



Removal of dyes from a synthetic textile dye effluent by biosorption on apple pomace and wheat straw

T. Robinson*, B. Chandran, P. Nigam

School of Biomedical Sciences, University of Ulster, Coleraine BT52 1SA, Northern Ireland, UK

Received 12 June 2001; received in revised form 26 October 2001; accepted 29 November 2001

Abstract

This paper deals with two low-cost, locally available, renewable biosorbents; apple pomace and wheat straw for textile dye removal. Experiments at total dye concentrations of 10, 20, 30, 40, 50, 100, 150, and 200 mg/l were carried out with a synthetic effluent consisting of an equal mixture of five textile dyes. The effect of initial dye concentration, biosorbent particle size, quantity of biosorbent, effective adsorbance, dye removal and the applicability of the Langmuir and Freundlich isotherms were examined. One gram apple pomace was found to be a better biosorbent, removing 81% of dyes from the synthetic effluent at a particle size of 2 mm × 4 mm and 91% at 600 μm. Adsorption of dyes by apple pomace occurred at a faster rate in comparison to wheat straw. Both the isotherms were found to be applicable in the case of dye adsorption using apple pomace. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Adsorption; Apple pomace; Dye removal; Textile dyes; Wheat straw

1. Introduction

Many industries, such as paper, plastics, food, cosmetics, textile, etc., use dyes in order to colour their products. The presence of these dyes in water, even at very low concentrations, is highly visible and undesirable [1,2]. Colour is the first contaminant to be recognised, and environmental regulations in most of the countries (EU directive 91/271) have made it mandatory to decolourise the dye wastewater prior to discharge [3]. Many dyes are difficult to degrade due to their complex structure and xenobiotic properties. Decolourisation of textile dye effluent does not occur even if the effluent is treated by municipal wastewater treatment systems [4].

The presence of dyes in water reduces light penetration and has a derogatory effect on photosynthesis. Dyes may also be problematic if broken down anaerobically in the sediment, leading to the production of toxic

amines. Lethal levels may be reached affecting aquatic systems and associated flora and fauna. Many treatments have been investigated regarding their effectiveness in either removing the dyes from dye-containing effluent, or decolourising dyes through liquid fermentations [5].

Currently, the most widely used and effective physical method in industry is activated carbon, although running costs are expensive. This is mainly due to the chemicals required for regeneration after dye removal [6]. Although activated carbon removes dyes from solution, they are then present in a more concentrated and toxic form, and so their safe disposal increases the costs further. Therefore, the potential exists for the process of dye removal by adsorption to be more economically feasible by looking at the use of lower cost biosorbents.

Since the formation of the Ecological and Toxicological Association of the Dyestuffs Manufacturing Industry (ETAD), in 1974, measures have been taken to minimise environmental damage [7]. In Great Britain, government legislation is becoming more and more stringent regarding dye removal and effluent toxicity.

*Corresponding author. Tel.: +44-28-7032-4053; fax: +44-28-7032-4965.

E-mail address: p.nigam@ulst.ac.uk (T. Robinson).

This tough stance on dye containing effluent was evident in the UK's 1997 environmental policy, stating that zero synthetic chemicals should be released into the marine environment [3,6].

This study investigated the use of a previously untried biosorbent, apple pomace and wheat straw for dye removal by adsorption. The aim of the study was to develop low-cost adsorbents for an inexpensive dye-removal technology. The effects of both the varying concentration of the dye effluent and the particle size of the substrates on dye removal were investigated.

2. Materials and methods

The reactive dyes used in this study were Cibacron Yellow C-2R, Cibacron Red C-2G, Cibacron Blue C-R, Remazol Black B and Remazol Red RB. The dyes were obtained from Fruit of the Loom, Buncrana, Rep. of Ireland. The wheat straw was obtained from a farm in County Armagh, N. Ireland and the apple pomace from Mulrines, Ballybofey, Rep. of Ireland. The substrates were dried to a constant dry weight.

The synthetic effluent was prepared by dissolving five dyes, in equal amounts, in distilled de-ionised water to produce a stock solution of 1000 mg/l (pH 7.2). From this, 100 ml volumes containing initial concentrations (C_0) of 10, 20, 30, 40, 50, 100, 150, 200 mg/l were prepared. A preliminary investigation on the effect of pH on effective adsorption showed that there was no significant difference in adsorption between pH ranges of 6–12 (results not shown). The substrates were tested for their adsorbance capacities at two different sizes: coarse (2 mm $\times$ 4 mm) and fine (600 μ m) by determining the concentration of dyes remaining in solution (C_e).

Different masses of each substrate were added to 100 ml of the synthetic effluent at varying concentrations. Coarse sized particles were chopped to approximate sizes and fine sized particles were blended in a Waring commercial blender and sieved through a 600 μ m sieve from Endecotts Ltd, London. Decolourisation was recorded using a Pharmacia Biotech, Novaspec II spectrophotometer. 1 ml samples were taken at regular intervals, centrifuged in a Sanyo Micro Centaur, and decolourisation was calculated from $\lambda_{\max}$ readings. Experiments were carried out in duplicate, at a room temperature of $20 \pm 2^\circ\text{C}$.

3. Results and discussion

3.1. Effect of initial concentration

The effect of initial concentration of the synthetic textile dye effluent on the percentage dye removed was studied. Two different concentration ranges were used;

one from 10 to 40 mg/l and the other from 50 to 200 mg/l. Five grams of the substrates at particle size of 2 mm $\times$ 4 mm were added separately to 100 ml of synthetic dye effluent at concentrations of 50, 100, 150 and 200 mg/l. The percentage of dye removal was low for lower concentrations, 10–40 mg/l (results not shown), when compared to that for the higher concentration range.

The equilibrium capacity of straw increased as the initial concentration (C_0) increased. Fig. 1 illustrates that 48% of dye was removed with an initial concentration of 50 mg/l, 64% at 100 mg/l, 75% at 150 mg/l and 80% at 200 mg/l. The time taken to attain equilibrium at 50 and 100 mg/l of initial concentration was 48 h and it was 72 h in the case of 150 and 200 mg/l. Nigam et al. [2], also found a similar percentage of dye removal with an

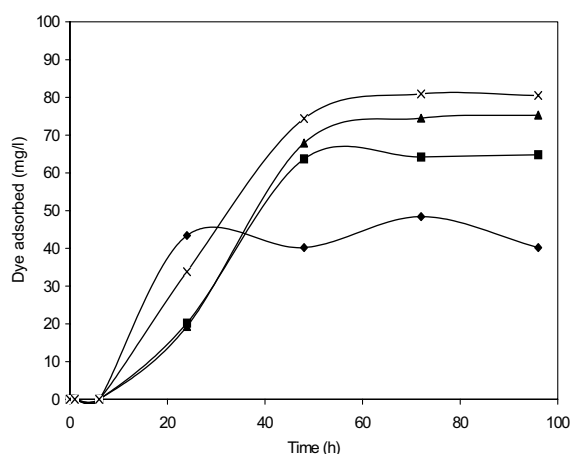


Fig. 1. Dye adsorbed by 5 g of wheat straw (2 mm $\times$ 4 mm) with concentrations of 50 mg/l (—◆—), 100 mg/l (—■—), 150 mg/l (—▲—), 200 mg/l (—×—).

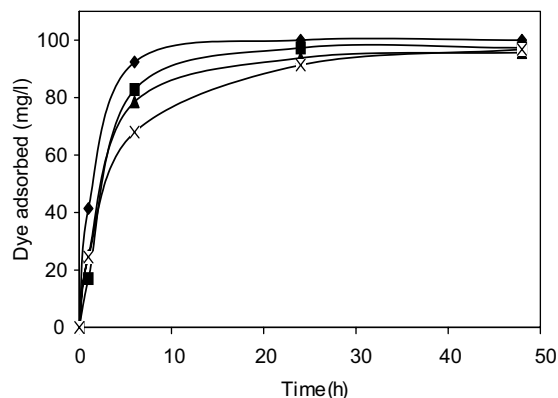


Fig. 2. Dye adsorbed by 5 g of apple pomace (2 mm $\times$ 4 mm) with concentrations of 50 mg/l (—◆—), 100 mg/l (—■—), 150 mg/l (—▲—), 200 mg/l (—×—).

initial concentration of 200 mg/l, using a synthetic textile dye effluent consisting of eight dyes.

For apple pomace the equilibrium capacity decreased with an increase in the initial concentration as shown in Fig. 2. At concentrations of 50, 10, 150 and 200 mg/l there was 100%, 98%, 96% and 96% decolourisation, respectively. The time taken to reach equilibrium (C_e) was 24 h in the case of apple pomace, compared to 50 h for wheat straw. Equilibrium was reached after 24 h at concentrations of 50 and 100 mg/l, and after 48 h for 150 and 200 mg/l. There is a sharp contrast in the appearance of the two graphs displayed in Figs. 1 and 2, with a gentle slope over a period of 48 h for straw and a much steeper slope over a shorter time period for the apple pomace. For both adsorbents, the concentration

of dye remaining in solution decreased with time, until a point was reached when no more dye can be adsorbed onto the sorbent.

3.2. Effect of particle size of the substrate

It can be seen that particle size of 600 μm straw removed more dye at all weights (Fig. 3). The 600 μm particle size showed an increase in percentage of dye removal at all substrate weights due to the increase in surface area allowing more dye molecules to be bound per gram of substrate.

Apple pomace removed more dye compared to straw regardless of particle size. The removal of dye was 100% in the case of 600 μm particle size for 5 and 2 g, and 91% in the case of 600 μm particle size for 1 g.

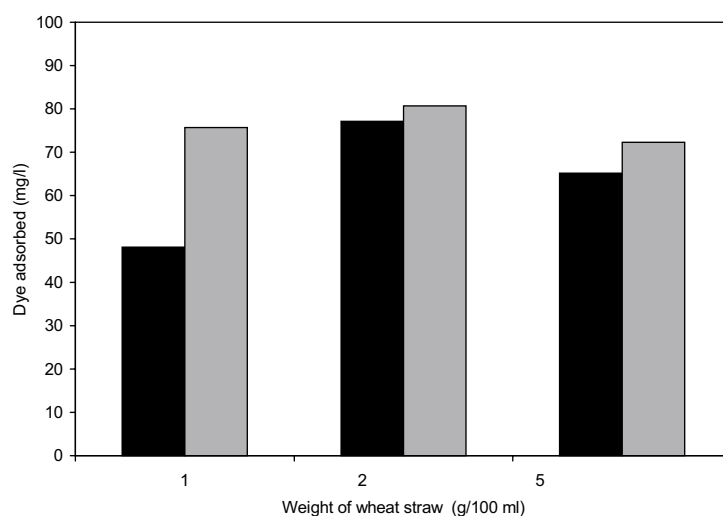


Fig. 3. Effect of particle size and weight (■ 2 mm × 4 mm, □ 600 μm) of wheat straw on dye removal.

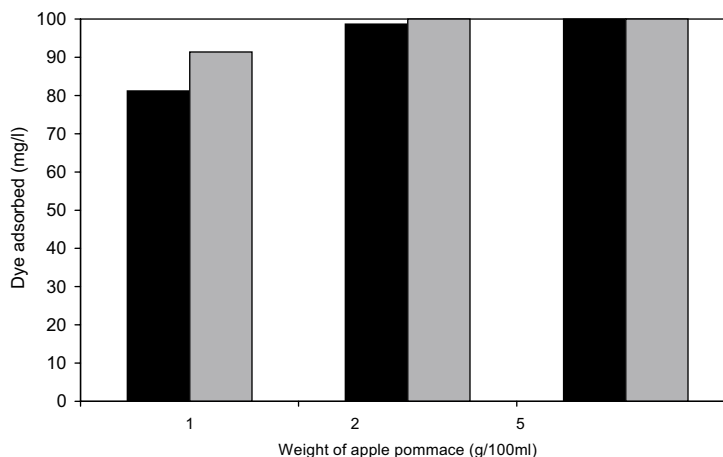


Fig. 4. Effect of particle size and weight (■ 2 mm × 4 mm, □ 600 μm) of apple pomace on dye removal.

for 1 g. Even though the amount of dye removed is almost equal by both particle sizes, the 600 μm particle size removed more dye with 1 g of substrate, compared to the amount removed by 2 mm $\times$ 4 mm, due to the increase in surface area (Fig. 4).

3.3. Quantity of substrate and effective adsorbance

Fig. 5 shows that the effective adsorption of straw was high when the weight of the substrate was 2 g at a particle size of 2 mm $\times$ 4 mm, which supported the high percentage dye removal shown in Fig. 3 for the same weight of substrate and particle size. Two grams of straw and apple pomace removes a similar amount of dye as 5 g, indicating that any further increase in weight did not have any effect on an increase in dye removal. Fig. 5 illustrates the amount of dye (mg/l) bound per gram of

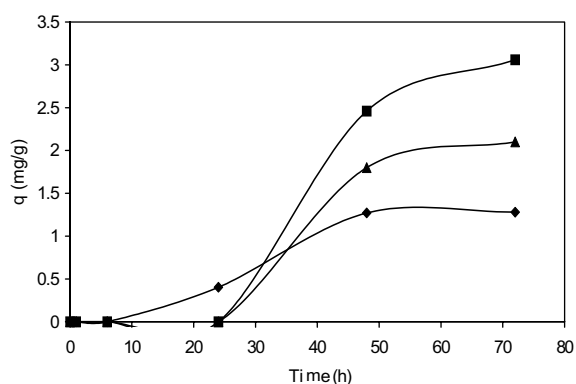


Fig. 5. Effect of weight of wheat straw (2 mm $\times$ 4 mm) on dye removal (mg/g). C_0 100 mg/l, 5 g (—◆—), 2 g (—■—), 1 g (—▲—).

substrate (q). Two grams of straw had the highest q value for 2 mm $\times$ 4 mm, showing that it removed more dye per gram than the other two weights.

Fig. 6 showed that by increasing the surface area of wheat straw, the amount of substrate for binding also increased. The q values were higher at all weights, with 1 g, 600 μm straw binding to more dye per gram of substrate. By increasing the surface area and making more of the substrate available for adsorption, the quantity of sorbent used can be reduced, without a significant reduction in total percentage dye removal. Similarly 1 g of apple pomace of both particle sizes (2 mm $\times$ 4 mm and 600 μm) had a high effective adsorbance capacity per gram of the substrate, as shown in Figs. 7 and 8, but removed less percentage of dye from solution in comparison to the other two weights at the same particle size due to the reduced quantity of substrate used.

The q -values are much improved by increasing the surface area and minimum effective substrate. Generally, the q values for apple pomace are much higher than straw at both particle sizes showing its ability to bind to more dye molecules per gram of substrate used. Apple also removed a higher percentage of dye from solution than wheat straw.

3.4. Kinetics of dye removal

The rate of dye adsorption increased as the initial concentration increased in both apple pomace and wheat straw at 1 g of 600 μm particle size (Fig. 9). The rate of dye adsorption was higher for apple pomace compared to wheat straw for all the concentrations.

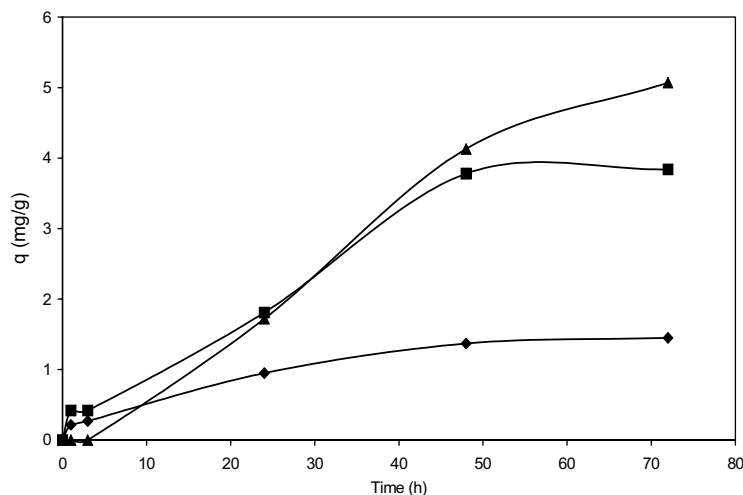


Fig. 6. Effect of weight of wheat straw (600 μm) on dye removal (mg/g). C_0 100 mg/l, 5 g (—◆—), 2 g (—■—), 1 g (—▲—).

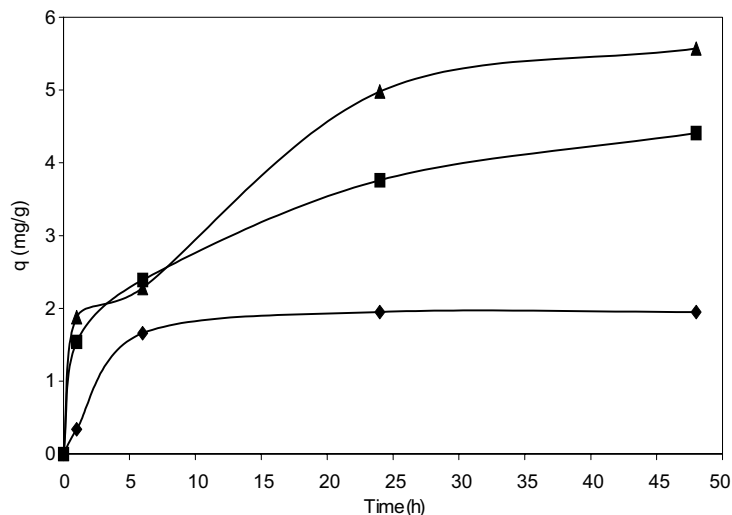


Fig. 7. Effect of weight of apple pomace (2 mm × 4 mm) on dye removal (mg/g). C_0 100 mg/l, 5 g (—◆—), 2 g (—■—), 1 g (—▲—).

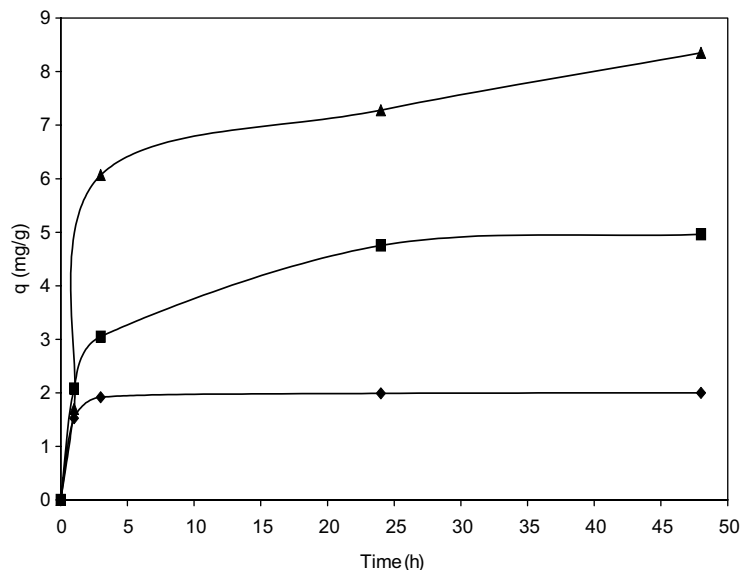


Fig. 8. Effect of weight of apple pomace (600 μm) on dye removal (mg/g). C_0 100 mg/l, 5 g (—◆—), 2 g (—■—), 1 g (—▲—).

3.5. Adsorption isotherms

The adsorption curves were applied to both the Freundlich and the Langmuir equations. The linear form of the Langmuir isotherm equation is represented as

$$\frac{1}{X/M} = \frac{1}{Q} + \left[\frac{1}{bQ} \right] \left[\frac{1}{C} \right]. \quad (1)$$

The linearised Freundlich isotherm equation is shown as

$$\text{Log} \left[\frac{X}{M} \right] = \text{log } K + \left[\frac{1}{n} \right] \text{log } C, \quad (2)$$

where X/M is the amount of solute absorbed per unit weight of adsorbent (q) (mg/g), C the concentration of solute remaining in solution at equilibrium (C_e) (mg/l), Q the amount of solute absorbed per unit weight of adsorbent in forming a complete monolayer on the surface (mg/l), b the constant related to the energy or net enthalpy and K and n are the Freundlich constants.

Table 1 gives the coefficients for the linearised form of the isotherm model for the adsorption of the synthetic effluent onto each of the substrates. Negative values for the Langmuir and Freundlich isotherm constants, as given in Table 1 indicate the inadequacy of the

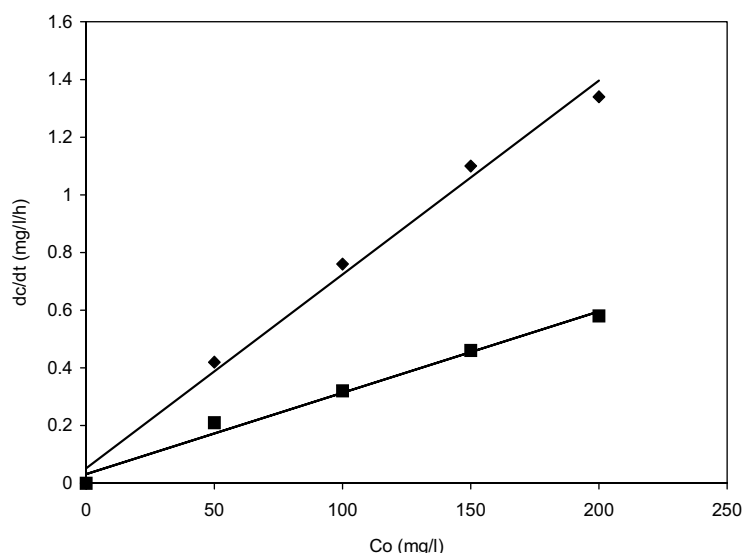


Fig. 9. Rate of removal of synthetic effluent by 1 g apple pomace ◆ and 1 g wheat straw ■ (600 μ m).

Table 1
Linearised isotherm coefficients for synthetic effluent

	Langmuir		Freundlich	
	Q	b	K	n
Apple pomace (g)				
5	1.1	2.6	−0.091	17.28
2	1.86	1.0	0.19	0.94
1	2.79	0.2	0.29	0.51
Wheat straw (g)				
5	−0.34	0.058	−1.09	0.7
2	−3.78	0.36	−4.1	3.42
1	−0.23	0.1	−0.89	0.92

isotherm models to explain the adsorption process. The positive values for the isotherm constants in the case of apple pomace (600 μ m) signifies monolayer adsorption and the data fitted reasonably well with the Freundlich model indicating heterogeneous surface binding also [8].

4. Conclusions

The experimental results showed that 1 g of apple pomace and 1 g of wheat straw, with a particle size of 600 μ m, were suitable adsorbents for the removal of dyes from a synthetic effluent. Apple pomace had a greater capacity to adsorb the five reactive dyes compared to wheat straw.

Apple pomace removed a larger amount of dyes from solution, and also binds to more dye molecules per gram of substrate. It also removed the dyes at a faster rate than straw. Further research is recommended to examine the possibility of solid state fermentation of the dye adsorbed material for either dye recovery or bioremediation purposes.

Acknowledgements

T.R. is thankful to the Department. of Education, Northern Ireland (DENI) for a research studentship to carryout this work towards his Ph.D. award.

References

- [1] Ramakrishna KR, Viraraghavan T. Dye removal using low cost adsorbents. *Water Sci Technol* 1997;36:189–96.
- [2] Nigam P, Armour G, Banat IM, Singh D, Marchant R. Physical removal of textile dyes and solid state fermentation of dye-adsorbed agricultural residues. *Bioresour Technol* 2000;72:219–26.
- [3] O'Neill C, Hawkes FR, Lourenco ND, Pinheiro HM, Delee W. Colour in textile effluents—sources. Measurement, discharge consents and simulation: a review. *J Chem Technol Biotechnol* 1999;74:1009–18.
- [4] Willmott N, Guthrie J, Nelson G. The biotechnology approach to colour removal from textile effluent. *J Soc Dye Colour* 1998;114:38–41.
- [5] Banat IM, Nigam P, Singh D, Marchant R. Microbial decolourisation of textile-dye-containing effluents: a review. *Bioresour Technol* 1996;58:217–27.

- [6] Robinson T, McMullan G, Marchant R, Nigam P. Remediation of dyes in textile effluent: a critical review on current treatment technologies with a proposed alternative. *Bioresour Technol* 2001;77:247–55.
- [7] Anliker R. Ecotoxicology of dyestuffs- a joint effort by industry. *Ecotox Environ Saf* 1979;3:59–74.
- [8] Weber WJ. *Physiochemical processes for water quality control*. New York: Wiley, 1972.