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Biosorption Studies for the Removal of Malachite Green from its Aqueous Solution by Activated Carbon Prepared from Cassava Peel

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Abstract: The association of dyes with health related problems is not a new phenomenon. The effectiveness of carbon adsorption for dye removal from textile effluent has made it an ideal alternative to other expensive treatment methods. The preparation of activated carbon from agricultural waste could increase economic return and reduce pollution. Cassava peel has been used as a raw material to produce activated carbon. The study investigates the removal of malachite green dye from its aqueous solution. The effects of condition such as adsorbent dosage, initial dye concentration, pH and contact time were studied. The adsorption capacity was demonstrated as a function of time for malachite green from aqueous solution by the prepared activated carbon. The results showed that as the amount of the adsorbent was increased, the percentage of dye removal increased accordingly. Higher adsorption percentages were observed at lower concentrations of malachite green dye. Silver nitrate treated cassava peel showed a better performance compared to Sulphuric acid treated and raw carbons, thus making it an interesting option for dye removal textile effluent.

Keywords*:* Malachite green, Adsorption, Cassava peel, Activated carbon

Introduction

The textile industry is, in the forefront, in the use of dyes in its operations[1] with more than 9,000 types of dyes incorporated in the colour index. Similarly, more than 70,000 tons of approximately 10,000 different types of dyes and pigments are produced annually worldwide, of which 20-30% are wasted in industrial effluents during dyeing and finishing processes in the textiles industries[2].

Dyes used in the textile industry are particularly difficult to remove by the conventional waste treatment methods because of their stability towards light and oxidizing agents and resistance towards aerobic digestion. For removal of colour from industrial wastewater, adsorption has become one of the most economic and effective methods[3-7]. The activated carbon adsorption treatment has been proven to be an effective replacement for the combined biological and chemical treatment although at a relatively high cost. The need of low cost replacements for activated carbon initiated a number of studies[8].

Adsorption process is one of the effective methods for removal of dyes from textile effluent. Since commercially available activated carbon is very expensive, now the research is focusing on the use of low cost adsorbents derived from agricultural and wood wastes, such as bagasse[9], coir pith[10], banana pith[11], tree fern[12], rice husk[13] *etc*. This investigation is aimed at examining the capacity and efficiency of dye removal from aqueous solution by activated carbon prepared from cassava peel. The effects of initial dye concentration, contact time, pH and carbon dosage are also assessed.

Experimental

The cassava peel was collected from the nearby sago industry in Salem District, Tamilnadu, India. Then it was washed thoroughly with water to get rid of dust particles. Then it was dried under the direct sunlight to remove the excess moisture. Then the dried peel was placed in a muffle furnace (Naber, Germany, Model: L51/S) for 24 h at 150 ^oC and this material is used as raw cassava peel carbon.

Silver nitrate treated cassava peel carbon

A part of the above carbon was ground to powder and then treated with 0.5 N $AgNO_3$ solution (1:1) for 8 h. Then the carbon was washed several times to remove excess $AgNO_3$ present in it. Then the dried peel was placed in a muffle furnace for 24 h at 150 ^oC and this material is used as Silver nitrate treated cassava peel carbon.

Sulphuric acid treated cassava peel carbon

Other part of raw cassava peel carbon was ground to powder and then mixed with concentrated sulphuric acid (1:1). Then the carbon was washed with distilled water and soaked in 1% sodium bicarbonate solution overnight to remove residual acid. The material was dried in a muffle furnace for 24 h at 150 ^oC and this material is used as sulphuric acid treated cassava peel carbon.

Preparation of adsorbate

The malachite green is a green coloured, basic cationic dye (Chemical formula: $C_{52}H_{54}N_4O_{12}$, Molecular Weight = 927.00, λ_{max} = 617 nm). An accurately weighed quantity of malachite green dye was dissolved in double distilled water to prepare the stock solution with a concentration of 500 mg/L. The stock solution was then properly wrapped with aluminium foil and stored in a dark place to prevent direct sunlight, which may cause decolourisation. Experimental solutions of the desired concentration were obtained by successive dilutions.

Batch biosorption studies

Effect of contact time

150 mL of dye solution with initial dye concentration (50 mg/L) was prepared in a conical flask with adsorbent concentration (0.5 g/150 mL) and kept inside the incubator shaker (Environmental orbital Shaker Incubator, Deneb Instruments) at 120 rpm and 27 °C. Dye concentration was estimated spectrophotometrically at the wavelength corresponding to maximum absorbance, λ_{max}, using a spectrophotometer (JASCO UV/Vis-550). The sample was withdrawn from the shaker at predetermined time intervals. The dye solution was separated from the adsorbent by bench top centrifuge (Remi Laboratory Instruments, R41) and the absorbance of solution is measured. The dye concentration is to be measured after 15, 30, 45, 60, 90 and 120 min for the equilibrium to be attained. The equilibrium adsorption capacity (q_e) is expressed as

$$q_e = \frac{C_0 - C_e}{X}$$

Where, q_e = Amount of dye adsorbed per unit mass of adsorbent at equilibrium (mg/g). C_0= Initial dye concentration (mg/L). C_e= Final dye concentration (mg/L). X = Dose of adsorbent (g/L).

Effect of initial dye concentration

250 mL of dye solution was prepared in conical flasks with a dye concentration of 50 mg/L and adsorbent dose (0.5 g/150 mL) and kept inside the incubator shaker at 120 rpm and 27 °C. The final dye concentration readings were taken at corresponding equilibrium time. The final concentration of dye was measured using a spectrophotometer. The same procedure was followed for concentrations of 100, 150, 200 and 250 mg/L.

Effect of initial pH

150 mL of dye solution was prepared in a conical flask with dye concentration of 50 mg/L and adsorbent dose of 0.5 g/150 mL and initial pH of the conical flask is to be measured. The pH of the dye solutions was adjusted to different pH values of 3, 5, 7, 9 and 11 with dilute HCl (0.05 N) or KOH (0.05 N) solution and the value was measured by using a pH meter (Eutech Instrument, pH 510). The prepared solutions were kept inside the incubator shaker at 120 rpm and 27 °C. The final concentration of dye was measured using a spectrophotometer.

Effect of adsorbent dose

150mL of dye solution was prepared in different conical flasks with dye concentration of 50 mg/L and adsorbent doses of 0.5, 1, 2, 5, 8 g/150 mL. The solutions were kept inside the incubator shaker at 120 rpm and 27 °C. The final concentration of dye was measured using a spectrophotometer.

Results and Discussion

Effect of initial dye concentration

The influence of the initial concentration of malachite green in the solution on the rate of adsorption on silver nitrate treated, sulphuric acid treated and raw cassava peel carbons were studied. The experiments were carried out at fixed adsorbent dose (0.5 g/150 mL) in the test solution, 27 °C room temperature, pH (7.0) and at different initial concentrations of malachite green (50, 100,150, 200 and 250 mg/L) for different time intervals (15, 30, 45, 60, 90 and 120 min). Result indicating the effect of initial methyl red concentration on the dye adsorption with contact time is shown in Table 1.

Table 1. Effect of initial methyl red concentration on the dye adsorption with contact time

Initial dye concentration, mg/L	Percent dye removal with time, min					
	15	30	45	60	90	120
Silver nitrate treated cassava peel carbon						
50	90.3	92.7	93.0	93.0	93.0	93.0
100	89.7	90.4	91.0	91.0	91.0	91.0
150	85.4	87.4	89.2	89.2	89.2	89.2
200	78.2	81.1	84.2	84.2	84.2	84.2
250	70.6	73.8	78.7	78.7	78.7	78.7
Sulphuric acid treated cassava peel carbon						
50	77.4	78.8	80.6	82.7	82.7	82.7
100	66.8	68.4	69.8	70.9	70.9	70.9
150	57.8	58.9	60.9	61.7	61.7	61.7
200	44.9	48.9	50.7	52.6	52.6	52.6
250	24.7	28.9	30.8	32.8	32.8	32.8
Raw cassava peel carbon						
50	43.3	50.7	52.6	53.5	53.7	53.7
100	38.8	42.7	45.9	46.6	47.7	47.7
150	36.7	40.9	43.8	44.7	46.8	46.8
200	30.7	33.3	36.9	37.5	37.9	37.9
250	25.6	26.9	28.4	29.6	30.8	30.8

It is evident that the percent adsorption efficiency of silver nitrate treated, sulphuric acid treated and raw cassava peel carbons decreased with the increase in initial dye concentration in the solution. However, for silver nitrate treated and sulphuric acid treated cassava peel, equilibrium was achieved only after 60 and 90 min, respectively. This may be due to the fact that silver nitrate treated and sulphuric acid treated cassava peel has macro and meso pores, resulting in longer contact time between the dye molecules and the adsorbent. In the process of dye adsorption, initially dye molecules have to encounter the boundary layer effect before diffusing from boundary layer film onto adsorbent surface. This is followed by the diffusion of dye into the porous structure of the adsorbent. This phenomenon will take relatively longer contact time. 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[14]. From Figure 1, it is evident that the dye adsorption is higher than silver nitrate treated cassava peel carbon than sulphuric acid treated and raw cassava peel carbons.

Effect of adsorbent dose

The adsorption of Malachite green on silver nitrate treated and sulphuric acid treated cassava peel carbons were studied by changing the quantity of adsorbent (0.5, 1, 2, 5, 8 g/150 mL) in the test solution while keeping the initial dye concentration (50 mg/L), temperature (27 ^{o}C) and pH (7.0) constant. Experiments were carried out at different contact time.

As shown in Figure 2, the percent adsorption increased with increasing adsorbent dose. The adsorption increased from 48.9 to 94.1%, as the Silver nitrate acid treated dose was increased from 0.2 g to 1.0 g/150 mL at equilibrium time 120 min). For sulphuric acid treated cassava peel, adsorption increased from 36.4 to 83.1% as the adsorbent dose was increased from 0.2 to 1.0 g/100 mL. Maximum dye removal was achieved within 90-120 min after which malachite green concentration in the test solution was almost constant. Increase in the adsorption with adsorbent dose can be attributed to the increase in adsorbent surface area and availability of more adsorption sites.

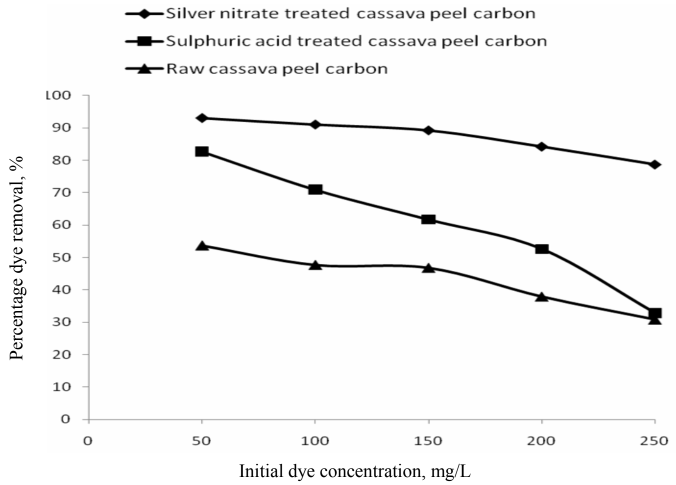

Figure 1. Effect of initial methyl red concentration on the dye adsorption

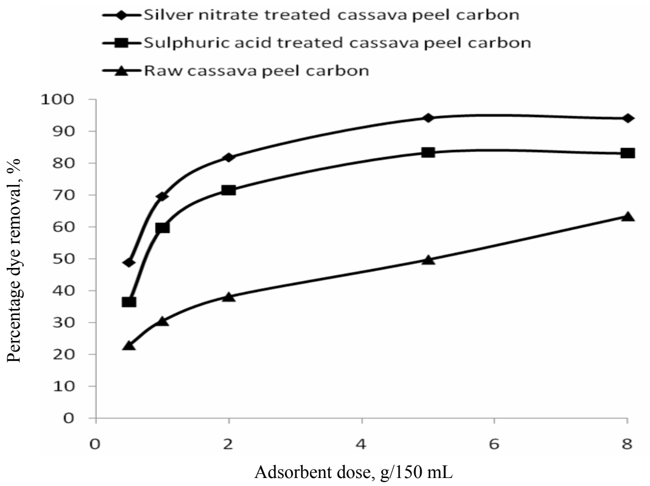

Figure 2. Effect of adsorbent dose on the dye adsorption

Effect of pH

In order to study the effect of pH on malachite green adsorption on silver nitrate treated cassava peel and sulphuric acid treated cassava peel, experiments were carried out at 50 mg/L initial dye concentration with 0.5 g/150 mL adsorbent mass at room temperature of 27 ^{o}C. Results are presented in Figure 3. In the case of raw cassava peel carbon, maximum dye removal of 59.6% was recorded at pH 11. Between pH range of 2-7, the percentage of dye removal was nearly equal. Significant increase in dye removal efficiency for sulphuric acid treated cassava peel was observed between pH ranges from 3 to 7. Although dye adsorption efficiency for Silver nitrate treated cassava peel is higher than the untreated and sulphuric acid treated cassava peel, it was not significantly affected by pH. This may be due to hydrolysis of the adsorbent in water, which creates positively charged sites[14]. Overall, the dye adsorption by silver nitrate treated was 79-96% in the studied pH range followed by sulphuric acid treated (75-89%) and raw cassava peel (44-60%).

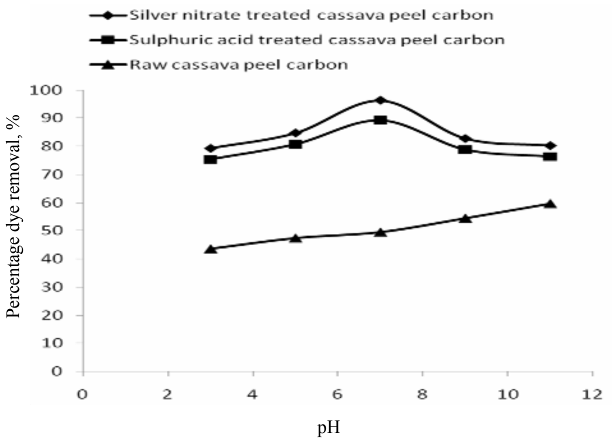

Figure 3. Effect of pH on methyl red adsorption

Conclusion

Activated carbons in different forms have a great role in modern life and help in providing energy efficient and trouble free living in clean environment. Cassava peel is a common biomass waste material and is easily available at low to negative costs. The removal of malachite green from simulated wastewater using chemical treatment of cassava peel with sulphuric acid and silver nitrate has been investigated under different experimental conditions in batch mode. The adsorption of methyl red was dependent on the contact time, adsorbent dose and initial Malachite green concentration in the wastewater. The results show that as the amount of the adsorbent was increased, the percentage of dye removal increased accordingly. Higher adsorption percentages were observed at lower concentrations of malachite green. Silver nitrate treated cassava peel showed a better performance compared to sulphuric acid treated cassava peel. This study proved that cassava peel is an attractive option for dye removal from dilute industrial effluents.

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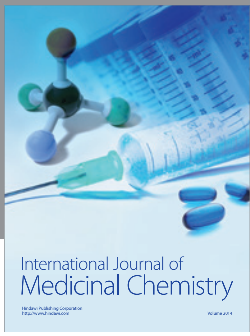
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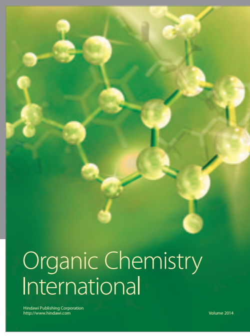
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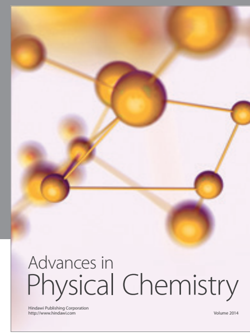
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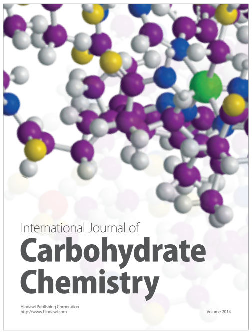
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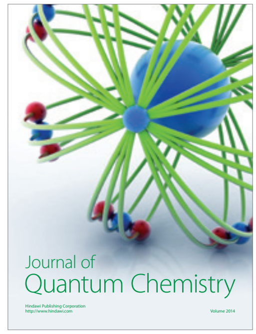
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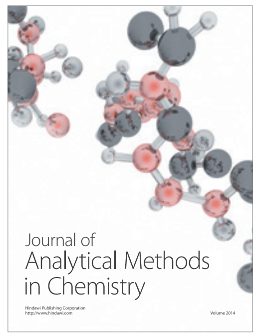
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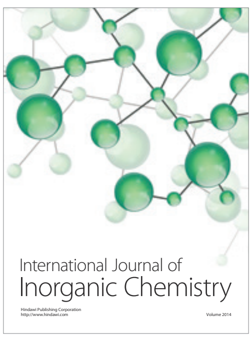
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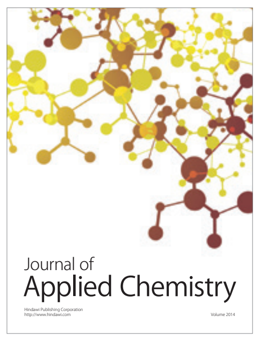
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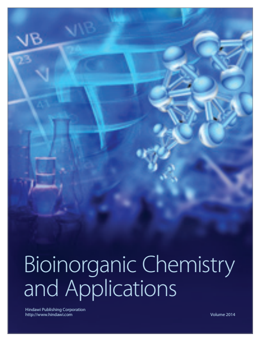
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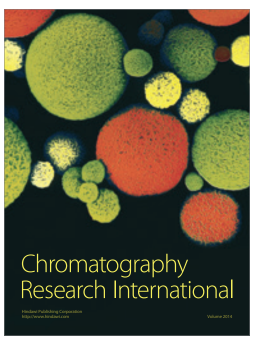
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