

Role of tapioca peel activated carbon (TPAC) in decolourisation of Red Brown C4R reactive dye

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Abstract

A carbon sorbent derived from an agricultural waste, tapioca peel was applied to study the removal of a reactive dye, Red Brown C4R from aqueous solution. Batch experiments were performed as a function of process parameters like agitation time, initial dye concentration and carbon dose. Modified Ritchie second order equation better predicted the kinetic results compared to other rate equations (pseudo first order & pseudo second order) tested. Among the isotherm models applied to the equilibrium data Freundlich model better predicted the experimental values. The adsorption capacity was 121.47 mg g⁻¹ at an initial pH of 6 and at 32±0.5°C. The adsorption capacity increased with increase in temperature. The influence of pH on dye removal was not significant. An optimum carbon dose of 1.2 g L⁻¹ was required for the maximum removal (96%) of dye from its 60 mg L⁻¹ solution.

Keywords: Adsorption, Red Brown C4R, tapioca peel, activated carbon, kinetics, isotherms

Introduction

Activated carbon has widely been used for the removal of inorganic and organic pollutants from aqueous solution. In a continuing search for the adsorbents, various lignocellulosic materials or agriculture wastes such as coconut shell, rice husks, saw dust, and wheat straw were used (Srivastava *et al.*, 1987; Usmani, 1988; Rahman, 2000). These materials were pyrolysed or carbonized in an inert atmosphere in order to remove volatile organic constituents, leaving behind a highly porous carbonaceous residue, followed by either chemicals, steam or gas activation for removal of the pollutants. Red Brown C4R has long been used as a model for the adsorption of organic pollutants from aqueous solution. A number of studies on the removal of Red Brown C4R from aqueous solution by using corncobs (El-Hendawy *et al.*, 2001), palm-tree cobs (Avon, 1997) oil palm nut shells (Chan, 1980) olive-waste (Bcaoui *et al.*, 2001) oil shale rock (Abu-El-Shar *et al.*, 2000) and chitin (Annadurai *et al.*, 1999) were reported.

Activated carbons have been prepared from the above materials by application of both physical and chemical activations. Activation and pyrolysis of rice husks with ZnCl₂, H₃PO₄ or CO₂ have been used for the adsorption of Red Brown C4R (Tanin & Gurgey, 1987) and benzene (Tanin & Gurgey, 1988). Separate and sequential application of physical activation with steam and chemical activation with H₃PO₄ were also reported (Lafi, 2000; El-Hendawy *et al.*, 2001). Hu and Srinivasan (2001) employed simultaneous activation by using ZnCl₂ and CO₂ to produce activated carbon from coconut shells and palm seeds.

Tapioca peels are agricultural by-product that is currently of no economic value. They consist of tiny bean-

like particles and are disseminated throughout the tapioca pulp, and are considered as waste product during sago production. It was reported (Bourgeois *et al.*, 2001) that the peels consist of high amount of lignocellulosic materials. Thus, it should be possible to carbonize or pyrolyse the material to form a porous carbon that is suitable to be used as adsorbent. In this work, we used tapioca peels as a raw material to produce activated carbons. We used physical activation (carbonization or pyrolysis) in an inert gas, followed by sequential chemical (Sulphuric acid) and physical activations to produce activated carbon. The use of such materials for the production of activated carbon has not been reported before.

Materials and methods

Tapioca peels were collected from nearby industries and then cleaned. It was dried in sunlight for 6 hr and then powdered in a domestic Sumeet mixie. It was washed with water to remove unwanted materials present in it and then filtered. Again, it was dried for 4 h and then activated with concentrated sulfuric acid before carbonization. Then, the material was carbonized at 200°C in a hot air oven under controlled conditions. Then to get rid of excess sulfuric acid, the carbon was repeatedly washed and finally dried. The carbonized material was sieved to 100 microns using Lawrence and Mayo sieve shaker and used for adsorption.

Adsorption studies

Various concentrations of Red Brown C4R solutions ranging from 10 -100 mg dm⁻³ were prepared by dissolving Red Brown C4R crystals in distilled water. A calibration curve of absorbance versus concentration was constructed, using a UV Spectrophotometer (Hitachi model, U-2000) at maximum wavelength of 670 nm.

Adsorption isotherm of Red Brown C4R were obtained by adding 0.1 g of TPAC sample to a 0.250 dm³ flask containing 0.100 dm³ of 10 mg dm⁻³ aqueous solution of Red Brown C4R. The flask was kept in a thermostat shaker at 30°C for 45 min. The suspension was then filtered, and the concentration of the Red Brown C4R was determined by difference. The procedure was extended to determine optimum shaking time, concentration and the amount of adsorbent used.

Results and discussions

Effect of mixing time

The adsorption behaviours of the samples were studied by evaluating the removal efficiency, R_E , of Red Brown C4R, calculated as:

$$R_E = (C_o - C)/C_o \times 100 \quad (1)$$

Where, C_o is the initial concentration of aqueous solution of Red Brown C4R replaced in a flask and shaken at room temperature for a certain time with a weighed sample, and C is the solution concentration after adsorption, R_E is expressed in term of percentage. The removal percentage increases with an increase in time (Fig.1).

The adsorption mechanism of the above data can be expressed in-terms of logarithmic plot of R_E versus mixing time in hour as:

$$\log R_E = m \log t + \log K \quad (2)$$

Where, m is the slope and may represent adsorption mechanism while K is a constant may represent rate factor (Bourgeois *et al.*, 2001). Regression analysis of the data reveals that increase in the surface area of the samples results in a decrease in slope values with corresponding increase in the factor K . Smaller values of m for larger surface areas indicate better adsorption, whereas higher values of rate factor, K , indicate a faster rate of Red Brown C4R removal (Table 1). Additional experiment showed that a relatively

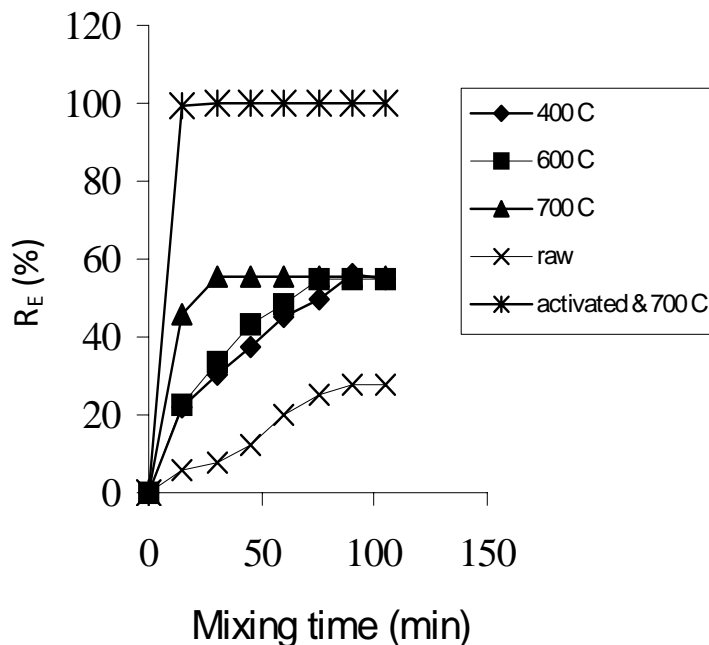
Table 1. Parameters for the $\log R_E$ Vs $\log t$ ($C = 10 \text{ mg dm}^{-3}$, volume 0.100 dm^3)

Surface area ($\text{m}^2 \text{g}^{-1}$)	Slope m	$\log K$	r^2
13	0.89	1.25	0.94
178	0.49	1.64	0.99
308	0.49	1.67	0.99
314	0.09	1.74	0.96

small quantity of activated sample with surface area of $600 \text{ m}^2 \text{g}^{-1}$, required only 0.3 g to remove all Red Brown C4R (10 mg dm^{-3}), as compared to 2 g required for the raw sample. Smaller values of K for comparatively smaller surface area may be due to the comparatively smaller pore volume or active sites on the tapioca peels.

On pyrolysis of tapioca peels up to 700°C, organic constituents were decomposed, leaving behind porous materials containing exposed active sites. However, the surface areas at these temperatures were relatively low and the materials were able to remove Red Brown C4R up to ~55%. Since only pores larger than the size of adsorbate molecule were accessible to the adsorbate, it is believed that the some pores in the pyrolysed samples were blocked by decomposition products of the organic constituents, thus inhibiting the accessibility of the active sites for the adsorption. After activation of the sample with sulphuric acid, a double increase in surface area was

Fig. 1. Removal efficiency of Red Brown C4R versus time.



observed, resulting in complete removal of Red Brown C4R. The effectiveness of sulphuric acid as activation agent was widely noted in the literature (Chan, 1980; Usmani, 1988; Hu & Srinivasan, 2001).

The adsorption isotherms of Red Brown C4R onto the activated guava seeds were carried out by applying the linear Langmuir equation

$$\frac{C_e}{X_e} = \frac{1}{X_m K} + \frac{1}{X_m} C_e \quad (3)$$

and the Freundlich equation

$$\log X_e = \log K_F + 1/n \log C_e \quad (4)$$

Where, C_e is the amount of adsorbate in the solution at equilibrium, X_e is the amount of adsorbate adsorbed, X_m is the amount of adsorbate adsorbed to form monolayer coverage, and K_L , n and K_F are the equation constants.

When the adsorption data was tested using equations (3) and (4), they best fitted to the Freundlich model as indicated by its relatively higher linear correlation coefficients (Table 2). Fig. 2a & b represent comparison of the experimental data of activated carbons with Langmuir and Freundlich equations. The results show that activated carbon prepared from tapioca peels exhibit good capacity to remove the bulky dye molecule through chemical activation followed by pyrolysis at 700°C.

Conclusions

We demonstrated the production of activated carbon derived from tapioca peels. Carbonization in inert gas produced poorly activated carbons due to the incomplete decomposition of organic constituents as carbonization by-products blocked the pores. However, activation by

Fig. 2. Fitting adsorption data with (a) Langmuir model and (b) Freundlich model

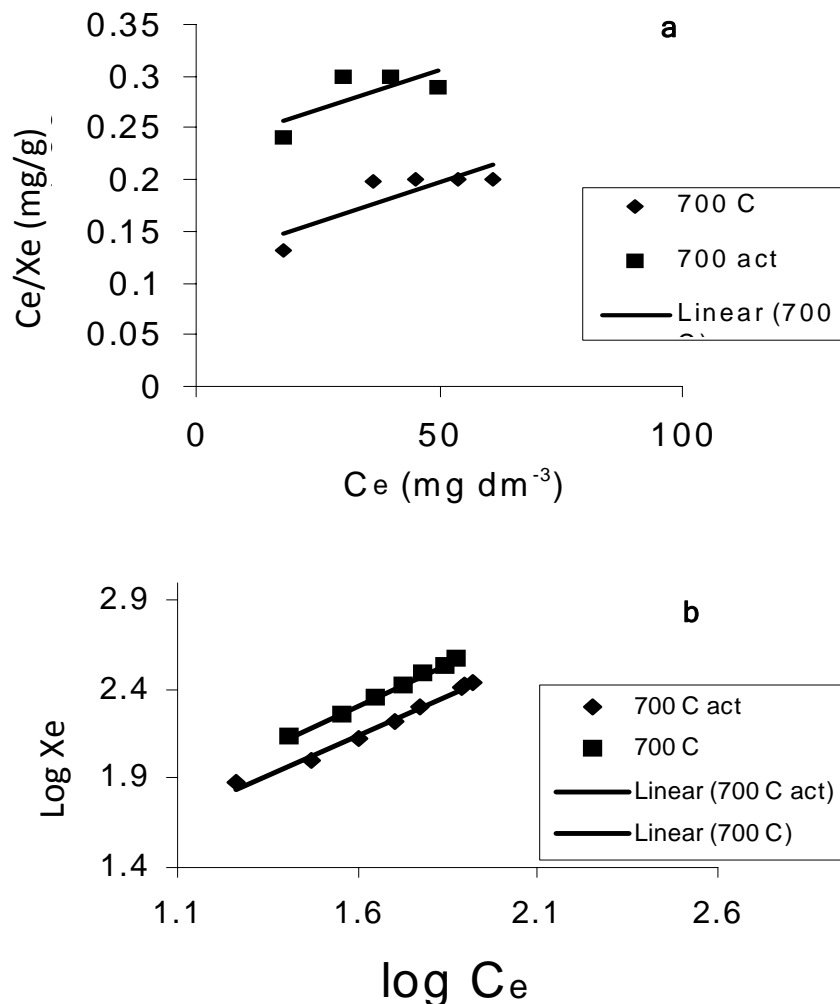


Table 2. Parameters for the adsorption of Red Brown CAR

		Samples	
Model	Parameter	700°C	700°C activated
Langmuir	r^2	0.508	0.713
	K_L	6.504	13.400
	X_m	0.667	0.625
	r^2	0.988	0.999
	K_F	5.261	6.174
	n	1.052	1.122

sulphuric acid followed by pyrolysis at 700°C proved very effective in producing better quality activated carbon with well-developed porosity and optimum adsorption capacity.

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