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RESEARCH ARTICLE

Study of the Removal of Direct dye from Aqueous Solution by using Solid Agricultural Waste

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ABSTRACT

The study investigates the removal of direct red 80 dye from its aqueous solution by using Tapioca peel activated carbon . 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 direct red 80 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 direct red 80 dye. Silver nitrate treated Tapioca peel showed a better performance compared to Sulphuric acid treated and raw carbons, thus making it an interesting option for dye removal textile effluent.

INTRODUCTION

Dyes are extensively used in the textile industry. One of the major problems concerning textile wastewater is colored effluent. The discharge of color waste is not only damaging the aesthetic nature of receiving streams but also it may be toxic to aquatic life. The color in the effluent is mainly due to unfixed dye. Many methods are available for the removal of dyes from waters. Among these methods, adsorption is by far the most versatile and widely used method because of its low cost, ease of operation. Considerable work has been carried out on the removal of dye from wastewater such as peanut hulls, maize bran, sawdust, sugar beet pulp, crab shell, cornstarch, rice husk, chitin, orange waste, lemon peel, granular kohlrabi peel, raw barley straw, sago waste, yellow passion fruit peel (Brown *et al*., 2000; Singh *et al*., 2006; Taty-Costodes *et al*., 2003; Reddad *et al*., 2002; Vijayaraghavan *et al*., 2006; Kweon *et al*.,2001; Kumar *et al*., 2006; Ghimire *et al*., 2001; Dhakal *et al*., 2005; Vasanth Kumar 2007; Renmin Gong *et al*., 2007; Husseien *et al*., 2007; Maheswari *et al*., 2008; Pavan *et al*., 2008). Therefore, there is the need to look for low cost alternatives in easily available biomaterials, which can absorb dyes from wastewaters. In this paper, we attempt to use an agricultural by product, peel of Tapioca, as adsorbent for the removal of dyes from water. These adsorbents can be used once, and then disposed as a fermentation substrate to produce fertilizer for vegetable cultivation. The present study was undertaken to explore the feasibility of finding a low cost effective adsorbent, Tapioca peel for the treatment of direct red 80 dye from aqueous solution as a function of initial concentration, contact time, pH and carbon dosage are also assessed.

MATERIALS AND METHODS

Preparation of Adsorbents

Raw Tapioca Peel Carbon

The Tapioca peel was collected from the nearby sago industry in Salem District, Tamil Nadu. 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°C and this material is used as raw Tapioca peel carbon. The Characteristics of the activated carbon prepared from Tapioca peel had been subject to various characterization parameter and the results are shown in Table 1.

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Table 1. Characteristic of TPAC

S.No.	Parameters	Obtained Result
1	pH solution	8.57
2	Water soluble matters (%)	43.86
3	Moisture content (%)	4.97
4	Ash content (%)	35.46
5	Apparel density (g/cc)	2.18
6	Iodine value (mg/gm)	9.93
7	HCL Soluble matter (0.25N)(%)	13.99
8	Calcium (mg/l)	52447.5
9	Sodium (mg/l)	5894.1
10	Potassium (mg/l)	5094.9
11	Phenol (mg/l)	184.81
12	Iron (mg/l)	958.49
13	Electrical conductivity (ms/cm)	10.64
14	Volatile matter (%)	21.8
15	Surface area(m2/g)	211-254

Silver Nitrate Treated Tapioca 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°C and this material is used as Silver nitrate treated Tapioca peel carbon.

Sulphuric Acid Treated Tapioca Peel Carbon

Other part of raw Tapioca 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°C and this material is used as sulphuric acid treated Tapioca peel carbon.

Preparation of Adsorbate

The Direct red 80 dye is a dark brown coloured, basic dye (Chemical formula: $C_{45}H_{26}N_{10}Na_6O_{21}S_6$, Molecular Weight = 1373.07, λ_{max} = 528 nm) was procured from Sigma-Aldrich Chemicals Pvt Limited, Bangalore, India. An accurately weighed quantity of direct red 80 dye 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 (50mg/L) was prepared in a conical flask with adsorbent concentration (0.5g/150mL) and kept inside the incubator shaker (Environmental orbital Shaker Incubator, Deneb Instruments) at 120rpm 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 (0.5g/150mL) and kept inside the incubator shaker at 120rpm 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 P^H^

150mL of dye solution was prepared in a conical flask with dye concentration of 50mg/L and adsorbent dose of 0.5g/150mL 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 (0.05N) or KOH (0.05N) 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 120rpm 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 50mg/L and adsorbent doses of 0.5, 1, 2, 5, 8g/150mL. The solutions were kept inside the incubator shaker at 120rpm 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 direct red 80 in the solution on the rate of adsorption on Silver nitrate treated, Sulphuric acid treated and raw Tapioca peel carbons were studied. The experiments were carried out at fixed adsorbent dose (0.5g/150mL) in the test solution, 27°C room temperature, pH (7.0) and at different initial concentrations of Direct red 80 (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 direct red 80 dye concentration on the dye adsorption with contact time is shown in Table 2. It is evident that the percent adsorption efficiency of Silver nitrate treated, Sulphuric acid treated and raw Tapioca peel carbons decreased with the increase in initial dye concentration in the solution. However, for Silver nitrate treated and Sulphuric acid treated Tapioca 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 Tapioca 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 (Garg *et al*., 2004).

Table 2. Effect of initial direct red 80 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 Tapioca peel carbon						
50	89.5	91.2	94.0	94.0	94.0	94.0
100	87.7	88.1	92.3	92.3	92.3	92.3
150	85.1	86.4	88.3	88.3	88.3	88.3
200	76.9	82.3	83.8	83.8	83.8	83.8
250	71.1	73.8	76.4	76.4	76.4	76.4
Sulphuric acid treated Tapioca peel carbon						
50	76.2	77.4	80.1	81.0	81.0	81.0
100	65.8	67.2	68.3	70.1	70.1	70.1
150	57.4	58.3	59.9	60.3	60.3	60.3
200	43.4	47.6	50.1	51.2	51.2	51.2
250	23.8	27.8	30.8	31.6	31.6	31.6
Raw Tapioca peel carbon						
50	42.6	49.2	51.4	52.3	52.3	52.3
100	37.4	41.1	42.8	44.1	45.3	45.3
150	34.5	38.9	40.9	41.7	41.8	41.8
200	30.7	33.3	36.9	37.5	36.4	36.4
250	25.4	26.5	28.3	29.4	30.7	30.8

From Fig 1, it is evident that the dye adsorption is higher than Silver nitrate treated Tapioca peel carbon than Sulphuric acid treated and raw Tapioca peel carbons.

Effect of Adsorbent Dose

The adsorption of Direct red 80 on Silver nitrate treated and Sulphuric acid treated Tapioca peel carbons were studied by changing the quantity of adsorbent (0.5, 1, 2, 5, 8g/150mL) in the test solution while keeping the initial dye concentration (50 mg/L), temperature (27°C) and pH (7.0) constant. Experiments were carried out at different contact time. As shown in Fig 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 Tapioca 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 Direct red 80 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.

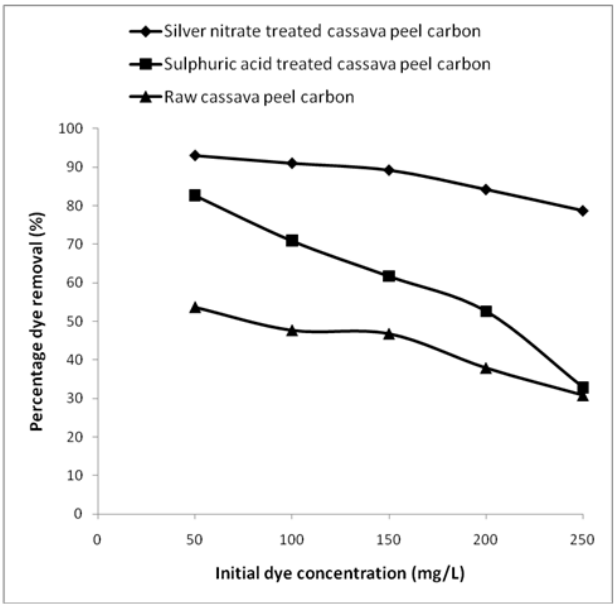

Fig. 1: Effect of initial direct red 80 red concentration on the dye adsorption

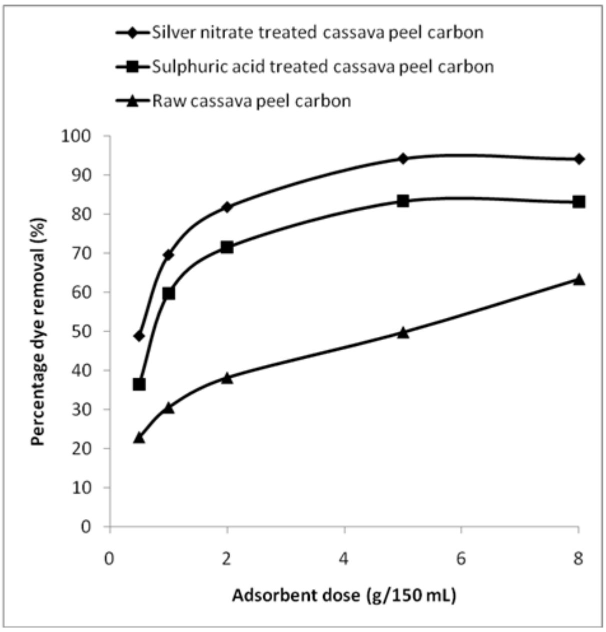

Fig. 2: Effect of adsorbent dose on the direct red 80 dye adsorption

Effect of pH

In order to study the effect of pH on Direct red 80 adsorption on Silver nitrate treated Tapioca peel and Sulphuric acid treated Tapioca peel, experiments were carried out at 50mg/L initial dye concentration with 0.5g/150mL adsorbent mass at room temperature of 27^{o}C. Results are presented in Fig 3. In the case of raw Tapioca 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 Tapioca peel was observed between pH ranges from 3 to 7. Although dye adsorption efficiency for Silver nitrate treated Tapioca peel is higher than the untreated and Sulphuric acid treated Tapioca peel, it was not significantly affected by pH. This may be due to hydrolysis of the adsorbent in water, which creates positively charged sites (Garg *et al*., 2004). 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 Tapioca peel (44-60%).

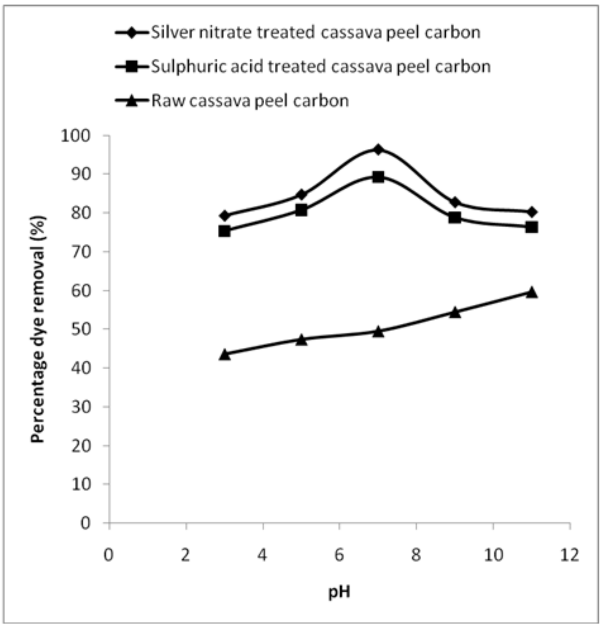

Fig. 3: Effect of pH on direct red 80 adsorption

Conclusions

The present study deals with the removal of direct red 80 on SATC, TAC, and DAC for the effect of initial concentration (Ci), contact time, dose of adsorbent and pH. The removal of direct red 80 from simulated wastewater using chemical treatment of Tapioca peel with Sulphuric acid and Silver nitrate has been investigated under different experimental conditions in batch mode. The adsorption of direct red 80 was dependent on the contact time, adsorbent dose and initial direct red 80 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 direct red 80. Silver nitrate treated Tapioca peel showed a better performance compared to Sulphuric acid treated Tapioca peel.

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