentrations. The percentage adsorption efficiency of PCSDC and PCSD decreased with increase in initial dye concentration in the solution (Figs. 3 and 4). Adsorption and initial dye concentration correlation was exponential in nature for PCSDC and PCSD. This accord well with the findings of other investigators [17]. Though the percentage adsorption was decreased with increase in initial dye concentration but the actual amount of dye adsorbed per unit mass of adsorbent was increased with increase in dye concentration in the test solution. Maximum dye was sequestered from the solution with in 30 mm after the beginning for every experiment. After that, the concentration of malachite green in the liquid phase remained almost constant. The equilibrium was established quickly within 15 min at all the studied concentrations by GAC. However, PCSDC and PCSD took about 45 and 60 min, respectively for equilibrium attainment. This may be due to the fact that PCSDC and PCSD have macro and micro pores. In the process of dye adsorption, initially dye molecules have to first encounter the boundary layer effect and then it has to diffuse from boundary layer film onto adsorbent surface and then finally it has to diffuse into the porous structure of the adsorbent. This phenomenon will take relatively longer contact time [15]. 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 [15].

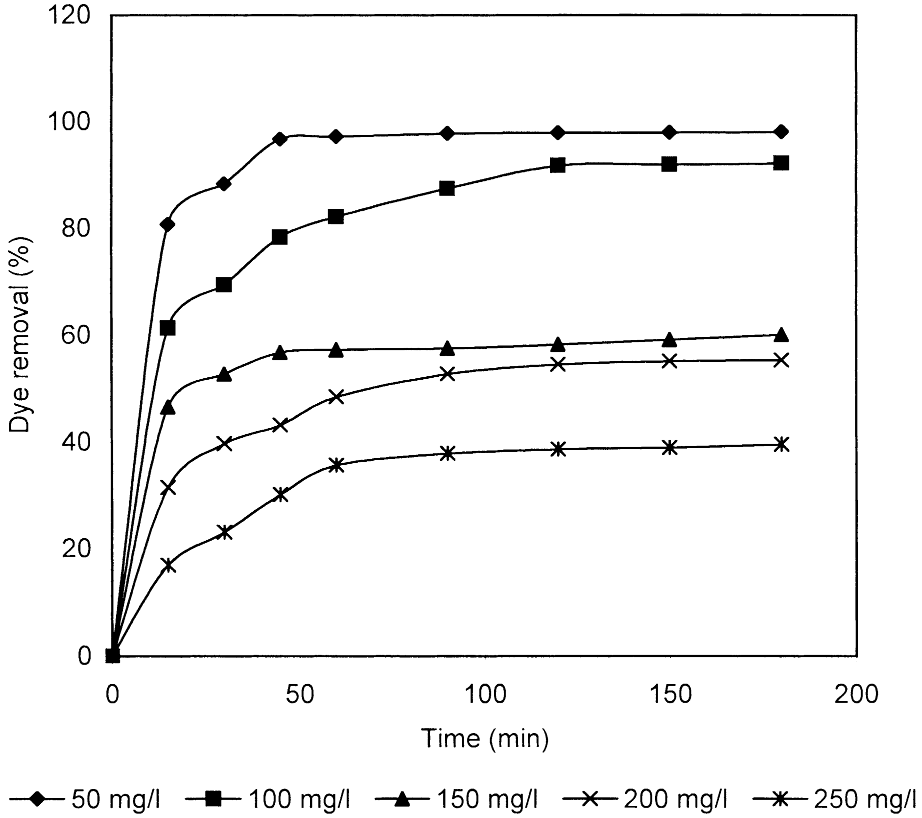

Fig. 4. Effect of initial dye concentration on the adsorption of malachite green on PCSD (adsorbent dose = 0.4 g/100 ml, pH = natural).

3.4. Effect of adsorbent mass

The adsorption of malachite green on GAC, PCSDC and PCSD was studied by changing the quantity of adsorbent (0.2, 0.4, 0.6, 0.8 and 1.0 g/100 ml) in the test solution while keeping the initial dye concentration (250 mg/l), temperature (27±1 °C) and pH (natural) constant at different contact times for equilibrium time (3 h). The percent adsorption was increased and equilibrium time was decreased with adsorbent dose (Figs. 5 and 6). The adsorption was 100% by GAC even at the minimum studied adsorbent dose (0.2 g/100 ml) within 15 min. The adsorption increased from 52.6 to 100%, as the PCSDC dose was increased from 0.2 to 1.0 g/100 ml at equilibrium time. For PCSD, adsorption increased from 22.3 to 73.2% as the adsorbent dose was increased from 0.2 to 1.0 g/100 ml. Maximum dye removal was achieved within 30–45 min after that malachite green concentration in the test solution was almost constant. Increase in the adsorption with adsorbent dose can be attributed to increased adsorbent surface area and availability of more adsorption sites. But unit adsorption was decreased with increase in adsorbent dose. For, PCSDC, unit adsorption was decreased from 65.8 to 25.0 mg/g as the adsorbent dose was increased from 0.2 to 1.0 g/100 ml in the test solution. This may be attributed to overlapping or aggregation of adsorption sites resulting in decrease in total adsorbent surface area available to malachite green and an increase in diffusion path length. Equilibrium time was lesser at higher adsorbent doses.

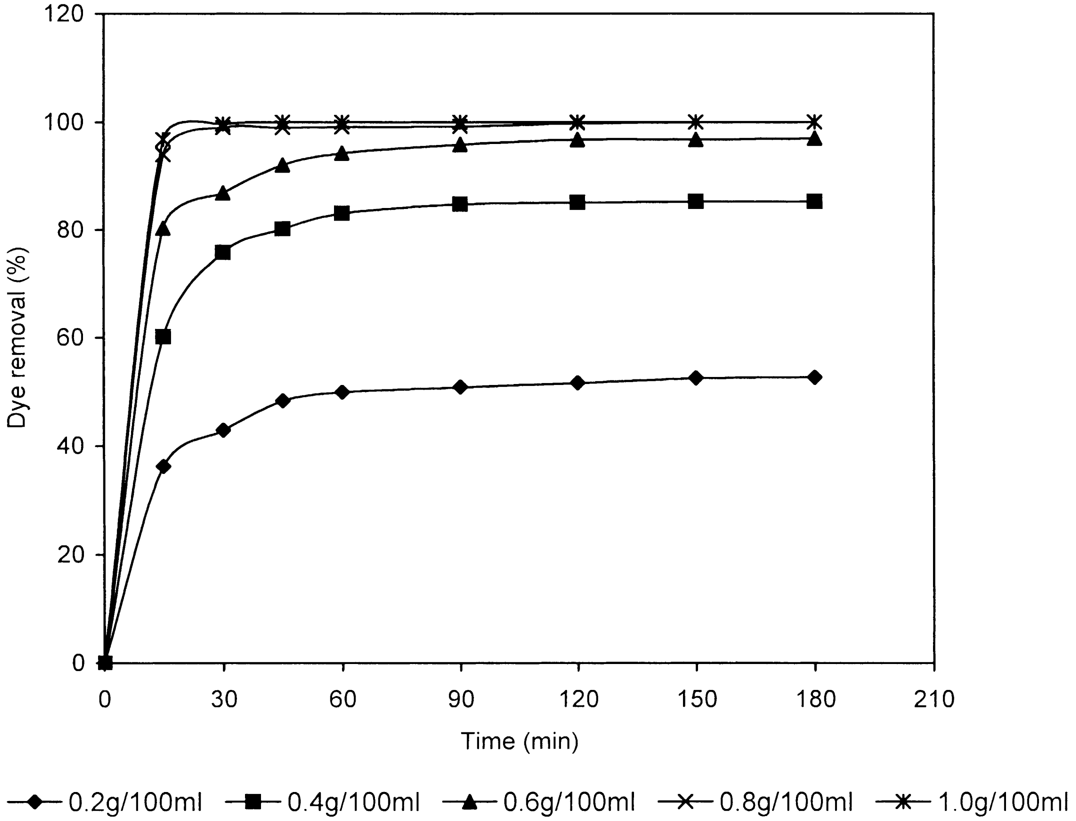

Fig. 5. Effect of adsorbent mass on the adsorption of malachite green on PCSDC (dye concentration = 250 mg/I, volume of sample = 100 ml, pH = natural).

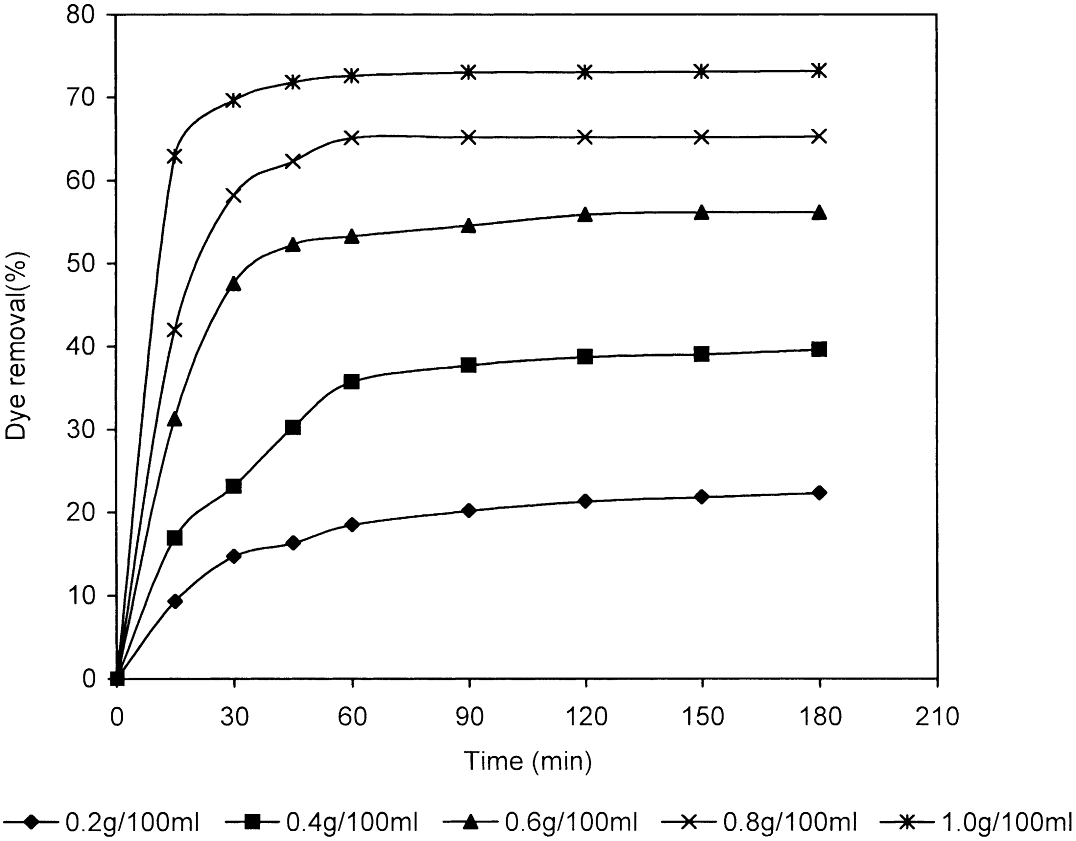

Fig. 6. Effect of adsorbent mass on the adsorption of malachite green on PCSD (dye concentration = 250 mg/l, volume of sample = 100 ml, pH = natural).

3.5. Adsorption dynamics

The specific rate constants, k_{ad}, for the adsorption of malachite green on PCSDC and PCSD were calculated using the pseudo-first-order Lagergren equation.

$$\mathrm{Log}_{10}(qe - q) = \log_{10} qe - \frac{k_{ad} \times t}{2.303}$$

where qe and q (both in mg/g) are the amounts of malachite green adsorbed at equilibrium time and at any time 't' respectively. The straight line plot of log (qe–q) vs. t indicated the validity of Lagergren equation for the present system and also explained that process followed the pseudo-first order kinetics. The values of k_{ad} calculated from the slopes of the plots were 0.0268 and 0.0534 min^{-1} for PCSDC at 0.2 and 0.4 g adsorbent doses per 100 ml of the test solution; and 0.0215 and 0.0332 min^{-1} for PCSD at similar adsorbent doses. These values are comparable with the results of other investigators [7,8,12,15].

The plot of adsorbate uptake vs. square root of time ($t^{1/2}$) has commonly been used to describe whether adsorption process is controlled by diffusion in the adsorbent particles and consecutive diffusion in the bulk of solution [18]. Fig. 7 shows that there are two separate regions in the curve. The initial portion is attributed to the bulk diffusion and the linear portion to intra-particle diffusion [19].

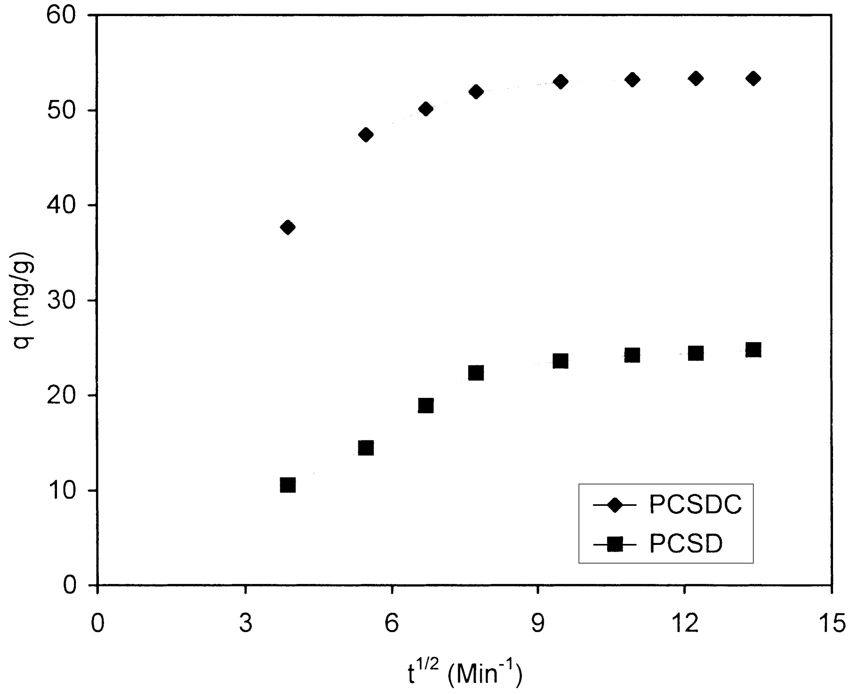

Fig. 7. Test of intraparticle diffusion model for adsorption of malachite green on PCSDC and PCSD.

4. Conclusion

The result of present investigations showed that PCSD and PCSDC prepared from *Prosopis cineraria* sawdust, have lower adsorption efficiency than GAC at higher dye concentrations. The adsorption was highly dependent on pH, initial dye concentration and adsorbent mass. The optimum pH for dye removal by PCSD and PCSDC was 6–10. Higher dye removal by PCSDC and PCSD was possible provided the initial dye concentration was low in solution. Adsorption kinetics followed Lagergren first-order kinetics model. GAC is an expensive material and regeneration is essential, where as PCSDC and PCSD are cheap so regeneration is not necessary. *Prosopis cineraria* is a commonly grown agro-forestry tree in Northern States of India and its saw dust is easily available in the countryside, so the use of these low-cost materials by small scale dyeing unit using batched or stirred-tank flow reactors is recommended for dilute solution.

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